Review

Weathering of rocks and neogenesis of minerals associated with lichen activity

Paola Adamo [*], Pietro Violante

Dipartimento di Scienze Chimico-Agrarie, Università di Napoli ''Federico II'', Portici, Italy

Abstract

The weathering action of lichens on rocks and the biogeophysical and biogeochemical alteration of rock-forming minerals, their influence in dissolution and precipitation reactions and in bioformation of new minerals are reviewed. The intimate adhesion of lichen thalli to the rock surface and the hyphal penetration in less coherent areas of the rock cause a physical disaggregation and fragmentation of the mineral surface. Chemical weathering is essentially due to the excretion of organic acids. Depending on the nature of the minerals, etching patterns and decomposition features are formed by biosolubilisation processes. The presence of calcium, magnesium, manganese and copper oxalate crystals at the rock–lichen interface and in the lichen thalli suggests that oxalic acid, secreted by the mycobiont, is one of the most active agents of chemical alteration. Transformation of minerals to siliceous relicts, precipitation of iron oxides and hydroxides and formation of alumino-silicates are presumably related to the activity of organic acids in complexing and removing elements from the substrate. The involvement of the so-called 'lichen acids', a group of mainly polyphenolic compounds, as bioweathering agents has been only recently well documented. Present and further progresses in the study of the lichen–rock relationship rely on application of modern instrumental and analytical techniques. The relevance of lichen weathering to the biodeterioration of stoneworks of artistic value is considered. © 2000 Elsevier Science B.V. All rights reserved.

---

[*] Corresponding author. Fax: +39-081-7755130; E-mail: adamo@unina.it

1. Introduction

1.1. Main characteristics of lichens

Lichens are composite organisms comprising a fungal component, the mycobiont, and an alga or cyanobacteria, the photobiont. Most of the mycobionts are ascomycetes and do not occur in a non-lichenized state. Several photobionts, members of chlorophyta or of cyanobacteria, can be encountered in a free-living condition. The two bionts live in symbiotic relationship forming a heterogeneous structure, the thallus, with a distinct anatomy, morphology and physiology (Ozenda and Clauzade, 1970; Ahmadjan and Hale, 1973).

Most lichens have a stratified structure. The photobionts are restricted generally to a particular layer in the thallus. Besides the algal zone there is the medulla, which consists of loosely interwoven hyphae. A cortical layer, formed by closely organised hyphae, always covers the upper side of the thallus and sometimes also the lower surface.

On the basis of the growth form lichens are divided into three main groups: crustose, foliose and fruticose. Crustose lichens never possess a lower cortex. They are firmly attached to soil, rock, or tree bark by the hyphae of the medulla. Species growing inside rock are called endolithic. The thallus of foliose lichens is formed by flattened lobes. It adheres more or less firmly to the substrata by bundles of tendentially parallel aligned hyphae called rhizines or rhizoidal hyphae. Either the whole lower surface is in contact with the substrate or the margin of the lobes becomes free and bends upwards. Fruticose lichens have strap-shaped or threadlike lobes. The thalli are attached to the substrata with the base and can be branched, erect, ascending or pendulous. In some lichens the thallus consists of a horizontal part lying on the substrate and of a vertical, fruticose part, bearing the fruiting bodies. The horizontal thallus may disappear as the lichen matures. The fruticose stalk is called podetium or pseudopodetium when formed from the generative or vegetative primary thallus tissue, respectively. Squamulose or placodioid thalli are intermediate between crustose and foliose lichens.

1.2. Rock weathering induced by lichens

The effectiveness of lichens as agents of rock weathering and soil formation has long been recognised (Syers and Iskandar, 1973; Jones, 1988; Jones and Wilson, 1985; Gehrmann et al., 1988; Ascaso and Wierzchos, 1995; Wilson, 1995). Unlike the situation in soil, where there are more complicating and interacting factors, the zone of contact between saxicolous lichens and their rock substrate provides an ideal environment for studying the biological weathering of minerals.

The close and intimate contact by the fungus with the underlying substratum and the location of the algal cells in the upper layers of the lichen thallus suggest

that the weathering ability of lichens is essentially due to the mycobiont (Wilson and Jones, 1983). Differences in thallus morphology related to more or less firm adhesion to the substrate do not necessarily imply differences in the capacity of lichens to alter the substrate, which more likely are related to physiological differences among species (Adamo et al., 1993). Some squamulose or placodioid lichens, however, produce significant root-like structures (rhizomorphs in sensu lato) that may greatly extend the lichen–substrate contact zone (Sanders et al., 1994).

The weathering action of lichens involves both biogeophysical and biogeochemical processes (Syers and Iskandar, 1973). Rhizine and rhizoid exploration and adhesion or, more generally, fungal hyphae penetration and thallus expansion and contraction (a consequence of the wetting and drying of its gelatinous or mucilaginous substances) are the most important mechanisms involved in physical weathering. The excretion by the mycobiont of low molecular weight organic carboxylic acids, such as oxalic, citric, gluconic, lactic acids, with combined chelating and acidic properties, and the production of slightly water-soluble polyphenolic compounds called 'lichen acids', [1] able to form complexes with the metal cations present in the rock-forming minerals, are phenomena of high local intensity. These substances promote the chemical processes by means of which lichens are able to decompose lithic constituents. The ability of lichens to absorb and retain water allows chemical weathering reactions to proceed for

---

[1] Depsides and depsidones, usually referred to as 'lichen acids', although not all of them are in fact acids, are the most commonly encountered secondary products of lichen metabolism. They may account for up to 8% of the dry weight of the lichen and are usually present in the medulla (Syers and Iskandar, 1973). Several studies have indicated that some of these substances are involved in biological weathering. Depsides and depsidones are esters and oxidative coupling products of variously substituted phenolic acids (Sundholm and Huneck, 1980; Huneck and Yoshimura, 1996). Their general structure may be of type A (which form the orcinol series) or B (which form the β-orcinol series with a one-carbon substituent, R^1, in the 3-position).

A   B
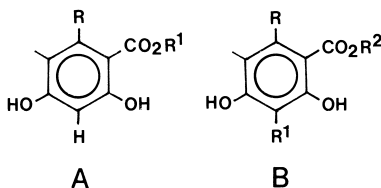
The simplest depside of the orcinol series is lecanoric acid. The most frequently encountered depside in the β-orcinol series is atranorin. Depsidones derive from oxidative ring closure of depsides. The cyclization usually takes place between the C-2 and C-5′ positions. A number of depsidones (fumarprotocetraric acid, stictic acid, norstictic acid, psoromic acid and salazanic acid), reported as able to affect the lichenised rock substrate, are aldehydes.
The occurrence in ortho (adjacent) positions of certain electron donors polar groups, such as -OH, -COOH and -CHO, largely determine the water solubility and the metal complexing capacity of the 'lichen acids' acting as biogeochemical weathering agents (Iskandar and Syers, 1972).

longer than on bare rock. The dissolution of respiratory carbon dioxide in absorbed water, leading to the formation of carbonic acid, seems to play only a minor role in the weathering occurring beneath encrusting lichens (Syers and Iskandar, 1973).

Lichen–substrate interactions result in the disruption of the rock surface, in extensive etch markings on rock minerals and in the extracellular and/or intracellular formation of a range of biogenic minerals (Jones and Wilson, 1986). Due to the abundance of biomolecules, crystallisation processes are extremely slow at the rock–lichen interface. Typically, weathering induced by lichens is considered to be combined with the presence of non-crystalline or poorly-ordered secondary products and organo-mineral complexes (Wilson and Jones, 1983). Nevertheless, the neoformation of crystalline phases may result from differentiation of the contact zone between rock and lichen in microsites with particular pH, humidity and redox potential conditions (Adamo et al., 1997).

The weathering effects caused by lichens have been most extensively studied using microscopic, submicroscopic and analytical methods. In particular, fractured surface lichen-encrusted rock samples and polished surfaces, thin and ultra-thin sections of undisturbed resin-embedded samples have allowed the observation in situ of the rock–lichen contact zone, showing its complexity and uniqueness. Optical microscopy (OM), electron microscopy (SEM/TEM), equipped with diffraction accessory (ED) and microprobe (EDXRA), X-ray diffractometry (XRD) and IR spectrometry have revealed the nature and composition of the secondary products formed at the rock–lichen interface or, indeed, within the lichen thallus itself (Jones and Wilson, 1985; Jones et al., 1981; Modenesi and Lajolo, 1988; Ascaso et al., 1990; Purvis et al., 1990; Nimis and Tretiach, 1995; Adamo et al., 1997). Additional information has recently been revealed by the applications of SEM in the back-scattered electron (BSE) emission mode (Ascaso and Wierzchos, 1994; Wierzchos and Ascaso, 1994, 1996) and using high-resolution transmission electron microscopy (HRTEM) (Wierzchos and Ascaso, 1998).

In this chapter, some aspects of the bioweathering phenomena are described and data regarding the biominerals resulting from the growth of lichens on various rock substrates are reported.

2. Biogeophysical weathering

Due to the lack of suitable instruments to investigate microscale chemical transformations, earlier researches on rock alteration by lichens were mainly focused on physical weathering, which was considered as more important than chemical decomposition (Mellor, 1923; Fry, 1924, 1927; Polynov, 1945; Jones, 1959).

The mechanical action of lichen thalli on the rock generally consists of a more or less extensive disaggregation and fragmentation of the lithic surface immediately below the lichen crust. The intensity of disintegration is a result of both the physico-chemical properties of the rock (compactness, hardness, lamination or preexisting surface alteration), and the nature of the lichen thallus.

For example, the presence in leucitic lavic rock of Mt. Vesuvius (Italy) of many vesicles and less coherent areas makes the penetration of the lichen *Stereocaulon vesuvianum* in the substrate easier (Adamo and Violante, 1991). In thin sections, the organ of adhesion of the lichen — the pseudopodetium — and its ramifications were observed to penetrate down to 30 mm in the rock (Adamo et al., 1997) (Fig. 1a).

In the case of *Squamarina cartilaginea* growing on a calcareous rock from the hills surrounding the town of Cuenca (Spain), elaborations of the thallus — the rhizomorphs — and their ramifications penetrate the substrate preferentially along the interfaces of rock and mineral fragments embedded within the conglomerate and appear to bore unimpeded through the extensive calcareous cement (Sanders et al., 1994) (Fig. 1b). On siliceous schist or when the thallus covers a zone of rock rich in micaceous material, hyphal penetration mainly occurs between laminae, which are increasingly separated with continued hyphal proliferation (Sanders et al., 1994; Wierzchos and Ascaso, 1994, 1996) (Fig. 1c).

The detachment of mineral fragments and their incorporation into the thallus is often observed as a result of hyphal interpenetration of the substrate particles and of thallus swelling and shrinking with hydration cycles (Jones et al., 1981; Adamo and Violante, 1989; Ascaso et al., 1990; Sanders et al., 1994; Wierzchos and Ascaso, 1994, 1996) (Fig. 1d). These forces are often cited as an explanation for physical desegregation of mineral grains, but apparently their strength has never been measured. For rock surfaces the mechanical processes of disintegration (e.g., freeze–thaw cycles) and subsequent colonisation of freshly exposed minerals along grain boundaries are probably also important mechanisms of biogeophysical weathering.

Substrate disaggregation is not always more pronounced under crustose lichens, firmly and closely attached to the substrate via the entirety of the lower surface of the thallus. The adhesion of foliose species, by distinct clusters of hyphae (rhizine), can be equally strong (Adamo et al., 1993). The indeterminate growth and the proliferation of the rhizomorph system of some species of squamulose lichens, characterised by the presence of small scales or squamules, may produce an extensive substratic network of hyphae (Sanders et al., 1994). In the frigid desert of the Antarctic dry valleys the activity of cryptoendolithic lichens, able to grow embedded within the sandstone rock matrix between and around the crystals of the porous substrate, results in a characteristic exfoliative weathering pattern (Friedmann, 1982). The substance cementing the sandstone grains is apparently solubilized at the level of the lichen, which is exposed as the upper rock crust peels off. Hyphae then penetrate deeper and a new lichen zone
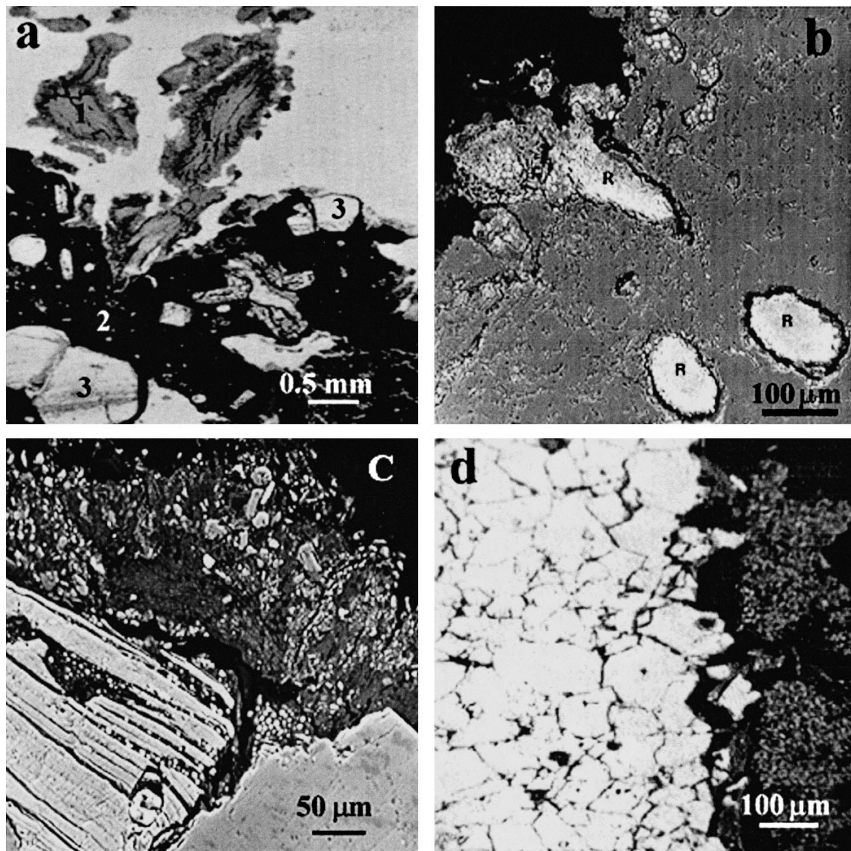
Fig. 1. Thin-section micrograph (plain polarized light) of (a) the interface between leucitic rock and *Stereocaulon vesuvianum* showing the deep penetration of the lichen in the lithic substrate: (1) lichen, (2) fine-grained rock matrix, (3) white trapezohedral leucite crystals (from Adamo et al., 1996). Scanning electron micrographs of: (b) rhizomorphs (R) of *Squamarina cartilaginea* penetrating calcareous conglomerate rock (from Sanders et al., 1994); (c) *Aspicilia intermutans* thallus on granitic rock (from Wierzchos and Ascaso, 1994); (d) dolomite rock– *Lepraria* genus lichen interface with detached and incorporated substrate fragments (from Adamo and Violante, 1989).

is formed at the appropriate depth, while on the surface a new rock crust is formed. In this way, subsequent layers are 'sliced off', resulting in steplike elevations on the surface of weathered rocks.

3. Biogeochemical weathering

3.1. Rock surface corrosion and mineral dissolution patterns

The chemical decomposition of rocks could proceeds at the same time as the physical disintegration. Microdivision of minerals is generally considered a

result of the mechanical action of the thalli, however, the participation of some type of chemical action cannot be discarded. In addition, mechanical fragmentation, increasing the surface area of the mineral or rock, accelerates chemical decomposition.

Dissolution processes, mainly by organic acids, occur at the microsites where lichens adhere to the rocks. These are manifested by extensive surface etching of the grains incorporated into the lichen thallus and of the rock surfaces immediately below the lichen thallus.

The etching pattern varies according to the type of mineral concerned. Labradorite grains embedded in the thallus of the crustose lichen *Pertusaria corallina* show surfaces with a ridge and furrow pattern, presumably representing a lamellar intergrowth between two components of different chemical composition (Jones et al., 1981) (Fig. 2a). Deep etch pits, sometimes with regular outlines along cleavage planes or pre-existing microfissures, have been observed by Adamo et al. (1993) on calcium-rich plagioclase feldspar at the interface between dolerite and the foliose *Xanthoria ectaneoides* lichen (Fig. 2b). Deeply penetrating rounded etch pits appear to be the decomposition features of leucite mineral under *Stereocaulon vesuvianum* (Adamo and Violante, 1991) (Fig. 2c). A split and twisted appearance is shown by the chrysotile fibres observed on the serpentinite rock surface on which the *Lecanora atra* lichen grows (Wilson et al., 1981) (Fig. 2d).

Due to their vulnerability to weathering, carbonate and ferromagnesian minerals are particularly corroded beneath lichens. The more rounded edges of dolomite rombohedric units under *Lepraria* sp. (Adamo and Violante, 1989) and of olivine grains in the thallus of *Pertusaria corallina* on basalt (Jones et al., 1980) give the impression of more rapid dissolution. Augite tends to etch out preferentially along cleavage planes in the form of narrow trenches (Jones et al., 1981; Adamo and Violante, 1991) (Fig. 2e). In calcite, the superficial dissolution of successive strata results in the appearance of forms that are close to scalenoedra (Robert et al., 1980; Adamo et al., 1993) (Fig. 2f).

The high solubility of calcium carbonate, compared to that of the minerals of other rocks, facilitates a deeper penetration of the hyphae (Syers and Iskandar, 1973). The direct perforation of calcareous substrata by lichen hyphae suggests chemical dissolution of the rock minerals, as well as mechanical deterioration (Sanders et al., 1994).

In spite of the well-known resistance to weathering, quartz grains with definite signs of fungal attack have been isolated from quartzites and quartzitic substrates colonised by lichens (Hallbauer and Jahns, 1977; Jones et al., 1981). Similar corrosion, attributed to 'lichen acids', were observed by Ascaso et al. (1976) on quartz samples treated with lichen extracts under controlled conditions.

The peculiar features of mineral surfaces due to biosolubilisation processes are thought to be related to the crystal structure of minerals, where more
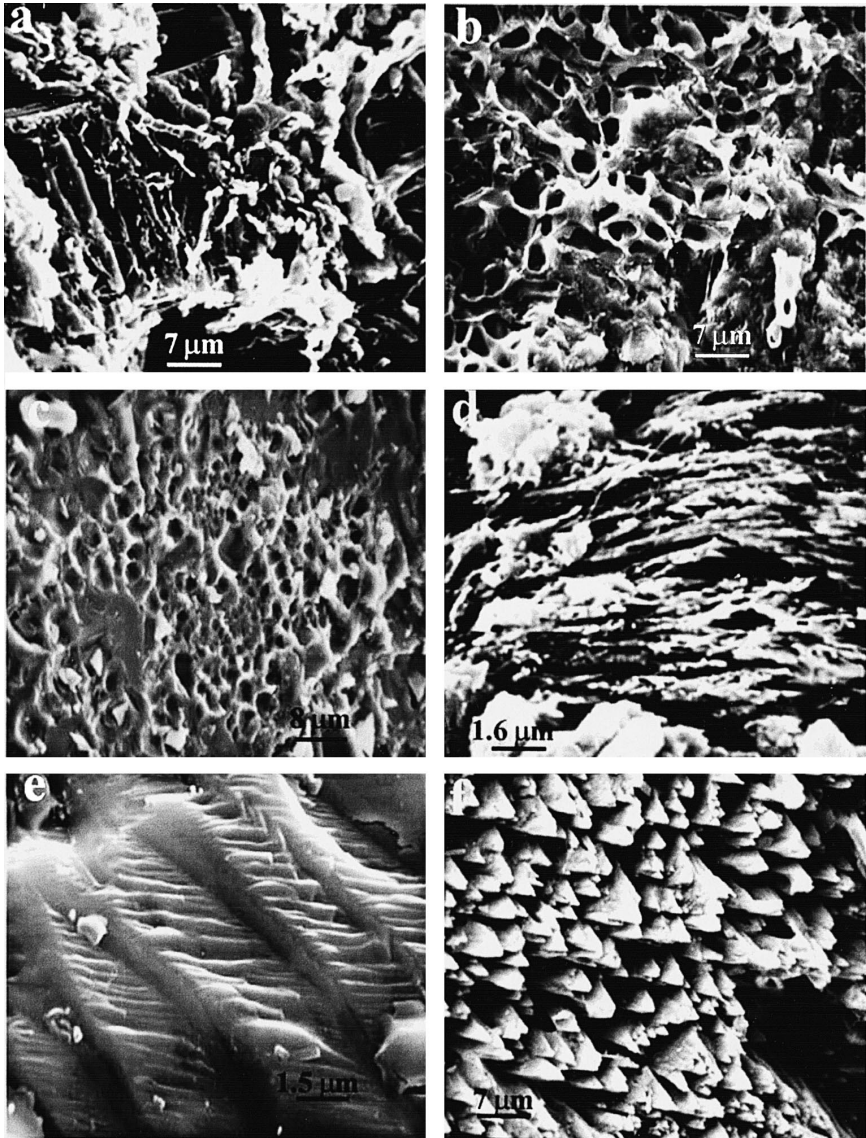
Fig. 2. Scanning electron micrographs showing surface etching patterns of: (a) labradorite grain embedded in the thallus of crustose lichen *Pertusaria corallina* on basalt (from Jones et al., 1981); (b) calcium-rich plagioclase feldspar localised at the dolerite rock–*Xanthoria ectaneoides* interface (from Adamo et al., 1993); (c) leucite mineral under *Stereocaulon vesuvianum* (from Adamo et al., 1991); (d) chrysotile fibres beneath *Lecanora atra* on serpentinite (from Wilson et al., 1981); (e) augite found at the vesuvite rock–*Stereocaulon vesuvianum* interface (from Adamo et al., 1991); (f) calcite under *Xanthoria ectaneoides* interface (from Adamo et al., 1993).

unstable areas of higher strain energy due to some kind of structural dislocation, behave as sites of preferential dissolution (Wilson, 1995; Wilson and Jones, 1983).

The amount of rock removed by corrosion caused by lichens can make a significant contribution to the small-scale formation of fine-grained material deposits. Recently, Garty (1992), taking into account the total volume of holes and pits produced by the growth of different lithobiontic microorganisms on chalk rock from a burnt forest area of the Carmel Mountains in the Beit-Oren Nature Reserve (Israel) and the *specific weight* of chalk, has estimated the amount of $CaCO_3$ removed by only one kind of endolithic lichen to yield up to some 1740 kg ha^{-1} of rock. Such amount, regarded by the author as irrelevant for the specific small study area in the Beit-Oren region, can give an idea of the possible contribution of endoliths to pedogenesis in the Mount Carmelo area as well as in other Mediterranean ecosystems in Israel or in similar ecosystems in the Mediterranean region. Findings of the same study indicate the importance of corrosion patterns in the postfire recolonisation of rock outcrops by lithobionts, because of the water-holding capacity of empty holes and pits and the possible deposition of soil and rock particles, organic matter and fire ash in this microrelief.

4. Neogenesis of minerals

In the weathered material localised at the rock–lichen interface and in the thallus itself, secondary products can be formed by dissolving and chelating actions of the biological processes associated with lichen growth. In the following paragraphs we report about the principal biominerals groups mentioned in the literature as formed as a result of lichen growth on rocks. It should be emphasised that unless ''in situ'' techniques are not applied to detect and determine these new mineral phases, two potential sources of misinterpreted results should always be taken into account. The first is the possible wind- or rainwater-born ''contamination'' along with the serious difficulty in distinguishing between weathering and bio-weathering products. The second could arise from procedures for samples preparation. Typically, the removal of organic matter through H_2O_2 treatment which leads to oxalic acid production (Farmer and Mitchell, 1963; Jackson, 1975). In lichen–mineral studies the formation of insoluble oxalates might be possible as a result of this treatment.

4.1. Oxalates

The reaction of oxalic acid secreted by many lichen-forming fungi with the minerals of the rock leads to the precipitation of oxalates. A close relationship exists between the chemical composition of the substratum and the type of insoluble oxalate accumulating immediately beneath or within the thallus.

On calcareous rocks, such as limestone and dolomite, as well as on rocks containing calcium-bearing minerals, calcium oxalate is predominant, usually whewellite, $CaC_2O_4 \cdot H_2O$, sometimes weddellite, $CaC_2O_4 \cdot (2+x)H_2O$, (Syers

and Iskandar, 1973; Jones et al., 1980; Ascaso et al., 1982, 1990; Vidrich et al., 1982; Adamo and Violante, 1989; Adamo et al., 1993; Wierzchos and Ascaso, 1994). The monohydrate form has monoclinic symmetry and a flat, platy morphology (Fig. 3a). Its main diagnostic X-ray reflections are at 0.593, 0.365 and 0.297 nm. The polyhydrate has tetragonal symmetry, tends to show bipyramidal- or tetragonal-prismatic habits (Fig. 3b) with strong reflections at 0.618, 0.442 and 0.278 nm.

The occurrence of calcium oxalates on the outer surface of hyphae within the lichen thallus or on the upper cortex suggests the extracellular formation of the crystals. As observed in several higher plants, it has been suggested that the crystals are initially formed intracellularly, within the wall of the hyphae, and, as they increase in length, their distal ends protrude through the hyphal wall (Pinna, 1983). In lichenized rock thin sections calcium oxalate crystals in the thallus and in the contact zone can be easily detected with the optical microscope by their high interference colours in crossed polarised light (Fig. 3c).

A need for the lichen to dispose of an excess of calcium is probably the main reason for the formation of calcium oxalate. Nevertheless, there is evidence of calcium oxalate occurrence in lichens colonising substrates, including brick, wood and bark, where calcium is almost absent (Wadsten and Moberg, 1985). These cases might be due to a reaction between oxalic acid produced by the lichen and calcium present in run-off.

The factors determining the formation of either the monohydrate or the polyhydrate phase are yet to be clarified. Whewellite is the stable phase of the system calcium oxalate/water. Weddellite is metastable. It tends to disappear from the system if 'stored' in water. A solid-state transformation of the polyhydrate structure into that of the monoclinic monohydrate structure is not possible. Weddellite may transform into whewellite only through dissolution of the polyhydrate crystals (Frey-Wyssling, 1981). Horner et al. (1985) have suggested that high pH and a high Ca/oxalic acid ratio are generally necessary for weddellite formation. At low pH the polyhydrate dissolves and is reprecipitated as whewellite. According to Ascaso et al. (1982) the two forms are related to the amount of water. In the absence of hydration water on the rocks, calcium oxalate monohydrate rather than calcium oxalate polyhydrate is preferentially formed.

The various hydrates may have some role in the water balance of the lichens, known to be very tolerant to desiccation (Wadsten and Moberg, 1985). Weddellite accommodates in the structure mobile zeolitic water molecules, which can be lost becoming available to the lichen. The presence of the polyhydrate phase in dry sites may therefore serve as a source of water.

From substrate rocks, where calcium is present in low amounts, other oxalates may originate.

In the Grampian Region (Scotland) on outcrop of serpentinite, a rock consisting almost entirely of magnesium silicate minerals with very low calcium
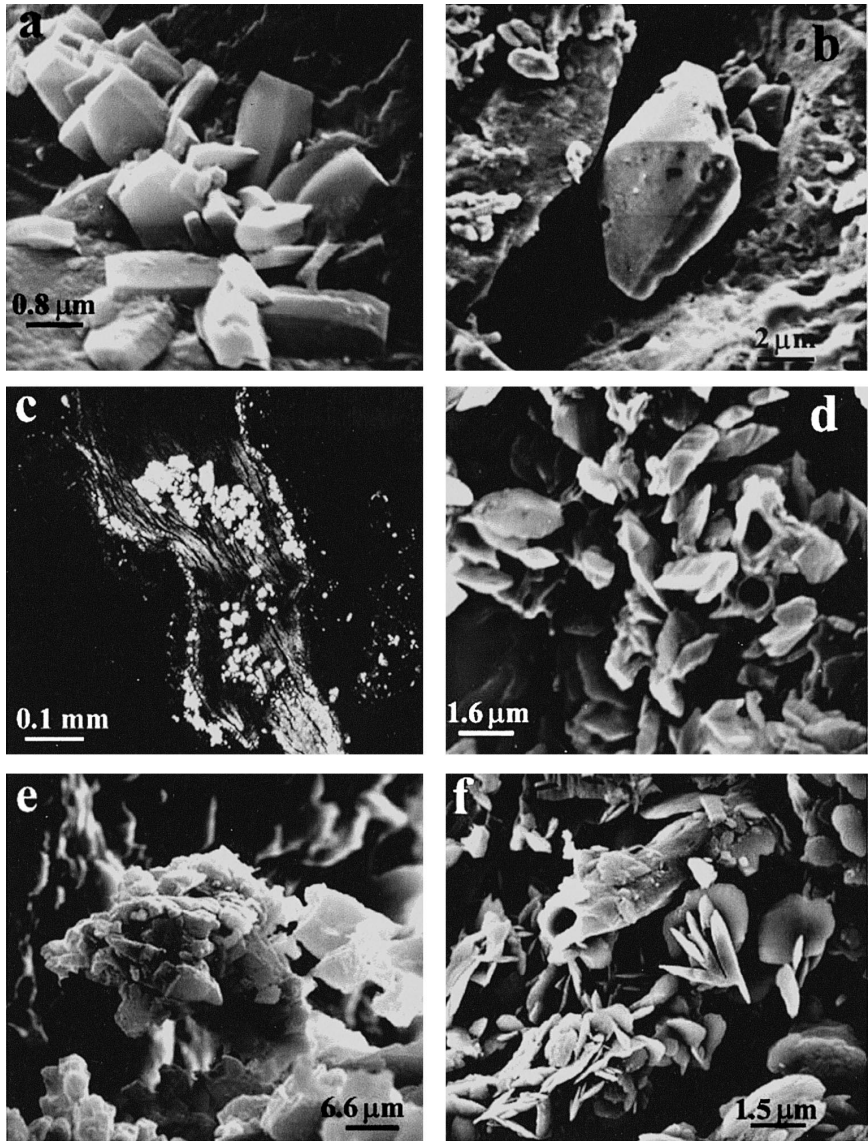
Fig. 3. Scanning electron micrographs of: (a) platy crystals of calcium oxalate monohydrate (whewellite) at the dolerite rock– *Parmelia subrudecta* interface (from Adamo et al., 1993); (b) bypiramidal crystals of calcium oxalate dihydrate (weddellite) at the dolomite rock– *Lepraria* genus lichen interface (from Adamo and Violante, 1989). Thin-section micrograph (crossed polarized light) of (c) calcium oxalate crystals in the thallus of *Stereocaulon vesuvianum* (from Adamo, 1996). Scanning electron micrographs of: (d) crystals of magnesium oxalate dihydrate (glushinskite) in the thallus of *Lecanora atra* encrusting serpentinite (from Wilson et al., 1981); (e) manganese-rich crystals in the thallus of *Pertusaria corallina* growing on manganese ore (from Wilson and Jones, 1984); (f) copper oxalate crystals (moolooite) encrusting medullary hyphae within *Acarospora rugulosa* growing on cupriferous substrates (from Purvis, 1984).

content, appreciable amounts of crystalline magnesium oxalate dihydrate — the mineral glushinskite (Wilson et al., 1980) — were found in the thallus of *Lecanora atra* as well as at the rock–lichen interface (Wilson et al., 1981). The mineral occurs as tiny crystals ranging from 2 to 5 μm in size, the majority showing a distorted pyramidal form (Fig. 3d). Its main X-ray reflections are found at 0.489, 0.317, 0.238, 0.204 and 0.186 nm. Microprobe analysis of the glushinskite shows that it contained significant amounts of nickel, iron and manganese. More recently $MgC_2O_4 \cdot 2H_2O$ has been described from the Island of Rhum in the Inner Hebrides of Scotland where it may form by lichen activity on magnesium-rich rocks (Wilson and Bayliss, 1987).

Accumulations of poorly formed sub-equant, blocky manganese-rich crystals, which have been proved to be manganese oxalate dihydrate by X-ray diffraction (main X-ray powder reflections at 0.483, 0.472, 0.301 and 0.267 nm), have resulted from the interaction between a manganese ore, consisting of hard cryptomelane, KMn_8O_{16}, and powdery lithiophorite, $(Al,Li)MnO_2(OH)_2$ and the lichen *Pertusaria corallina* (Fig. 3e) (Wilson and Jones, 1984).

The occurrence of vivid blue inclusions of copper oxalate hydrate, later recognized as the mineral moolooite (Chisholm et al., 1987), in lichens growing on cupriferous substrates has been revealed by the work of Purvis (1984). The blue crystalline material consists of aggregates of platy crystals 1–3 μm in diameter encrusting medullary hyphae (Fig. 3f). The X-ray diffraction pattern is characterised by a very strong reflection at 0.388 nm and medium intensity reflections at 0.194, 0.177 and 0.171 nm, all other reflections being weak or very weak.

In principle, it seems likely that a range of previously unreported oxalate minerals may exist where oxalic acid-secreting lichens have colonised substrates of appropriate composition. On the basis of the crystallographic studies of Lagier et al. (1969) and Dubernat and Pezerat (1974), Wilson et al. (1980; 1981) suggested that magnesium could be substituted by nickel, cobalt, iron, zinc and manganese in the glushinskite structure, similar to, and isomorphous with, the dihydrated oxalates of these elements. Purvis (1984) also considers the feasibility of the precipitation of the relatively insoluble oxalates of barium, lead and silver.

So far, only the detection of non-hydrated ferric oxalate $(C_6O_{12}Fe_2)$, giving X-ray peaks at 0.530, 0.438 and 0.348 nm, in *Caloplaca callopisma* growing on Fe-rich dolomite has been reported (Ascaso et al., 1982). Apparently ferrous iron oxalate, the already well-known mineral humboldtine, is absent in the weathering zone between lichen and rock. The oxidation, possibly microbial, of organic molecules complexing Fe^{2+}/Fe^{3+}, with subsequent hydrolysis and precipitation of more or less crystalline iron oxides has been claimed as a probable process to which the finding may be ascribed (Jones and Wilson, 1986; Adamo et al., 1997).

The incorporation of heavy metal ions into oxalates within the lichen thallus, but external to the protoplasm, seems to be related with the well-known ability of lichens to avoid the effects of toxic elements (Jones and Wilson, 1985; Wilson, 1995; Purvis, 1996; Purvis and Halls, 1996). Recently, extracellular immobilisation of Zn and Pb as oxalate salts in the lichen metal hyperaccumulator *Diploschistes muscorum*, collected in the vicinity of a (Zn,Pb)S smelter located at Auby in the North of France, has been revealed by Sarret et al. (1998), coupling powder X-ray diffraction (XRD) by extended X-ray absorption fine structure (EXAFS) spectroscopy.

4.2. Iron oxides and hydroxides

The biogenic formation of iron oxides and hydroxides minerals is obvious from the colour of the rock surface beneath the lichen thallus. In 1970, Jackson and Keller found a considerable enrichment in Fe of the reddish weathering crust of *Stereocaulon vulcani*-covered Hawaii lava flows. An unidentified, poorly crystallised form of ferric oxide, metastable with respect of hematite, and distinctly different from the iron oxide occurring in the lichen-free rock crust was detected. Possibly this amorphous ferruginous oxide may be the actually well known mineral ferrihydrite, more recently reported in a thin ochreous layer at the interface between *Pertusaria corallina* and a weathered basalt substrate in Western Scotland (Jones et al., 1980) and in the rusty ferruginous material frequently located in the zone of contact between the thallus of *Stereocaulon vesuvianum* and the leucite-bearing rock of Mt. Vesuvius (Adamo et al., 1997). Ferrihydrite is a short-range order iron oxyhydroxide structurally resembling hematite. It forms very small spherical particles, 3 to 7 nm in diameter, which usually are highly aggregated (Fig. 4a). According to its crystallinity, it gives rise to XRD and electron diffraction patterns characterised by a variable number of very broad peaks at about 0.25, 0.22, 0.197, 0.173 and 0.147 nm (Fig. 4b). Unlike most other Fe oxides it is nearly completely soluble in acid ammonium oxalate in the dark. Differential X-ray diffraction (DXRD) of an untreated and an oxalate-treated sample may be required for positive identification. The difficulty of distinguishing between ferrihydrite and feroxyhite, with similar structures and X-ray lines, implies the possibility that this iron oxyhydroxide may also be significantly present among the secondary products formed as a result of lichen weathering.

Goethite is by far the most common form of crystalline iron oxide occurring at the rock/lichen interface. On several occasions Ascaso et al. (1976) have observed twinned crystals of α-FeOOH beneath the thallus of *Rhizocarpon geographicum* growing on granite (Fig. 4c). An aluminium-containing goethite has been detected by Jones et al. (1981) in an ochreous coating on the surface of *Tremolecia atrata* (as ''*Lecidea dicksonii*'') encrusting a biotite chlorite schist. Again, Galvan et al. (1981) find considerable amounts of iron oxides (goethites)
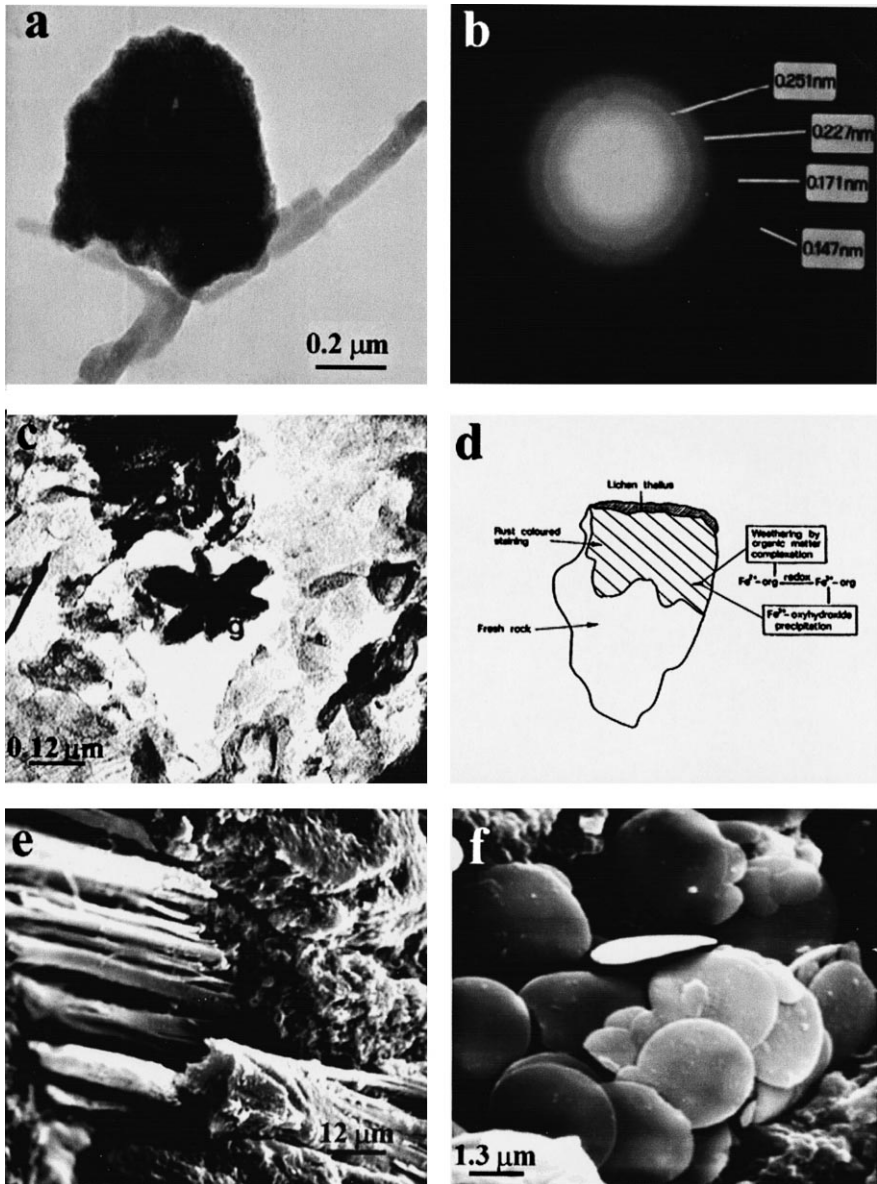
Fig. 4. Transmission electron micrograph (a) and electron diffraction pattern (b) of ferrihydrite from the rusty interface between *Stereocaulon vesuvianum* and volcanic rock (from Adamo et al., 1997). (c) TEM of twinned goethite at the interface between the thallus of *Rhizocarpon geographicum* and granite substrate (from Ascaso et al., 1976). (d) Diagrammatic representation of iron complexation and translocation under lichen thallus (from Adamo et al., 1993). Scanning electron micrographs of: (e) fibrous silica gel at interface between serpentinite rock and lichen *Lecanora atra* (from Jones et al., 1981); (f) Silica-rich microdiscs at serpentinite rock–*Caloplaca* sp. interface (from Adamo et al., 1993).

in the material from the interfaces between various lichens and a garnet-chloritoid and quarzite schist. However, the authors do not ascribe any significance to this finding because the mineral was already present in the parent rock.

Recently, small (0.1–0.3 μm) hexagonal plates of hematite, as well as acicular shaped goethite crystals, have been found by Adamo et al. (1997) in the iron-rich material surrounding the basal part of *Stereocaulon vesuvianum* thallus.

In iron-rich dark sandstones of the Antarctic cold desert iron solubilisation has been observed to take place in the cryptoendolithic lichen zone (Friedmann, 1982). As a result, the thin crust above the lichen and the rock substrate a few millimeters below appear darker because of iron deposition. Precipitated iron compounds (probably hematite or goethite, or both) have been found to cover the colourless fungal hyphae penetrating the rock substrate.

It seems likely that the organic acids produced by lichens play a key role in the formation and enrichment of poorly-ordered and crystalline Fe phases at the rock–lichen interface. Presumably the biomolecules complex Fe, primarily released from Fe(II) silicates on weathering, and link the small ferrihydrite particles, preventing, in both cases, the formation of more crystalline iron oxides (Schematization shown in Fig. 4d). Processes of transformation of poorly-ordered oxyhydroxides as well as reactions of oxidation/precipitation of Fe^{2+} would account for the neoformation of more crystalline phases. Differentiation of the rock–lichen interface into microsites each with separate pH, humidity and redox potential conditions may result in the genesis of either goethite or hematite (Schwertmann et al., 1986).

4.3. Siliceous relicts

The formation of siliceous relicts as a result of the intense mineral decomposition produced by lichens has been widely reported (Ascaso et al., 1976; Jones et al., 1981; Wilson et al., 1981). The preferential extraction of structural magnesium from the silicate chrysotile by oxalic acid secreted by the mycobiont of *Lecanora atra* left behind an X-ray amorphous silica gel often retaining the fibrous morphology of the parent mineral (Fig. 4e) (Wilson et al., 1981).

Microprobe analysis of individual flakes of biotite, incorporated into a culture medium of an oxalic acid producing fungus, shows that the decomposition of the layer silicate resulted in the removal of all elements, with the exception of silicon, and reveals that acid attack generally proceeded from the edge of the flake and progressed towards the centre (Jones et al., 1981).

Amorphous silica has been found to be associated with *Parmelia conspersa* growth on granite and gneiss. Thallus fragments from the same lichen are even able to generate in vitro SiO_2 from the three primary rock forming minerals, quartz, micas and feldspars (Ascaso et al., 1976).

Silica in the form of microdiscs a few microns in diameter has been observed at the interface between quartz and *Acarospora hospitans* and between serpentinite rock and *Caloplaca sp.*, suggesting, as for phytoliths, dissolution, absorption and excretion of the element (Fig. 4f) (Robert et al., 1983; Adamo et al., 1993).

4.4. Alumino-silicates

Poorly ordered alumino-silicates, intimately admixed with rock-forming minerals, phyllosilicates and ferrihydrite, have been found in the weathering crust at the rock–lichen interface (Jones et al., 1980; Adamo and Violante, 1991). Electron micrographs (Fig. 5a) show that these amorphous Al–Si materials consist of microaggregates of very finegrained particles yielding a diffuse and poorly defined electron diffraction pattern (Adamo and Violante, 1991). According to Wilson and Jones (1983) their formation is presumably related to the effectiveness of lichens in complexing and removing aluminium from the substrate minerals by organic compounds. The biotic oxidation of these organo-mineral complexes would liberate Al in a reactive form to combine with silica. Farmer (1979) reports a similar mechanism of formation in the podzolic B horizons of an X-ray amorphous alumino-silicate complex called proto-imogolite allophane. Recently, allophanes and imogolite fibres have been detected by electron microscopy under the thallus of *Xanthoria elegans* growing on volcanic andesite in maritime Antarctica (Ascaso et al., 1990).

Many authors (Jackson and Keller, 1970; Jones et al., 1980; Wilson et al., 1981; Vidrich et al., 1982) suggest caution in considering possible the neogenesis of well-ordered alumino-silicates in the zone of contact between lichen and rock substrate. 'Biochemical' weathering, differently from 'geochemical', oc-
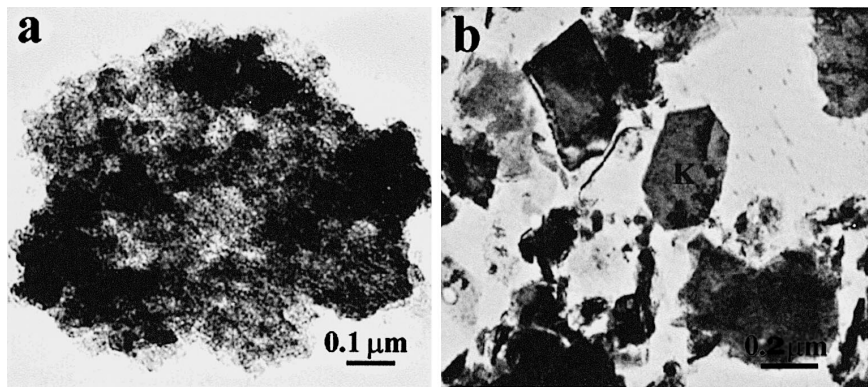

Fig. 5. Transmission electron micrographs of: (a) amorphous alumino-silicates of the fine clay fraction ($\varnothing < 0.5$ μm) from the volcanic rock–*Stereocaulon vesuvianum* interface material (from Adamo and Violante, 1991); (b) kaolinite (K) crystals at the interface between the thallus of *Parmelia conspersa* and granite substrate (from Ascaso et al., 1976).

curs through the mediation of complexing organic acids and this condition would severely limit the crystallisation to clay minerals leading rather to the preferential formation of poorly ordered phases.

On the other hand, various phyllosilicates have been identified in the weathered material accumulated at the rock–lichen interface. Halloysite and kaolinite have been frequently noted by Ascaso et al. (1976) under the thalli of *Parmelia conspersa* and *Rhizocarpon geographicum* either on granite or gneiss substrate (Fig. 5b). Furthermore, these newly formed minerals and montmorillonite, have been generated in laboratory experiments by incubating fragments of the lichen thalli or extracts of selected lichen compounds (atranorin, usnic acid, stictic acid and norstictic acid) with either rock samples or their primary minerals (albite, orthoclase, biotite and muscovite) (Ascaso and Galvan, 1976; Ascaso et al., 1976). Some micas of the illite type, which may be degradation products of various phyllosilicates in the rock, have been identified beneath of the thallus of *Lecidea lapicida* collected from volcanic andesite in South Shetland Islands (Ascaso et al., 1990). X-ray diffractometer traces of the fine fraction separated
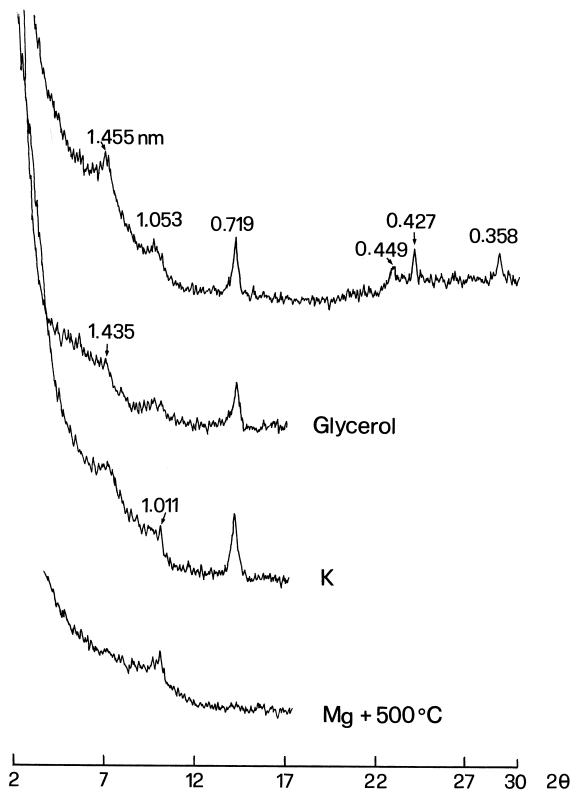

Fig. 6. X-ray diffractometer traces (CoK_α radiation) of the clay fraction ($\varnothing < 2.0$ μm) from the weathered material beneath the lichen *Stereocaulon vesuvianum* colonising leucitic rock of Mt. Vesuvius (from Adamo, 1996).

from the weathered material beneath the lichen *Stereocaulon vesuvianum* colonising leucitic rock of Mt. Vesuvius revealed the occurrence of various clay minerals. Ethylene glycol solvation and heating at 550°C demonstrated kaolinite, illite and a 1.4 nm intergrade mineral presence (Fig. 6) (Adamo, 1996; Adamo and Violante, 1991). These clay minerals commonly occur in Andisols of temperate climate regions and particularly have been found in the clays of soils developed on central-southern Italy volcanic materials of petrological composition similar to that of Mt. Vesuvius. With the exception of illite, probably inherited from mica in the parent material, they are believed to originate to a large extent by neoformation reactions, rather than by transformation of pre-existing phyllosilicate structures (Violante and Wilson, 1983). Recently, Wierzchos and Ascaso (1996) have observed distinct depletion of interlaminar potassium in adhesion zones of *Parmelia conspersa* and *Aspicilia intermutans* thalli, on granitic biotite sheets (Fig. 7a and b). On the bases of the geochemical mass
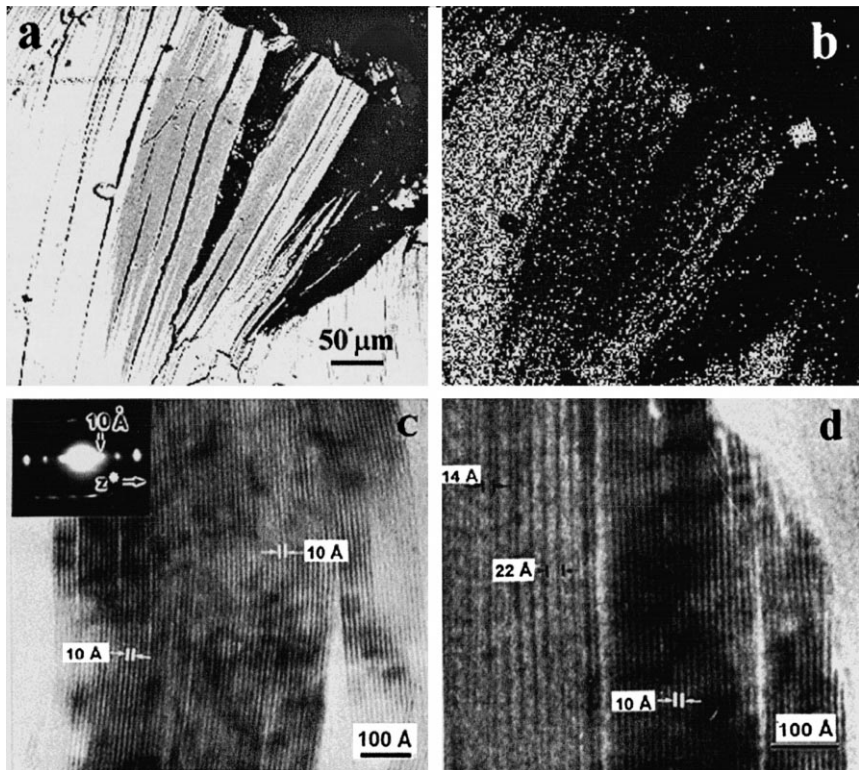

Fig. 7. SEM back-scattered electron image of (a) the interface zone between the *Parmelia conspersa* thallus and granitic biotite sheets. (b) X-ray distribution map of K in (a). HRTEM images of lattice fringes of octadecylammonium ion treated (c) unaltered biotite revealing the 10 Å basal spacing and (d) ordered bioweathered biotite, interstratified biotite (10 Å) and vermiculite (14–30 Å) phases from the lichen–biotite contact area (from Wierzchos and Ascaso, 1996, 1998).

balance of the K-rich and K-poor biotite zones, the authors suggest the transformation of K-rich biotite to scarcely altered biotite with a biotite–vermiculite (hydrobiotite-like) intermediate interstratified phase. In a more recent high resolution transmission electron microscopy (HRTEM) study of the carefully extracted mineral material Wierzchos and Ascaso (1998) have further demonstrated the biogenetic vermiculitization of biotite. A homogenous 10 Å *d(001)*-space, unaffected by octadecylammonium chloride treatment, was observed for unweathered biotite samples within and on the surface of the fresh parent granitic rock (Fig. 7c). Nevertheless, HRTEM image of lattice fringes of biotite taken from the lichen–biotite contact zone after ODA treatment revealed large area of both unexpanded (10 Å) and expanded (14–30 Å) layers of phyllosilicates identified as interstratified biotite/vermiculite (Fig. 7d).

It is difficult to be certain whether clay minerals are newly formed in the rock–lichen contact area or whether they derive from extraneous sources in the form of wind-borne dust trapped by lichen thalli. Their ordered nature makes it unlikely their formation in the same environment that favours the formation of amorphous and poorly ordered materials. Nevertheless, the possibility that at the rock–lichen interface the accumulation of various cations and organic compounds, with peculiar number and location of hydroxyl and carboxyl groups and stability of their complexes, combined with specific physico-chemical parameters might create conditions favorable to phyllosilicate genesis cannot be discounted entirely.

4.5. Carbonates

Calcite, in form of rhizomorphic features and cytomorphic sands, has been frequently observed at the surface of hyphae or roots and inside hyphae (Robert and Berthelin, 1986); however, until recently, only two cases of carbonates formation by lichen activity on rocks have been reported. The first is the detection of hydrocerussite, a basic lead carbonate $[Pb_3(CO_3)_2(OH)_2]$, in the thallus of *Stereocaulon vesuvianum* growing on siliceous limestone in the ruins of a flue from a lead-smelting mill (Jones et al., 1982). Although no obvious crystalline form yielding a lead signal on probing was discernible by scanning electron microscopy, the X-ray diffraction pattern obtained from tufts of mycelium sampled near the rock surface, almost identical to that of the mineral hydrocerussite, proves the occurrence of the carbonate mineral (Table 1). The second example is the identification by X-ray analysis and IR spectroscopy of a small amount of calcite in the contact area between the endemic Antarctic lichen *Bacidia stipata* and its rock substrate, a volcanigenic sediment classified as clastic (Ascaso et al., 1990). In this study many bacteria were found underneath and inside the lichen thallus in the weathered area of the rock. This observation could suggest a contribution of the co-existing microorganisms (bacteria, cyanobacteria, algae or fungi) to the alteration of the substrate. Lichens,

Table 1

X-ray powder data for (1) Hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] from the JCPDS Powder Diffraction File Card No. 13-131, and (2) hyphal tufs from *Stereocaulon vesuvianum* near rock surface (from Jones et al., 1982)

(1)		(2)	
d (Å)	I/I_1	d (Å)	I
7.80	5	–	
4.47	60	4.46	m
4.25	60	4.26[a]	
3.61	90	3.61	s
3.29	90	3.27	m
2.715	20	2.719	w
2.623	100	2.629	v.s.
2.491	30	–	
2.261	10	–	
2.231	50	2.237[a]	
2.120	30	2.128[a]	
2.099	20	2.106	w
2.046	30	2.053	m
1.884	20	–	
1.856	30	–	
1.696	40	1.701	m

[a]These reflections are also partly attributed to quartz. v.s. = very strong, s = strong, m = medium, w = weak, d = spacings in Angstroms (Å). I = intensity.

according to Viles (1987), may be best viewed as one component in a complex weathering system which in some circumstances play a dominant role.

4.6. Lichen acid–metal complexes

The formation of soluble, frequently coloured complexes resulting from the reaction of certain lichen compounds, or ground lichens with water suspensions of minerals and rocks, represented the first indirect evidence of mineral weathering by 'lichen acids' (Schatz, 1963; Syers, 1969; Iskandar and Syers, 1972). Later, Ascaso and Galvan (1976) and Ascaso et al. (1976) observed the morphological and structural alterations of granite, gneiss and their primary minerals due to treatment with saturated solutions of lichen compounds (atranorin, norstictic acid, stictic acid and usnic acid). These substances, after promoting the release of cations, give rise to new minerals in the laboratory. However, only recently, Purvis et al. (1985; 1987; 1990) have conclusively demonstrated the formation of lichen acid–metal complexes under natural conditions. As a tentative and new hypothesis, they have suggested that the unusual green surface coloration and copper contents of c. 5% of the dry weight observed in specimens of *Acarospora smaragdula* and *Lecidea lactea* collected from cupriferous substrata could be due to the presence of a Cu-norstictic acid
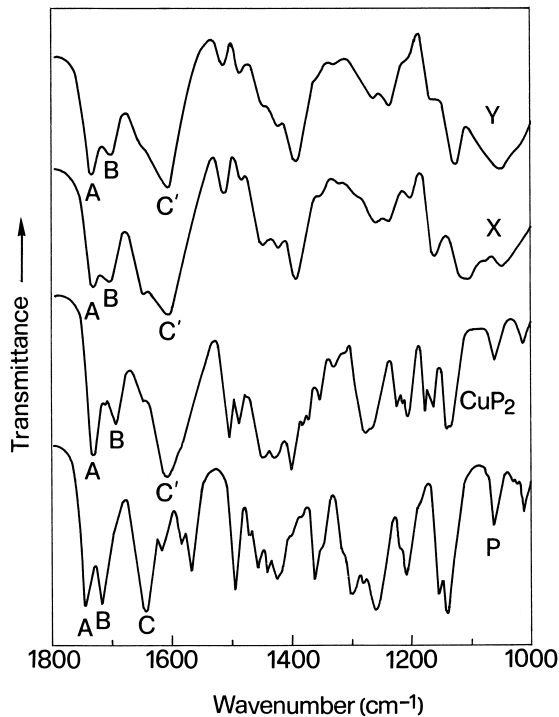
Fig. 8. IR absorbance spectra of psoromic acid (P), a synthetic copper-psoromic acid complex (CuP$_2$) and copper-rich material from the lichens X = *Lecidella bullata* and Y = *Tephromela testaceoatra* (from Purvis et al., 1990).

complex (Purvis et al., 1985). This compound has been conclusively identified by infrared absorption spectroscopy. Optical microscopy, scanning electron microscopy and electron microprobe analysis have shown that complexetion of copper by norstictic acid occur within the cortex of the lichens (Purvis et al., 1987). More recently, complexation of copper by psoromic acid in the apothecia of *Lecidella bullata* and in the thallus of *Tephromela testaceoatra* from similarly cupriferous substrata has been further demonstrated (Purvis et al., 1990) (Fig. 8). Purvis et al. (1987) have suggested that, like the extracellular metal-oxalates formation, a wide variety of hitherto unidentified compounds can be found as a result of the interaction between lichen biochemistry and the geological environment. Nevertheless, lichen acid–metal complexes, although seem to be crystalline observed in transversal lichen–rock sections in polarised light, have not yet been identified by X-ray diffraction.

5. Biodeterioration produced by lichens on historical monuments

In the past 20 years, notable attention has been given to the study of the relationships between lichens and man-made substrata. Lichens are very com-

mon on artistic stoneworks and contribute to their deterioration, frequently creating serious problems for their recovery, restoration and conservation. Lichen coverage alters monuments aesthetically, inducing colour changes and obscuring detail of sculpture and paintwork. Recent literature on this topic has been reviewed by Piervittori et al. (1994; 1996; 1998).

Biogeophysical and biogeochemical deterioration has been mainly identified in the fracturing of substratum surfaces and in the build-up of encrustations formed as a result of the reaction between lichen by-products and the minerals in the stone. Extensive erosion of the material has been often observed.

Conventional and Fourier Transform Raman spectroscopic methods, with visible and near infrared laser excitation, have been proved to be effective in the interpretation and characterisation of both the physical and chemical effects on historic monuments, frescoes and other works of art brought about by the action of certain aggressive lichens (Edwards et al., 1991, 1992, 1997; Seaward and Edwards, 1995, 1997; Seaward et al., 1995). These techniques, which use very small amounts of material, in the nanogram–picogram range, and low laser power for sample illumination, are non-destructive of the valuable samples; they have permitted, for example, microscopical investigation of the chemical nature of the gradient through the lichen thallus, the substratum, and their interface. The detection of complex chelating ''lichen acids'' and the identification of the state of hydration of calcium oxalate in lichen encrustations have been achieved. In addition, the presence of incorporated material, such as calcite, gypsum and paint pigments has been shown.

The ambient urban climate and associated atmospheric pollutants dramatically affect the lichen flora. Strong evidence has been produced to suggest that modified environmental conditions have been conducive to increasing detrimental invasion by certain aggressive lichen species such as *Dirina massiliensis* forma *sorediata*. This lichen is extending its ecological range due to its reproductive strategy and its ability to exploit diverse substrata, facilitated by new environmental regimes, including qualitative changes in atmospheric pollution, which have frequently allowed it to dominate in the wake of the rapid disappearance of other more pollution-sensitive species. It is now commonly found on a range of works of art throughout Europe (Edwards et al., 1997).

In their first review of the literature, Piervittori et al. (1994) drew attention to the need to avoid generalization about the effects that lichens may have on stonework substrata. In interpreting and evaluating the role of lichens in the biodeterioration of monuments the species-specific differences in weathering ability, the physical and chemical nature of the substrata and the microclimatic conditions, particularly in terms of water retention, have to be carefully taken into consideration. The principal causes of lichen colonization, the factors that may accelerate the growth rate of the species involved, their reproductive strategies and the consequences arising from their elimination have to be systematically gathered.

It cannot always be said that lichen encrustations are detrimental to their immediate substrates. Indeed, it has been sometimes suggested that the organisms may play a protective role in this respect (Seaward et al., 1989). Biodeterioration and bioprotection are in an unstable equilibrium which can be unbalanced by environmental conditions, the substratum and the type of organisms colonising the monument. This has been exemplified in the sandstone pavement of the forum of the Roman city of Baelo Claudia (Cadiz, Spain), where the flagstones without lichen cover show higher deterioration than those colonised by lichens (Ariño et al., 1995). In this particularly aggressive environment the combined effects of wind, salt and water easily disintegrate a fragile substratum. Although the lichen–sandstone interface shows some weathering, namely disaggregation, calcium oxalate deposition and crystal etching, biodeterioration is a much slower process than physical and chemical deterioration: sometimes lichens can even represent a protective cover for the stones. In a porous substrate, like the sandstone of the Baelo Claudia forum pavement (Ariño et al., 1995), the presence of lichen retards rainwater absorption, partially lessening dissolution and precipitation processes, and it also prevents the abrasive action produced by airborne sand particles, the impact of raindrops and changes in temperature.

Extensive, homogeneous, yellow-brown films mainly composed of calcium oxalate, both monohydrate (whewellite) and bihydrate (weddellite) are frequently observed on artefacts of historic and artistic interest, on buildings, sculptures and archaeological remains independently of the substrate. One of the main hypotheses proposed for the formation of the films involves the production of oxalic acid by lichens which could have colonised the monuments presumably favoured by the unpolluted atmosphere of the past (Del Monte, 1991; Del Monte and Sabbioni, 1987; Del Monte and Ferrari, 1989; Seaward and Edwards, 1997). However, according to many authors, only in a limited number of cases can the origin of oxalate films be related to lichen activity (Franzini et al., 1984; Matteini and Moles, 1986; Alessandrini et al., 1989).

6. Conclusions

The weathering ability of lichens with respect to their mineral substrates has long been recognised and many papers have been published in this century documenting the physical and chemical processes involved. The bioweathering seems to consists of: (a) a more or less intense disaggregation and fragmentation of the rock surface immediately below the lichen by surface adhesion and hyphal penetration, (b) dissolution processes and (c) the precipitation and formation of new minerals. The detailed understanding of the mechanisms and processes involved in lichens weathering of mineral surfaces has given a most

significant contribution to explain the biodeterioration phenomena of stonework of monuments and other archeological materials.

Many of the papers referred to in this review indicate that oxalic acid and 'lichen acids' must be considered biomolecules extremely active as weathering agents. Oxalates, whose nature depends upon the composition of the substrate, are the best studied lichen biominerals and are commonly found in the thallus and/or at the rock/lichen interface. The suspected involvement of 'lichen acids' has been conclusively demonstrated in the last decade. Crystalline salts of ''lichen acids'' containing metal cations derived from the mineral substrate have been shown to occur in the thallus. It is likely that more oxalate/'lichen acid'-derived minerals could be described in the future. Furthermore, other simple low-molecular-weight organic acids (e.g., citric, lactic and tartaric acid), known to be produced by fungi, are presumably excreted by lichen mycobionts in much the same way as oxalic acids. Humic and fulvic acids could be produced from the decomposition of lichen residues. The effectiveness of these compounds in the decomposition of soil minerals by both the acidic effect and complex formation or chelation is well known. Although the lack of experimental evidence, they are expected to play an analogous important role in lichen weathering. Hence, much remains to be studied to fully elucidate the interaction between lichens and mineral surfaces. The application of more specialised instrumental and analytical techniques and the close collaboration among biologists, chemists and mineralogists are fundamental requisites for future progress.

Acknowledgements

References

Adamo, P., 1996. Ruolo dell'attività dei licheni nell'alterazione di substrati rocciosi e nella neogenesi di entità mineralogiche. Atti XIII Convegno Nazionale SICA, pp. 13–26.

Adamo, P., Colombo, C., Violante, P., 1997. Iron oxides and hydroxides in the weathering interface between *Stereocaulon vesuvianum* and volcanic rock. Clay Minerals 32, 275–283.

Adamo, P., Marchetiello, A., Violante, P., 1993. The weathering of mafic rocks by lichens. Lichenologist 25 (3), 285–297.

Adamo, P., Violante, P., 1989. Bioalterazione di roccia dolomitica operata da una specie lichenica del genere *Lepraria*. Agricoltura Mediterranea 119, 460–464.

Adamo, P., Violante, P., 1991. Weathering of volcanic rocks from Mt. Vesuvius associated with the lichen *Stereocaulon vesuvianum*. Pedobiologia 35, 209–217.

Ahmadjan, V., Hale, M.E., 1973. The Lichens. Academic Press, London, pp. 697.

Alessandrini, G., Bonecchi, R., Peruzzi, R., Toniolo, L., 1989. Caratteristiche composizionali e morfologiche di pellicole ad ossalato: studio comparato su substrati lapidei di diversa natura. In: Proc. Symp. Le pellicole ad ossalato: origine e significato nella conservazione delle opere d'arte, Centro CNR Gino Bozza, Milano, pp. 137–150.

Ariño, X., Ortega-Calvo, J.J., Gomez-Bolea, A., Saiz-Jimenez, C., 1995. Lichen colonization of the Roman pavement at Baelo Claudia (Cadiz, Spain): biodeterioration vs. bioprotection. The Science of the Total Environment 167, 353–363.

Ascaso, C., Galvan, J., 1976. Studies on the pedogenic action of lichen acids. Pedobiologia 16, 321–331.

Ascaso, C., Wierzchos, J., 1994. Structural aspects of the lichen–rock interface using back-scattered electron imaging. Botanica Acta 107, 251–256.

Ascaso, C., Wierzchos, J., 1995. Study of the biodeterioration zone between the lichen thallus and the substrate. Cryptogamic Botany 5, 270–281.

Ascaso, C., Galvan, J., Ortega, C., 1976. The pedogenetic action of *Parmelia conspersa*, *Rhizocarpon geographicum* and *Umbilicaria pustulata*. Lichenologist 8, 151–171.

Ascaso, C., Galvan, J., Rodriguez-Pascual, C., 1982. The weathering of calcareous rocks by lichens. Pedobiologia 24, 219–229.

Ascaso, C., Sancho, L.G., Rodriguez-Pascal, C., 1990. The weathering action of saxicolous lichens in maritime Antarctica. Polar Biology 11, 33–39.

Chisholm, J.E., Jones, G.C., Purvis, O.W., 1987. Hydrated copper oxalate, moolooite, in lichens. Mineralogical Magazine 51, 766–803.

Del Monte, M., 1991. Trajan's column: lichens don't live here anymore. Endeavour, New Series 15 (2), 86–92.

Del Monte, M., Ferrari, A., 1989. Patine da biointerazione alla luce delle superfici marmoree. In: Proc. Symp. Le pellicole ad ossalato: origine e significato nella conservazione delle opere d'arte, Centro CNR Gino Bozza, Milano, pp. 171–182.

Del Monte, M., Sabbioni, C., 1987. A study of the patina called ''*scialbatura*'' on imperial Roman marbles. Studies in Conservation 32, 114–121.

Dubernat, P.J., Pezerat, H., 1974. Fautes d'empilement dans les oxalates dihydratés des métaux divalents de la séries magnésienne (Mg, Fe, Co, Ni, Zn, Mn). Journal of Applied Crystallography 7, 387–394.

Edwards, H.G.M., Farwell, D.W., Seaward, M.R.D., Giacobini, C., 1991. Preliminary Raman microscopic analysis of a lichen encrustation involved in the biodeterioration of Renaissance frescoes in central Italy. International Biodeterioration 27, 1–9.

Edwards, H.G.M., Farwell, D.W., Jenkins, R., Seaward, M.R.D., 1992. Vibrational Raman Spectroscopic Studies of calcium oxalate monohydrate and dihydrate in lichen encrustations on Renaissance frescoes. Journal of Raman Spectroscopy 23, 185–189.

Edwards, H.G.M., Farwell, D.W., Seaward, M.R.D., 1997. FT-Raman spectroscopy of *Dirina massiliensis* f. *sorediata* encrustations growing on diverse substrata. Lichenologist 29 (1), 83–90.

Farmer, V.C., 1979. Possible roles of a mobile hydroxyaluminium orthosilicate complex (proto-

imogolite) in podzolization. In: Migrations organo-minérales dans les sols tempérés. International Colloquium of C.N.R.S., Nancy, No. 303, pp. 275–279.

Farmer, V.C., Mitchell, B.D., 1963. Occurrence of oxalates in soils clays following hydrogen peroxide treatment. Soil Science 96, 221–229.

Franzini, M., Gratzui, C., Wicks, E., 1984. Patine ad ossalato di calcio sui monumenti marmorei. Società Italiana di Mineralogia e Petrologia 39, 59–70.

Frey-Wyssling, A., 1981. Crystallography of the two hydrates of crystalline calcium oxalate in plants. American Journal of Botany 68, 130–141.

Friedmann, E.I., 1982. Endolithic organisms in the Antarctic cold desert. Science 215, 1045–1053.

Fry, E.J., 1924. A suggested explanation of the mechanical action of lithophytic lichens on rocks (shale). Annals of Botany 38, 175–196.

Fry, E.J., 1927. The mechanical action of crustaceous lichens on substrata of shale, schist, gneiss, limestone and obsidian. Annals of Botany 41, 437–460.

Galvan, J., Rodriguez, C., Ascaso, C., 1981. The pedogenetic action of lichens on metamorphic rocks. Pedobiologia 21, 60–73.

Garty, J., 1992. The postfire recovery of rock-inhabiting algae, microfungi and lichens. Canadian Journal of Botany 70, 301–312.

Gehrmann, C., Krumbein, W.E., Petersen, K., 1988. Lichen weathering activities on mineral and rock surfaces. Studia Geobotanica 8, 33–45.

Hallbauer, D.K., Jahns, H.M., 1977. Attack of lichens on quartzitic rock surfaces. Lichenologist 9, 119–122.

Horner, H.T., Tiffany, L.H., Cody, A.M., 1985. Calcium oxalate bipyramidal crystals on the Basidiocarps of *Geastrum minus* (Lycoperdales). Proc. Iowa Acad. Sci. 92, 70–77.

Huneck, S., Yoshimura, I., 1996. Identification of Lichen Substances. Springer Verlag, Berlin.

Iskandar, I.K., Syers, J.K., 1972. Metal complex formation by lichen compounds. Journal of Soil Science 23, 255–265.

Jackson, M.L., 1975. Soil Chemical Analysis — Advanced Course, 2nd edn., 10th printing. Published by the author, Madison, WI.

Jackson, T.A., Keller, W.D., 1970. A comparative study of the role of lichens and ''inorganic'' processes in the chemical weathering of recent Hawaiian lava flows. American Journal of Science 269, 446–466.

Jones, D., 1988. Lichens and pedogenesis. In: Galun, M. (Ed.), Handbook of Lichenology, CRC Press, Boca Raton, pp. 109–124.

Jones, D., Wilson, M.J., 1985. Chemical activity of lichens on mineral surfaces — a review. International Biodeterioration 21, 99–104.

Jones, D., Wilson, M.J., 1986. Biomineralization in crustose lichens. A Review. In: Leadbeater, B.S.C., Riding, R. (Eds.), The Systematics Association Symposium on Biomineralization in Lower Plants and Animals. Oxford Univ. Press, Oxford, pp. 91–105.

Jones, D., Wilson, M.J., McHardy, W.J., 1981. Lichen weathering of rock-forming minerals: application of scanning electron microscopy and microprobe analysis. Journal of Microscopy 124, 95–104.

Jones, D., Wilson, M.J., Tait, J.M., 1980. Weathering of a basalt by *Pertusaria corallina*. Lichenologist 12, 277–289.

Jones, D., Wilson, M.J., Laundon, J.R., 1982. Observations on the location and form of lead in *Stereocaulon vesuvianum*. Lichenologist 14, 281–286.

Jones, R.J., 1959. Lichen hyphae in limestone. Lichenologist 1, 119.

Lagier, J.P., Pezerat, H., Dubernat, J., 1969. Oxalates dihydratés de Mg, Mn, Fe, Co, Ni et Zn divalants: evolution vers la forme la plus ordonnée des composés presentant des fautes de'empilement. Rev. Chim. Miner. 6, 1081–1093.

Matteini, M., Moles, A., 1986. Le patine di ossalato sui manufatti in marmo, In: Restauro del marmo-Opere e Problemi. Numero speciale OPD Restauro, Opus Libri, Firenze, pp. 65–73.

Mellor, E., 1923. Lichens and their action on the glass and leadings of church windows. Nature 25, 299–300.

Modenesi, P., Lajolo, L., 1988. Microscopical investigation on a marble encrusting lichen. Studia Geobotanica 8, 47–64.

Nimis, P.L., Tretiach, M., 1995. Studies on the biodeterioration potential of lichens, with particular reference to endolithic forms. In: De Cleene, M. (Eds.), Interactive physical weathering and bioreceptivity study on building stones, monitored by computerized X-Ray Tomography (CT) as a potential non-destructive research tool. Protection and Conservation of the European Cultural Heritage, Research Report N. 2, University of Ghent, pp. 63–122.

Ozenda, P., Clauzade, G., 1970. Les Lichens — Etude Biologique et Flore Illustrée, Masson, Paris, pp. 801.

Piervittori, R., Salvadori, O., Laccisaglia, A., 1994. Literature on lichens and biodeterioration of stoneworks I. Lichenologist 26 (2), 171–192.

Piervittori, R., Salvadori, O., Laccisaglia, A., 1996. Literature on lichens and biodeterioration of stoneworks II. Lichenologist 28, 471–483.

Piervittori, R., Salvadori, O., Isocrono, D., 1998. Literature on lichens and biodeterioration of stoneworks III. Lichenologist 30 (3), 263–277.

Pinna, D., 1983. Fungal physiology and the formation of calcium oxalate films on stone monuments. Aerobiologia 9, 157–167.

Polynov, B.B., 1945. The first stages of soil formation on massive crystalline rocks. Pochvovedenie 7, 325–339.

Purvis, O.W., 1984. The occurrence of copper oxalate in lichens growing on copper sulphide-bearing rocks in Scandinavia. Lichenologist 16, 197–204.

Purvis, O.W., 1996. Interactions of lichens with metals. Science Progress 79 (4), 283–309.

Purvis, O.W., Halls, C., 1996. A review of lichens in metal-enriched environments. Lichenologist 28 (6), 571–601.

Purvis, O.W., Gilbert, O.L., James, P.W., 1985. The influence of copper mineralization on *Acarospora smaragdula*. Lichenologist 17, 111–116.

Purvis, O.W., Elix, J.A., Broomhead, J.A., Jones, G.C., 1987. The occurrence of copper-norstictic acid in lichens from cupriferous substrata. Lichenologist 19, 193–203.

Purvis, O.W., Elix, J.A., Gaul, L., 1990. The occurrence of copper-psoromic acid in lichens from cupriferous substrata. Lichenologist 22, 345–354.

Robert, M., Berthelin, J., 1986. Role of biological and biochemical factors in soil mineral weathering, In: Huang, P.M., Schnitzer, M. (Eds.), Interactions of Soil Minerals with Natural Organics and Microbes, Soil Sci. Soc. Am., Madison, WI, pp. 453–495.

Robert, M., Veneau, G., Berrier, J., 1980. Solubilisation comparée des silicates carbonates et hydroxydes en fonction del conditions du milieu. Bull. Miner. 103, 324–329.

Robert, M., Berrier, J., Eyralde, J., 1983. Rôle des êtres vivants dans les premiers stades d'altération des minéraux. Colloq. Int. CNRS Pétrologie des altérations et des sols, Paris. Sci. Geol. 73, 95–103.

Sanders, W.B., Ascaso, C., Wierzchos, J., 1994. Physical interactions of two rhizomorph-forming lichens with their rock substrate. Botanica Acta 107, 432–439.

Sarret, G., Manceau, A., Cuny, D., Van Haluwyn, C., Déruelle, S., Hazemann, J., Soldo, Y., Eybert-Berard, L., Menthonnex, J., 1998. Mechanisms of lichen resistance to metallic pollution. Environmental Science and Technology 32, 3325–3330.

Schatz, A., 1963. Soil microorganisms and soil chelation. The pedogenic action of lichens and lichen acids. Agricultural and Food Chemistry 11, 112–118.

Schwertmann, U., Kodama, H., Fischer, W.R., 1986. Mutual Interactions between organics and iron oxides, In: Huang, P.M., Schnitzer, M. (Eds.), Interactions of Soil Minerals with Natural Organics and Microbes, Soil Sci. Soc. Am., Madison, WI, pp. 223–250.

Seaward, M.R.D., Edwards, H.G.M., 1995. Lichen-substratum interface studies, with particular reference to Raman microscopic analysis: 1. Deterioration of works of art by *Dirina massiliensis* forma *sorediata*. Cryptogamic Botany 5, 282–287.

Seaward, M.R.D., Edwards, H.G.M., 1997. Biological origin of major chemical disturbances on ecclesiastical architecture studied by Fourier Transform Raman Spectroscopy. Journal of Raman Spectroscopy 28, 691–696.

Seaward, M.R.D., Edwards, H.G.M., Farwell, D.W., 1995. FT-Raman microscopic studies of *Haematomna ochroleucum* var. *porphyrium*. In: Knoph, J.G., Schrüfer, K., Sipman, H.J.M. (Eds.), Studies in Lichenology with Emphasis on Chemotaxonomy, Geography and Phytochemistry, Berlin-Stuttgart, Bibliotheca Lichenologica, Vol. 57, pp. 395–407.

Seaward, M.R.D., Giacobini, C., Giuliani, M.R., Roccardi, A., 1989. The role of lichens in the biodeterioration of ancient monuments with particular reference to Central Italy. International Biodeterioration 25, 49–55.

Sundholm, E.G., Huneck, S., 1980. ^{13}C NMR-spectra of lichen depsides, depsidones and depsones. Chemica Scripta 16, 197–200.

Syers, I.K., 1969. Chelating ability of fumarprotocetraric acid and *Parmelia conspersa*. Plant and Soil 31, 205–208.

Syers, J.K., Iskandar, I.K., 1973. Pedogenetic significance of lichens, In: Ahmadjian, V., Hall, M.E. (Eds.), The Lichens. Academic Press, London, pp. 225–248.

Vidrich, V., Cecconi, C.A., Ristori, G.C., Fusi, P., 1982. Verwitterung Toskanischer Gesteine unter Mitwirkung von Flechten. Zeitschrift für Pflanzenerneahrung und Bodenkunde 145, 384–389.

Viles, H.A., 1987. A quantitative scanning electron microscope study of evidence for lichen weathering of limestone, Mendip Hills, Somerset. Earth Surface Processes and Landforms 12, 467–473.

Violante, P., Wilson, M.J., 1983. Mineralogy of some italian andosols with special reference to the origin of the clay fraction. Geoderma 29, 157–174.

Wadsten, T., Moberg, R., 1985. Calcium oxalate hydrates on the surface of lichens. Lichenologist 17, 239–245.

Wierzchos, J., Ascaso, C., 1994. Application of back-scattered electron imaging to the study of the lichen–rock interface. Journal of Microscopy 175, 54–59.

Wierzchos, J., Ascaso, C., 1996. Morphological and chemical features of bioweathered granitic biotite induced by lichen activity. Clays and Clay Minerals 44, 652–657.

Wierzchos, J., Ascaso, C., 1998. Mineralogical transformation of bioweathered granitic biotite studied by HRTEM: evidence for a new pathway in lichen activity. Clays and Clay Minerals 46 (3), 446–452.

Wilson, M.J., 1995. Interactions between lichens and rocks; a review. Cryptogamic Botany 5, 299–305.

Wilson, M.J., Bayliss, P., 1987. Mineral nomenclature: glushinskite. Mineralogical Magazine 51, 327–328.

Wilson, M.J., Jones, D., 1983. Lichen weathering of minerals and implications for pedogenesis, In: Wilson, R.C.L. (Ed.), Residual Deposits: Surface Related Weathering Processes and Materials, Special Publication of the Geological Society, Blackwell, London, pp. 5–12.

Wilson, M.J., Jones, D., 1984. The occurrence and significance of manganese oxalate in *Pertusaria corallina*. Pedobiologia 26, 373–379.

Wilson, M.J., Jones, D., McHardy, W.J., 1981. The weathering of serpentinite by *Lecanora atra*. Lichenologist 13, 167–176.

Wilson, M.J., Jones, D., Russell, J.D., 1980. Glushinskite, a naturally occurring magnesium oxalate. Mineralogical Magazine 43, 837–840.