

Weathering of rocks induced by lichen colonization — a review

Jie Chen^{a,*}, Hans-Peter Blume^b, Lothar Beyer^b

^a *Institute of Soil Science, Chinese Academy of Sciences, East Beijing Road 71, P.O. Box 821, Nanjing 210008, People's Republic of China*

^b *Institute of Plant Nutrition and Soil Science, University of Kiel, D-24098 Kiel, Germany*

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Abstract

The evidence presented by numerous investigations of the interface between lichens and their rock substrates strongly suggests that the weathering of minerals can be accelerated by the growth of at least some lichen species. The effects of lichens on their mineral substrates can be attributed to both physical and chemical processes. The physical effects are reflected by the mechanical disruption of rocks caused by hyphal penetration, expansion and contraction of lichen thallus, swelling action of the organic and inorganic salts originating from lichen activity. Lichens also have significant impact in the chemical weathering of rocks by the excretion of various organic acids, particularly oxalic acid, which can effectively dissolve minerals and chelate metallic cations. As a result of the weathering induced by lichens, many rock-forming minerals exhibit extensive surface corrosion. The precipitation of poorly ordered iron oxides and amorphous aluminosilica gels, the neof ormation of crystalline metal oxalates and secondary clay minerals have been frequently identified in a variety of rocks colonized by lichens in nature. For a better understanding of the impacts of lichens on environments, further work on the comprehensive involvement of the lichen effects on weathering of natural rocks, deterioration of building stones and stonework, and formation of primitive soils should be carried out. © 2000 Elsevier Science B.V. All rights reserved.

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* Corresponding author. Tel.: +86-25-3361704; fax: +86-25-3353590.
E-mail address: jchen@issas.ac.cn (J. Chen).

1. Introduction

The occurrence of lichens may date from the Early Devonian (400 million years ago) (Taylor et al., 1995). As the earliest colonizers of terrestrial habitats on the earth, lichens are amongst the most successful forms of symbiosis (Galloway, 1994; Seaward, 1997). It is estimated that around 8% of the terrestrial surface of the earth is covered by lichen-dominated vegetation (Larson, 1987).

According to Ahmadjian (1993), a lichen may be described as “an association between a fungus, usually an ascomycete but in a few cases a basidiomycete or deuteromycete, and one or more photosynthetic partners, generally green algae or cyanobacteria. In all lichens the fungus forms a thallus or lichenized stroma that may contain unique secondary compounds”. The lichens occupying rocks as their substrates, generally known as saxicolous species, can be divided into three distinct groups: crustose, foliose, and fruticose, basically in the terms of the modes of attachment to the substrate (Jones and Wilson, 1985; Carcia-Rowe and Saiz-Jimenez, 1991). Crustose lichens may also be subdivided into epilithic (living on the surface of the rock) and endolithic (living in the interior of the rock) types. The latter may differ by mode of entry; cryptoendolithic forms occupy structural cavities and chasmoendolithic forms inhabit fissures and cracks within rocks, while euendolithic forms actively bore into rocks (Golubic et al., 1981; Bell, 1993). Not all lichens, however, can be classified by the inhabiting location of rock. In fact, some species of lichens are partially epilithic and partially endolithic, others have an epilithic phase and an endolithic phase in the course of their life cycle (Golubic et al., 1981). Furthermore, it has been reported that some endolithic lichens may have their chasmo- and euendolithic phases at different stages of colonization (Ascaso et al., 1995) (Fig. 1).

The fact that lichens affect their substrate rocks, both in their natural state and when used as building stones, has long been recognized (Seaward, 1997; Silva et al., 1997). Concerning the significance of lichens in affecting rock weathering and soil development, formerly there were different opinions. Some authors suggested that lichens are of significance in weathering and pedogenesis (e.g., Schatz, 1963a; Jackson and Keller, 1970; Syers and Iskandar, 1973), while others argued that the importance of lichens in this context has been exaggerated (Smith, 1962; Haynes, 1964; Culberson, 1970).

For the study of biological aspects of weathering of rocks and minerals, lichen-encrusted rocks provide an ideal environment, where a direct relationship between lichens and their substrates can be investigated with relative ease (Wilson and Jones, 1983; Wierzchos and Ascaso, 1996). The interface between lichen and rock is now known as a place of considerable physical and chemical activity, presenting a complicated heterogeneity in which primary and secondary minerals, organic acids and compounds, and living organisms including the myco- and photobionts of lichens, free-living algae and fungi, and bacteria, are all involved (Jones and Wilson, 1985; Wierzchos and Ascaso, 1994, 1996). The investigation of the lichen–rock interface has been of interest for many years (Ascaso et al., 1995). As early as the end of last century, the first light microscopy study of the lichen–rock interface was initiated (Bachmann, 1890). Since then, numerous investigations have been carried out in this field and a variety of microscopic and microanalytical techniques have been employed, including light microscopy (LM),

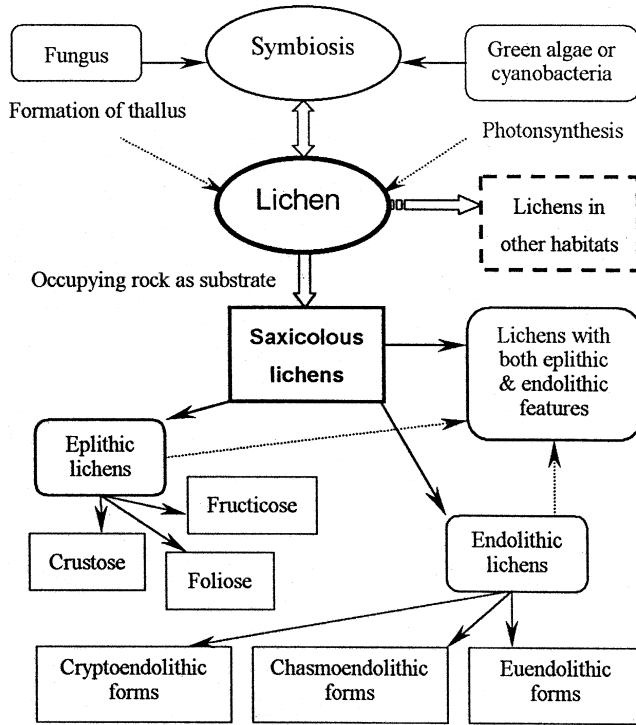


Fig. 1. Lichens and their classification based on habitat variation.

transmission electron microscopy (TEM), scanning electron microscopy (SEM), SEM in back-scattered electron emission mode (EDS), FT-Raman microscopy, infrared spectroscopy (IR), X-ray diffraction (XRD), energy dispersive X-ray Spectrometry (EDS, also known as EDXRA), X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy. As a result, a vast amount of observational and microanalytical evidence of the lichen–rock interface, showing the interaction between lichen thalli and mineral surfaces is available. At the same time, a large number of laboratory studies associated with the weathering of rocks and minerals induced by lichens and lichen compounds have been conducted. The experimental data obtained include: (1) the nature and solubility of lichen products (Smith, 1962; Haynes, 1964; Iskandar and Syers, 1971; Hawksworth, 1988); (2) chelating and complexing ability of lichen compounds (Schatz, 1963a; Syers, 1969; Iskandar and Syers, 1972; Williams and Rudolph, 1974; Ascaso and Galvan, 1976; Eckhardt, 1985); (3) mechanisms and kinetics of mineral dissolution and ion release by lichen-producing organic acids, especially oxalic acid (Jacks, 1953; Johnston, 1959; Henderson and Duff, 1963; Eckhardt, 1985; Mast and Drever, 1987; Song and Huang, 1988; Ganor and Lasaga, 1994); (4) nature of the weathered residues of the treated rocks and minerals and the neoformed products (Ascaso and Galvan, 1976; Varadachari et al. 1994).

2. Physical effects

Early investigations of lichen weathering of mineral substrates concentrated largely on mechanical aspects, leading to the conclusion that the effects of lichens might be mainly ascribed to physical causes (Fry, 1922, 1924, 1927; Perez-Llano, 1994), despite the fact that the first indication of mineral neoformation in the encrustation of building stones, probably induced by lichen activity, dates back to the middle of the 19th century (Liebig, 1853). It is now widely accepted that lichens can play an important role in both the processes of physical and chemical weathering of rocks and minerals. Generally, the physical weathering of rocks by lichens proceeds by the following mechanisms: (1) the penetration of hyphae through intergranular voids and mineral cleavage planes; (2) expansion and contraction of thallus by microclimatic wetting and drying; (3) freezing and thawing of lichen thallus and associated microenvironment; (4) swelling action of organic and inorganic salts originating from lichen activity, and (5) incorporation of mineral fragments into the thallus (Figs. 2 and 3).

2.1. Penetration of hyphae

Undoubtedly, physical effects of lichens on their substrates begin with penetration of hyphae of lichens through various voids in the rocks. As one of the most important mechanisms, hyphal penetration contributes directly to physical weathering and mechanical damage of both natural rocks and building stones, and also induces and accelerates other forms of physical weathering.

Disaggregation and exfoliation of a variety of rocks caused by hyphal penetration of numerous lichen species, especially crustose species, have been reported. By a microscopic examination, Prieto et al. (1994) revealed that hyphae of all five lichen species colonizing granite penetrated into the rock to a greater depth than usually expected, indicative of a significant contribution to disaggregation and detachment of mineral grains. In another case of colonized granite, Prieto Lamas et al. (1995) found that the growth and penetration of hyphae occurs both vertically and horizontally and may exceed 4 mm, mainly via intergranular voids, but in some cases, along the cleavage planes of mica and feldspar. As a result of hyphal growth and penetration, micas are broken down into minute crystals, while quartz and feldspar are broken down into grains. The depth of penetration of *Lecidea Sarcogynoides* in Clarens sandstone and Magaliesberg quartzite were compared. The average penetration depth of the hyphae in Clarens sandstone was 3.21 mm (Wessels and Schoeman, 1988) and in Magaliesberg quartzite 1.12 mm (Cooks and Otto, 1990). In the ultrastructural investigation of a granitic rock colonized by crustose lichens, Ascaso and Wierzchos (1994) found that the fragments of the well-developed thallus were present between the pieces of mineral plates detached from a micaceous material and the surface of the parent mineral. Thus, it was indicated that the hyphae could detach rock minerals by the penetration. Similar findings of detachment, separation and exfoliation of granitic biotite plates in adhesion zones of epilithic foliose and crustose lichen thalli also were reported by Wierzchos and Ascaso (1996), further confirming the mechanical action of hyphal penetration. In the case of other types of mineral substrate, Ariño et al. (1997) noted that the perforations

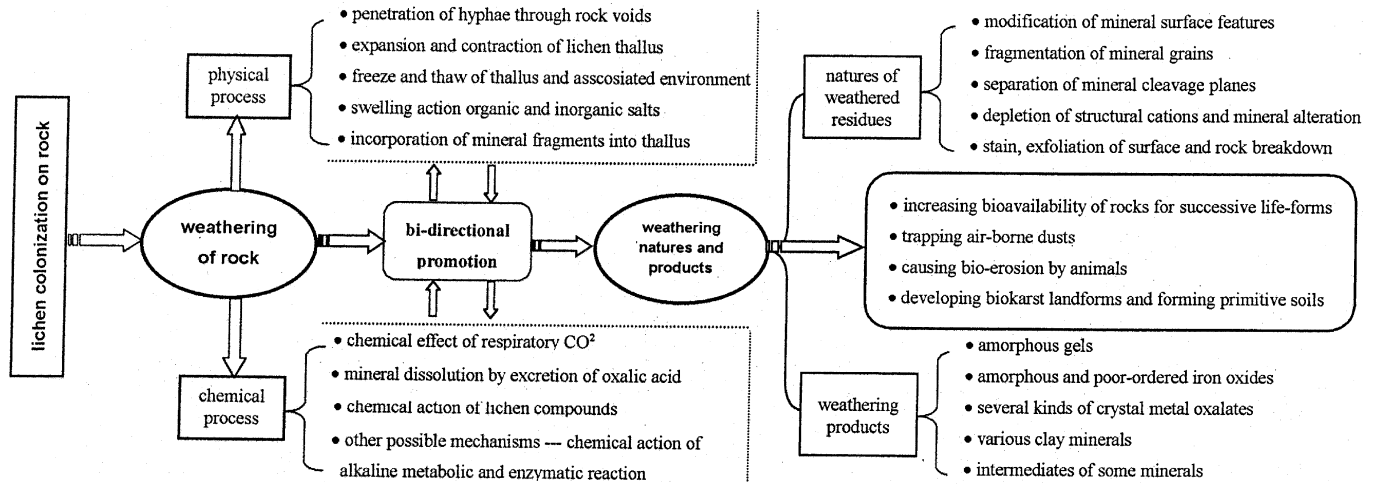


Fig. 2. Flow chart showing effects of lichens on their substrate rocks.

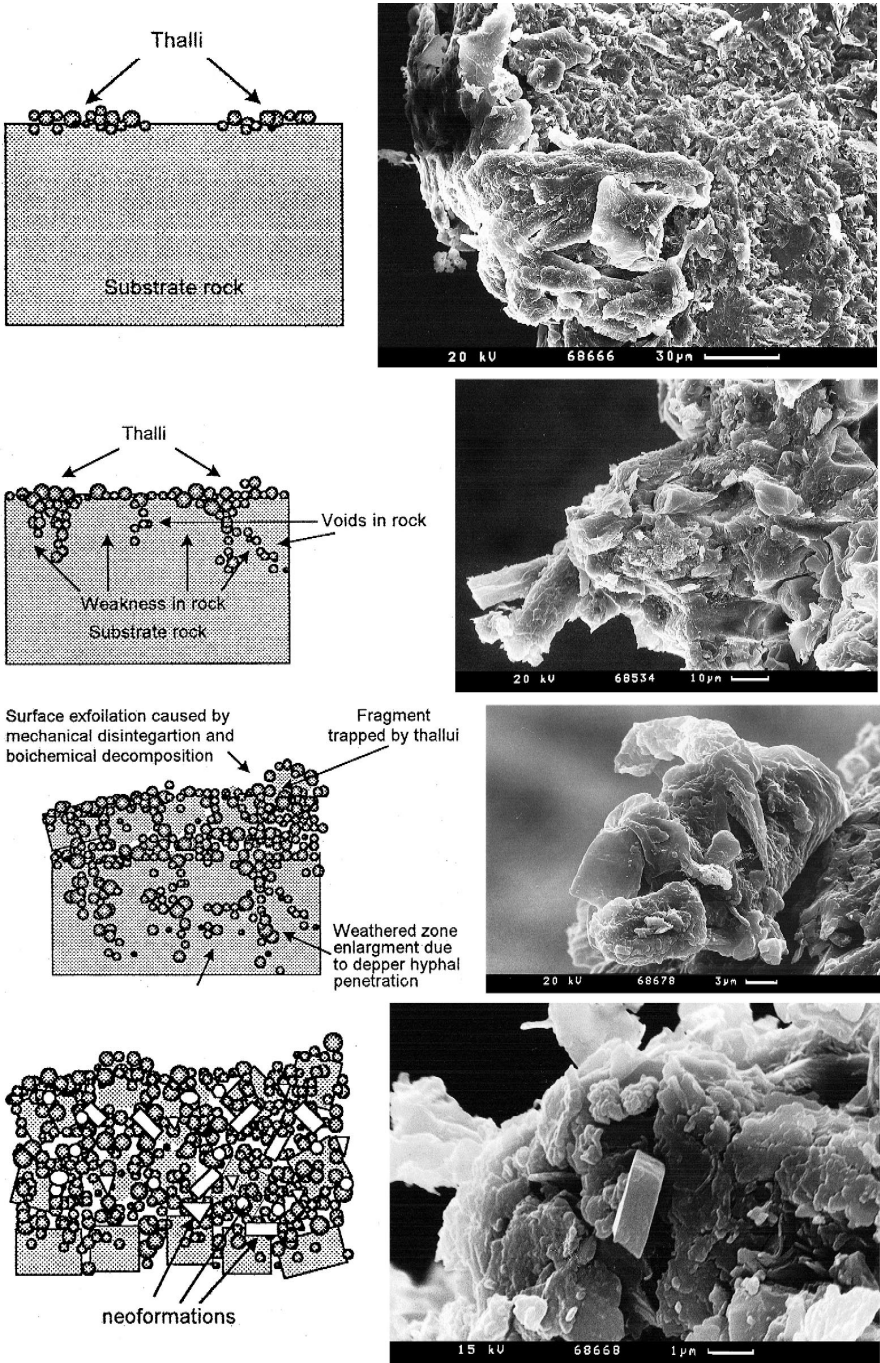


Fig. 3. Suggested sequence of the weathering effects of lichens on substrate rocks.

by the hyphae and hyphal bundles, and the development of the fruiting bodies of the lichens are responsible for the pits formed on the surface of colonized mortars. Within the superficial layer of building sandstone colonized by communities dominated by crustose lichens in arid environments, Ariño et al. (1997) reported the intensive disaggregation of rock grains due to hyphal penetration. In the Antarctic cold desert, Friedmann and Weed (1987) considered the growth of plectenchyma of endolithic lichens between rock crystals as one of the main factors in the flaking process of Beacon sandstone.

2.2. *Expansion and contraction of thallus*

The mechanical disruption of the substrate rocks caused by the expansion and contraction of lichen thallus has long been recognized. Fry (1924, 1927) investigated on a variety of colonized mineral substrates and suggested that the mechanical force exerted by the expansion and constriction of gelatinous and mucilaginous substances of medulla through wetting and drying of lichen thalli was significant in the physical weathering process of the substrates. It is known that the medulla of lichens is an excellent hygroscopic substance and has a great water holding capacity, up to 300% of the dry weight when enough moisture is available (Creveld, 1981). It can be expected, therefore, where alternate wetting and drying is frequent, considerable physical weathering of the substrate rocks by this mechanism may take place in a relatively short period of time. For studying the effect of the lichen *Collema auriforma* in solution basin development on a carboniferous limestone substrate in the west Ireland, Moses and Smith (1993) carried out an experiment in which the lichen was subjected to a number of wetting–drying cycles. SEM examination of the underside of the thalli lifted away from the rock surface during wetting–drying experiment revealed the presence of fragments of the substrate. These fragments, ranging from 10 to 50 μm in size along their longest axis, typically adhered to, or were embedded within, the fungal hyphae. These particles of rock likely plucked probably from the rock surface on contraction of the thalli of the lichen during the drying phase. It was concluded that in conjunction with chemical solution, this process could play a significant role in the formation of karstic features including solution basins. In Central Italy, the expansion and contraction of lichen thalli resulting from wetting and drying, combined with other forms of physical action, may lead to visible mechanical damage to stonework in 10 years or less (Seaward et al., 1989).

2.3. *Freezing and thawing of lichen thallus and associated microenvironment*

Freeze and thaw as an important mechanism of physical weathering and soil formation, especially in cold regions, has been well demonstrated. However, there have been few reported investigations of this mechanism associated with lichen colonization. Freeze and thaw resulting from temperature variation may occur in both the microenvironment created by the lichen community and in lichen thallus itself. As a result of hyphal penetration, surface water can reach a considerable depth, where the so-called ice-wedging action caused by freezing expansion of the thallus and surrounding mi-

croenvironment could take place when temperature drops below zero. In the alpine zone of South Norway, Creveld (1981) suggested that freeze and thaw action could play a significant role in the weathering process of lichen-colonized rocks. In Antarctica, freezing expansion associated with endolithic lichen communities and their microecological environments was said to be a cause of surface exfoliation of rocks (Friedmann, 1985; Friedmann and Weed, 1987). In temperate zones, the mechanical disruption to substrates by freeze and thaw of lichen thalli has also been recognized (e.g., Ariño et al., 1997).

2.4. Swelling action of organic and inorganic salts

It is well known that crystallization of salts within pores and cracks of rocks may exert sufficient pressure to separate mineral grains or rock fragments (Wellman and Wilson, 1965; Cooke and Smalley, 1968; Campbell and Claridge, 1987). As to the weathering process induced by microbial communities, Sand (1997) suggested that mechanical disaggregation and separation of rocks and minerals also might be caused by crystallization of the secondary salts originating from the reactions of organic and inorganic acids excreted by organisms with mineral substrates. At the lichen–rock interface and in the lichen thallus itself, universal occurrence of secondary crystalline salts, especially various oxalates, could have brought about mechanical disruption of the immediate substrate rock. To date, however, no known investigation concentrating on the swelling action of biogenetic salts resulting from lichen colonization has been reported.

2.5. Incorporation of mineral fragments into thallus

It has been demonstrated by a number of authors that lichen thalli can incorporate the separated or disaggregated rock and mineral fragments by these mechanical processes. In a SEM study, Ascaso and Wierchos (1994) found that, at the interface between thalli of the lichen *Parmelia conspersa* and granitic rock, one of two parts of the same mineral particle belongs to the rock while another appears embedded in the hyphae of the thalli. Thus, the observational evidence of the mechanism by which lichen hyphae detach rock and mineral fragments was presented. An investigation by Ariño et al. (1995) revealed that the contents of mineral grains or particles in the thalli of the lichen species *Calopaca variabilis* and *Lecanora albescens* colonizing sandstone could average 25 and 30 mg · m⁻², respectively. The mineral particles are composed mainly of quartz crystals detached from sandstone surfaces. In colonized granite, Prieto Lamas et al. (1995) reported that the thalli of five lichen species contained mainly quartz, feldspar, and mica, confirming that these loosened rock-forming mineral grains can be engulfed by the thallus.

3. Chemical effects

Previously, it was thought that lichens might play a minor role in the process of chemical weathering of rocks. This was because lichen compounds were thought to be

insoluble in water (Iskandar and Syers, 1972), and direct evidence of the chemical effects of lichens on their substrate rocks was very difficult to demonstrate because of the technique limitations in the early studies (Jones et al. 1981).

Recently, chemical effects of lichens on rocks and minerals have been intensively investigated, both for their pedogenic significance and their effectiveness in the biodeterioration of natural rocks and building stones. The lichen exudates, which have powerful chelating capacity, the widespread occurrence of mineral neoformation, particularly metal oxalates, together with the characteristics of weathered substrates, all confirm the significance of lichens as chemical weathering agents.

3.1. Mechanisms

The chemical weathering action of microorganisms is characterized by different solubilization mechanisms regarding mineral elements. According to Berthelin (1983), solubilization includes the processes of acidolysis, complexolysis, alkalinolysis, corresponding to the formation of acidic, complexing, and alkaline metabolic compounds. Lichens induce at least two of the above-mentioned three solubilization mechanisms. Syers and Iskandar (1973) suggested that the main chemical processes by which lichens solubilize minerals are (1) generation of respiratory CO_2 ; (2) the excretion of oxalic acid; and (3) the production of biochemical compounds with complexing ability (Fig. 2).

3.1.1. Respiratory CO_2

The dissolution of respiratory CO_2 in water held by lichen thalli results in the generation of carbonic acid, which advances solubilization processes by lowering the local pH values of the thallus and the related microenvironment. However, Jones and Wilson (1985) suggested that the type of weathering caused by carbonic acid should be one form of “geochemical” weathering (terminology from Duchaufour, 1982) and would be most significant only in a tropical climate and take place under conditions without the presence of organic acid anions. It was concluded, therefore, that simple or complex organic acids abundant in lichen thalli could be expected to dominate the weathering processes by dissolving minerals and chelating metallic cations. This type of weathering was referred as “biochemical” weathering, distinguished by the removal of Fe and Al and accumulation of Si, as well as by the occurrence of poorly crystallized neoformation. This conclusion, however, fails to get support from the results of some investigations. The study of Prieto Lamas et al. (1995) on granite colonized by lichens in Northwest Spain indicated that, organic complexes of Fe and Al were no more abundant at the lichen–rock interface than in the interior of the rock, and all non-crystalline iron and aluminium coatings on the void walls were in their inorganic forms. As suggested by many authors, the lichen thallus can create a characteristic chemical microenvironment and specific weathering conditions at the thallus–rock interface, particularly in the terms of water retention. The acceleration of this hydrolysis of minerals by metabolic CO_2 dissolved in water is to be expected (e.g., Creveld, 1981; Seaward et al. 1989; Wierzchos and Ascaso, 1996). In an investigation on lichen-colonized lava flows on the Island of Hawaii, by the contrast between the lichen-colonized and lichen-free weather-

ing crusts of lava flows, Jackson and Keller (1970) found that respiratory CO₂ of lichens could effectively result in localized pH reduction in the microenvironment and thus contribute to promotion of the rate of chemical weathering.

3.1.2. Oxalic acid

Oxalic acid secreted by the mycobionts of many lichens is commonly considered to play a crucially important role in the chemical weathering of rocks and minerals. This is confirmed by the universal occurrence of metal oxalates at the lichen–rock interface and in the lichen thallus itself, and by the fact that dissolution and precipitation of various rocks and minerals in the presence of oxalic acid can be demonstrated under experimental conditions.

Generally, the great effect of oxalic acid on dissolution of rocks and minerals is attributed to the presence of hydrogen ions and the formation of cation-complexes. The structural cations, released from minerals as a result of the attack of hydrogen ions, tend to form cation–organic complexes with oxalic acid, which has OH⁻¹ and COOH⁻¹ groups in the ortho position. The chemisorption of the cation–organic complexes on the mineral surfaces causes a shift of electron density toward the framework of the mineral. This charge transfer increases the electron density of the cation–oxygen bonds and makes them more susceptible to hydrolysis (Eick et al., 1996a,b).

As pointed out by Jones and Wilson (1985), it would be a great mistake to take oxalic acid as a universal agent for the weathering by lichens. On the one hand, many species of lichens do not produce any oxalic acid, but can still exert significant chemical effects on their substrate rocks. This is because lichen fungi can secrete other simple organic acids, such as citric, gluconic acids, which can also lead to the weathering of rocks through acidic attack and chelation. On the other hand, the weathering caused by oxalic acid is not necessarily attributed to lichen colonization of rocks. It has been recognized that a vast number of other microorganisms can secrete oxalic acid. These microorganisms, associated with lichen community or independently inhabiting rocks, include a number of blue-green algae, green algae, various fungi, and numerous bacteria (Currie and Tom, 1915; Jacquot, 1938; Nord and Vitucci, 1947; Tsu-Ning Tsao, 1963; Jacks, 1965; Friedmann et al., 1972; Urbanus et al., 1978; Del Monte et al., 1987). Furthermore, oxalic acid can be formed from the decomposition of some organic materials, such as polysaccharides and proteins, under acidic conditions (Lesquibe, 1963; Del Monte et al., 1987; Beyer et al., 1997).

3.1.3. Lichen compounds

The organic compounds abundant in lichens, referred to as lichen acids although not of all them are in fact acids, were thought to be responsible for the observed effects on rocks in some early studies (Schatz et al., 1954, 1956; Schatz, 1963a,b). However, due to their apparent insolubility in water, these organic compounds were not commonly considered to be of importance in terms of the weathering of rocks and soil-forming processes at that time (Smith, 1962; Haynes, 1964; Culberson, 1970). Later studies (e.g., Iskandar and Syers, 1971) revealed that lichen depsides and depsodones, commonly occurring lichen compounds, are slightly soluble in water. This finding, in conjunction

with the presence of polar groups such as OH, CHO, COOH in ortho positions of many lichen compounds, theoretically explains the chelating ability of these compounds. A more comprehensive experimental study by Iskandar and Syers (1972), using various lichen compounds with aqueous suspensions of biotite, granite and basalt, demonstrated the formation of soluble, coloured metal–organic complexes, indicative of the decomposition of the silicate minerals. Similar results were obtained by Ascaso and Galvan (1976). In contrast, using iron chelation as a measure of biochemical weathering, Williams and Rudolph (1974) found that the isolated symbionts of four lichen species investigated showed no chelating ability after growth on synthetic media. It was found by Ascaso and Galvan (1976), however, that squamatic acid, a depside present in *Cladonia squamosa* could solubilize iron, although at a rate less than that suggested by Iskandar and Syers (1972). Schatz (1963b) and Syers (1969) have suggested that the release of cations from silicates by lichen compounds is largely attributable to complex formation and not to reactions directly involving hydrogen ions.

Although the significant capacity of lichen compounds to dissolve and decompose rock-forming minerals by complexing structural metallic cations has been well demonstrated under laboratory conditions, it would be very difficult to investigate the effect of lichen compounds on rocks in nature. In fact, this process has not been conclusively demonstrated in field studies (Jones and Wilson, 1985; Wilson, 1995).

3.1.4. Other mechanisms

According to Berthelin (1983), alkalinolysis of mineral materials caused by alkaline metabolic products is one of the other mechanisms by which microorganisms solubilize their mineral substrates. For lichens, however, no evidence has been presented to show that these alkaline metabolites have directly participated in the weathering process of rocks and minerals. Nevertheless, some alkaline nitrogen compounds, such as NH_4OH , are believed to stimulate the dissolving of lichen compounds and therefore accelerate the weathering of minerals (Creveld, 1981). Furthermore, Prieto et al. (1997) reported the neoformation of calcium carbonate in the thalli of the lichens colonizing granite and attributed this to the local pH in the thalli having been raised due to the release of sodium from nearby plagioclase during weathering. But, in a few cases, the localized reduction in pH within the thalli could also be caused by alkaline metabolites of lichens, thus leading to the neoformation of calcium carbonate.

As one mechanism of microbial weathering, enzymatic reaction has been widely recognized, especially in the decomposition process of organic compounds (e.g., Berthelin, 1983; Eckhardt, 1985; Sand, 1997). However, there has been no report on the role of enzymes in the weathering induced by lichens so far, despite the fact that some microorganisms associated with lichens such as cyanobacteria probably produce enzymes, contributing to dissolution of lichen compounds and to other processes.

Microbial absorption and uptake (adsorption to cell surfaces or absorption by microorganisms) are also believed to be of importance in the terms of the weathering process by microorganisms (Berthelin, 1983). It has been well recognized that most lichens are specific to certain mineral substrates and their colonization depends on many factors including mineral requirements (Chisholm et al., 1987; Carcia-Rowe and Saiz-Jimenez, 1991; Purvis and Halls, 1996). Reasonably, the specific absorption and uptake

of some elements by lichens would result in the acceleration of solubilization of the related element-bearing minerals.

3.2. *Nature of weathered rocks and minerals*

The effects of lichen weathering processes on rock-forming minerals of natural rocks are generally shown morphologically and compositionally, including modification of surface features, fragmentation of grains, separation of layers, depletion of structural cations, dissolution of ultrafine crystals, and precipitation of amorphous gels on mineral surfaces. Due to the alteration of rock-forming minerals, the parent rocks correspondingly suffer surface stain, disintegration, exfoliation, and breakdown, at various degrees. Attributable to variation in mineral constituents, texture, and porosity, different types of rocks are affected in quite different ways during the weathering process (Fig. 2).

3.2.1. *Sandstone*

The weathering of various sandstones induced by endolithic microorganisms has been intensively investigated in diverse parts of the world, such as hot and cold deserts. In the Antarctic cold desert, Friedmann (1982) and Friedmann and Weed (1987) demonstrated a characteristic weathering pattern in which the surfaces of Beacon sandstone are exfoliated. By this process exudates from cryptoendolithic lichens dissolve the cementing substance between sandstone grains, thus reducing the cohesion of sandstone grains in the upper level of the lichen-colonized zone, resulting in surface exfoliation. Iron compounds within the sandstone are mobilized and moved to the surface or to the deeper part, where they are precipitated. Iron chromatography of water extracts from the lichen-colonized zones suggests that oxalic acid secreted by lichen mycobionts is an Fe mobilizing agent in these rocks (Weed and Norton, 1991). Similar exfoliative weathering patterns by the cryptoendolithic community, together with the exudation process, were also found in the case of sandstones in other regions, for instance, the Clarens sandstone in South Africa (Wessels and Büdel, 1995) (Fig. 3).

3.2.2. *Basalt*

It has been experimentally revealed that pyroxene, olivine and feldspar, the main rock-forming minerals of basalt, are all subject to the attack of organic acids. For instance, the pyroxene surface exposed to oxalic acid treatment shows side-by-side etching along the boundaries of basal lamellae while olivine grains exhibit a pitted or wavy surface (Eick et al. 1996a). The petrographic analysis by Varadachari et al. (1994) showed that after treatment with oxalic acid of higher concentration for longer time, a very large number of small crystals appeared and parts of the original grains became amorphous. As a result of dissolution of these minerals, it would be expected that Fe and Mg, major constituents of pyroxene and olivine could be released in the greatest amounts, followed by Ca and Al (Iskandar and Syers, 1972; Eick et al., 1996a).

Therefore, in basalt colonized by lichens, the weathering process is characterized, in many cases, if not most, by mobilization of the iron and magnesium and release of calcium and aluminium from the primary minerals, and by coating of hydrous ferric

oxide on mineral surfaces and formation of amorphous materials. Jones et al. (1980) reported that in the colonized basalt lichen growth resulted in extensive corrosion of the primary minerals, principally ferromagnesian minerals and calcium-rich plagioclase, and ferruginous clay minerals present in the unweathered rock had completely disappeared. The complete decomposition of clay minerals present in unweathered basalt as a result of lichen colonization was previously reported in an earlier study by Jackson and Keller (1970). It was suggested, therefore, that oxalic acid and other organic acids secreted by the mycobionts had reacted with the rock-forming minerals, resulting in their dissolution and etching. Fe, Mg, Ca, and Al were released and the poorly ordered gels, iron oxides and calcium oxalate were subsequently precipitated. The accumulation of amorphous hydrous ferric oxide in the surface weathered crust implies that the mobilized or chelated iron may be transformed over small distances before being oxidized and precipitated on the rock surface (Wilson and Jones, 1983).

3.2.3. *Granitic rocks*

In granitic rocks weathered by lichens, micaceous minerals seem to be the most significantly affected. Among them, biotite is shown to be most subject to attack by organic acids under laboratory conditions (Song and Huang, 1988). As a result, flakes of biotite suffer much more extensive morphological and chemical alteration. An examination of weathered biotite residues by Varadachari et al. (1994) revealed that great changes in crystal morphology take place due to weathering. The flakes that show perfect layering in the original mineral become smaller in size, the edges are etched, the thickness of the layers is reduced and numerous fragmented particles are present. These morphological features of altered biotite have also been observed in granitic rocks naturally colonized by various lichens (Prieto et al., 1994; Wierzchos and Ascaso, 1994, 1996; Ascaso et al. 1995; Silva et al., 1997). Furthermore, the release of structural cations from biotite is also noticeable. Wierzchos and Ascaso (1996) reported that in the contact zone between the lichen thallus and granitic biotite, considerable depletion of potassium from the interlayer positions occurred, together with removal of other elements, corresponding to a 9.7% loss in matter. In a case of severely weathered granitic rock, Prieto et al. (1994) found that the biotite has been transformed into hydroxy aluminium vermiculite, a biotite–vermiculite intermediate, which has been cited as a characteristic product of mica (especially biotite) weathering in Al-rich environments (such as granite) and in the presence of organic acids (Vicente et al., 1977; Pozzuoli et al., 1994). This finding has been confirmed by other reports from weathered granitic rocks (Wierzchos and Ascaso, 1996; Prieto et al., 1997). Besides biotite, alteration of other minerals in the colonized granitic rocks has been observed. For example, Prieto et al. (1994) found that disintegration and surface dissolution of feldspar grains were also apparent where there is direct contact with lichens.

3.2.4. *Calcareous rocks*

In comparison with other types of rocks, calcareous rocks are believed to suffer much more severe weathering induced by lichens. Oxalic acid, if secreted by the mycobionts, would be expected to play a particularly active role in dissolution of the primary

minerals of calcareous rocks (Syers and Iskandar, 1973), and this has been confirmed by many other investigations (e.g., Vidrich et al., 1982; Edwards et al., 1991, 1993).

In the study of the weathering of limestone and dolomite by the lichens *C. callopisma*, *Diploschistes ocellatus*, *Squamarina oleosa*, and *Protoblastemia testacea*, Ascaso et al. (1982) found that all species effectively dissolved calcite by secretion of oxalic acid, leading to considerable decrease of this mineral. The species producing the most important effects on two calcareous rocks is *D. ocellatus*. At the lichen–rock interfaces, calcite is completely absent. Precipitation of calcium oxalate has been found both in the thalli and interfaces in various amounts. Ariño et al. (1995) investigated the weathering of mortar used as building material, composed mainly of calcite and quartz. It was found that the dissolution of minerals induced by lichens is evident both on the surface and inside the mortar, and produces clear alteration patterns such as micropitting and etching of the calcite crystals. At the lichen–rock interface, the concentrations of calcium carbonate, feldspar and mica decrease, while quartz appears to be more or less constant. In some samples, a superficial orange patina about 0.1 mm thick, composed mainly of calcium carbonate and oxalate, was found to cover the sandstone surface. This patina was previously reported by Del Monte et al. (1987), who found that the interface between the patina and the marble appears irregular, thus indicating the transformation of the marble into calcium oxalate by biological activities.

3.2.5. Other rocks

Besides the rock types described above, the weathering of other types of rocks associated with a variety of lichen species has also been investigated in different regions, further demonstrating the widespread effects of lichens on their substrates.

In South Africa, the study of Hallbauer and Jahns (1977) revealed that, at the lichen–rock interface quartzitic rocks and lichen *Dimelaena oreina*, quartz grain surfaces exhibited obvious corrosion features. In Spain, the effects of lichens on metamorphic rocks including various kinds of schists and gneisses were investigated by Galvan et al. (1981), who showed that the mineralogical features of the rock immediately beneath the lichens are quite different from those of the fresh rock. Feldspars and chlorite were observed to be altered to a considerable extent, and secondary minerals and amorphous gels were formed. Generally, it is suggested that metamorphic rocks undergo a more intense lichen weathering process than igneous rocks (Jones and Wilson, 1985). The weathering of serpentinite caused by the lichen *Lec. atra* was reported by Wilson et al. (1981). Microprobe study showed that depletion of magnesium in chrysolite reached the depths up to 100 μm below the rock surface. In Italy, the weathering effectiveness of the lichen *Sterocaulon vesuvianum* on volcanic vesuvite, a rock composed mainly of leucite and augite, was investigated by Adamo and Violante (1991). Using SEM, it was observed that the rock–lichen interface is characterized by extensive disintegration of the rock surface with separation of numerous rock fragments. The surfaces of mineral grains found at the interface or embedded in the thallus are extensively etched. Leucite is characterized by rounded etch pits and augite by two sets of cleavage planes at right angle to each other. The secondary products of poorly ordered aluminosilicate materials and various clay minerals were found to occur intimately admixed at the lichen–rock interface. In the Antarctic cold desert, besides the

exfoliation of sandstone described in the foregoing, Campbell and Claridge (1987) noted that the growth of some crustose lichens also may bring about surface exfoliation of dolerite. Ascaso et al. (1990) demonstrated the weathering action of several lichens on volcanic andesite and volcanigenic sediment in maritime Antarctica. It was shown that different species had rather different effects on the rocks. Generally, feldspars were found to be present at the lichen–rock interface to a smaller degree than in the underlying rock.

3.3. Secondary weathering products

3.3.1. Metal oxalates

Various metal oxalates, resulting from the reaction of oxalic acid with the minerals of the rock substrates, are known as the most frequent forms of secondary crystalline products of the weathering by lichens. Experimentally, it is suggested that all the cations except Si^{4+} are probably present as oxalates. Among them, the divalent ions can form insoluble oxalates whereas the monovalent ions and the trivalent Al^{3+} and Fe^{3+} can only form soluble oxalate salts (Eckhardt, 1985; Varadachari et al., 1994). This is why all the oxalates identified in the lichen thalli and the rock substrates are present as divalent salts of metals.

It is known that calcium oxalate is the most common form of oxalate identified in nature. It has been experimentally demonstrated that calcium oxalate will precipitate at Ca^{2+} concentrations as low as $90 \mu\text{mol}$ (Eick et al., 1996a). Calcium oxalate, therefore, may be formed even on colonized rocks poor in calcium, such as granite (Prieto et al., 1997). Calcium oxalate generally accumulates within, and immediately beneath, the lichen thallus. In some cases, however, the presence of calcium oxalate on the surface of the lichens has also been confirmed (Edwards et al., 1991, 1993). In nature, calcium oxalate occurs as the hydrated salt, usually as whewellite (monohydrate) but sometimes as the weddellite (dihydrate). These two oxalates can be distinguished by their morphology, with whewellite present in the form of plates and weddellite exhibiting a bipyramidal form (Jones et al., 1981; Ascaso and Wierzchos, 1994).

Beside calcium oxalate, other secondary crystalline metal oxalates, associated with lichen growth, have been identified in nature. For example, the glushinskite, crystalline magnesium oxalate dihydrate, was found by Wilson et al. (1980, 1981) at the interface between *Lec. atra* and serpentinite, a rock consisting almost entirely of magnesium silicate and containing little calcium. Jones et al. (1981) demonstrated the presence of calcium and magnesium oxalates in powdered lichen thalli from a lichen colonized allivalite, an ultrabasic rock rich in calcium and magnesium. An occurrence of manganese oxalate dihydrate as a natural mineral was first reported by Wilson and Jones (1984) in *Pertusaria corallina* growing on manganese ore. Similarly, the hydrated copper oxalate, moolootite, was identified within the medulla of the lichen species *Acarspora rugulosa*, *L. lactea*, *L. inops* growing in areas of copper mineralization (Purvis, 1984; Chisholm et al., 1987). According to Wilson and Jones (1984), all the above-mentioned findings suggest the possible existence of a variety of hitherto-unreported metal oxalates associated with the weathering activities of the lichens colonizing

rocks and ores, since the dihydrate oxalates of magnesium, ferrous iron, manganese, nickel, zinc and cobalt have all been shown to be completely isomorphous with respect to each other. However, by treating basalt respectively with 20 and 2 mM oxalic acid, Eick et al. (1996a) found that almost 99% Fe^{2+} exists as free metal in both solutions, indicating little possibility for ferrous iron to be complexed with oxalate anion. In fact, until now the naturally occurring ferrous iron oxalate has not been found associated with lichens. In contrast, in the study of the weathering of calcareous rocks by lichens, Ascaso et al. (1982) reported the precipitation of non-hydrated ferric oxalate at the interfaces between dolomite rock and the lichen species *C. callopisma* and *D. ocellatus*. This finding may be open to question and needs further investigation and consideration. First, the experimental results obtained by Harrison and Thyne (1991) and Eick et al. (1996a,b) showed that in aqueous solutions, the divalent free Fe^{2+} ion demonstrates species distribution in the presence of oxalic acid up to and including pH 7, only very little, if any, ferric iron ion may be available for the formation of oxalate salt. Second, ferric iron can only form a soluble complex with oxalic acid as mentioned in the foregoing. Therefore, it seems impossible that ferric iron oxalate accumulates at the lichen–rock interface in a considerable amount. The mobilization and precipitation of iron during the weathering of the rocks by lichens have been investigated by many authors (e.g., Jackson and Keller, 1970; Jones et al., 1980; Friedmann and Weed, 1987; Weed and Norton, 1991), however, neither ferric nor ferrous iron oxalates have been further identified in nature so far.

3.3.2. Iron oxides

Poorly ordered iron oxides are among the characteristic secondary products of the weathering processes in the presence of organic acids. It has been experimentally shown that iron released from silicate minerals by organic acids is in the form of Fe^{2+} and, with time, Fe^{2+} ions are oxidized and precipitated as ferric oxyhydroxides (Siever and Woodford, 1979; Eick et al., 1996a). In nature, ferric oxyhydroxides associated with lichens have been identified by many investigators, including Weed and Norton (1991) who revealed that they dominate the iron oxides in the surface crust of the sandstones weathered by endolithic lichens in the Antarctic cold desert. Prieto Lamas et al. (1995) also noted the segregation of ferric oxyhydroxides from granitic biotite colonized by lichens.

Hydrous ferric oxide known as ferrihydrite, however, has been detected in the rust-coloured weathering crusts on basalt respectively by Jackson and Keller (1970) and Jones et al. (1980). According to Jackson and Keller (1970), the observation that iron oxides of the weathering crusts are hydrous oxides rather than oxyhydroxides may be explained by the continual exposure of the rock surfaces to the drying action of the air.

Ferrihydrite is usually known as the major component of the stains and varnishes of the rocks from the cold and dry environments, such as Antarctica (Johnston and Cardile, 1984) and alpine regions (Kock et al., 1995). In tropical areas like Hawaii, where Jackson and Keller (1970) conducted their study of the weathering of basalt, there is little doubt that the ferric oxide is composed entirely, or almost entirely, of hematite which is believed to form via a precursor oxide (ferrihydrite). Ferrihydrite is normally absent due to high transformation rates of the precursor. This has been confirmed by the

mineralogy of iron oxides in the lichen-free weathering crusts of basalt at the same site. Ferrihydrite associated with lichens was referred to by Jackson and Keller (1970) as “cold precipitated hydrated ferric oxides”. Possibly, the formation of this mineral is an epitaxial phenomenon in which some organic compounds excreted by lichens and their microflora predetermines the crystal structure of the ferric oxides. This is supported by the results of the study of Schwertmann et al. (1968) who demonstrated that organic compounds can influence the crystallization of ferric oxides.

3.3.3. *Amorphous alumino-silicate gels*

Chemical weathering by the presence of organic matter and living organisms has been known to be characterized by the removal of metallic cations and the accumulation of silica, as well as the occurrence of amorphous alumino-silicate gels (Duchaufour, 1982; Jones and Wilson, 1985).

Under laboratory conditions, many investigators have revealed that structural cations such as Fe and Ca are strongly depleted relative to Si from the parent silicate minerals, in the presence of organic acids. For example, Barmen et al. (1992) noted that, after treatment with oxalic acid for 5 days, only 14.1% of the Si^{4+} from olivine is solubilized, much less than metallic cations. The siliceous residues formed by the attack of organic acids such as oxalic acid indicate more extensive cation depletion compared to those formed in response to HCl at the same pH, due to the complexation of metallic cations (Shotyk and Nesbitt, 1992). By reacting a variety of minerals, including olivine, biotite, epidote and hornblende, microcline and tourmaline, with oxalic and citric acids Varadachari et al. (1994) showed that amorphous materials were commonly neoformed in all residues except biotite. Associated with lichens, the experimental results presented by Ascaso and Galvan (1976) suggested that when rocks and minerals were allowed to react with lichen compounds, they would suffer morphological alteration and release metallic cations. In the cases of the most altered minerals, amorphous SiO_2 can be identified on the parent mineral surfaces.

Although a considerable amount of Al^{3+} may be released from silicate minerals under the attack of oxalic acid, it has been suggested that Al^{3+} is probably not present as an oxalate but is a part of the unattached residues in the normal conditions (Varadachari et al., 1994). In many cases, therefore, amorphous gels are identified in the alumino-silicate forms. Silica gel, or amorphous SiO_2 , is likely to derive from the eventual disintegration and dispersion of the siliceous relics (Jones and Wilson, 1985). In nature, amorphous alumino-silicate gels associated with the weathering action of lichens have been identified in various rocks, for instance, in basalt (Jackson and Keller, 1970; Jones et al. 1980), and in volcanic vesuvite (Adamo and Violante, 1991). The study of Wilson et al. (1981) on the weathering of serpenitite rock by oxalic acid showed that fibrous chrysolite, the main magnesium silicate in this rock, was decomposed to an X-ray amorphous gel which may retain the fibrous aspect of the parent mineral, although at the interface with lichen, its morphology becomes more indeterminate. Of special interest is the formation of the surface rinds of the sandstone from the Antarctic cold desert, described by Weed and Norton (1991). The silica derived from the dissolving action of endolithic lichen community is transported to the sub-aerially exposed surfaces. Then due to wet–dry and warm–cold cycling microenvironments, it is

precipitated and trapped in pre-existing grain pores, thereby preserving biogenic patterns in the colonized rocks as the trace of endolithic microorganisms.

3.3.4. Clay minerals

A variety of clay minerals associated with lichen weathering have been identified in many types of rock substrates, including kaolinite, halloysite, vermiculite, goethite, illite, allophane and imogolite. The types of secondary clay minerals formed depend upon not only substrate rocks and minerals, but also lichen species. For example, the interface between *R. Geographicum* and granite contains halloysite and goethite whilst the interface between *P. Conspera* and granite is characterized by kaolinite and halloysite (Ascaso and Galvan, 1976).

In many cases, however, halloysite and kaolinite are the most common forms of secondary clay minerals formed in the weathering crusts associated with lichen growth. Experimentally, Ascaso and Galvan (1976) revealed that halloysite was a characteristic alteration product when albite, orthoclase, biotite, muscovite and quartz reacted with lichen compounds. Galvan et al. (1981) studied the weathering of metamorphic rocks and found that halloysite was also commonly formed at the lichen–rock interface, although the formation of clay minerals was characterized by goethite. Jackson and Keller (1970) reported that the lichen-covered crust of Hawaiian basaltic lava flows was apparently devoid of clay minerals due to the leaching of Si, frequent rainfall, and excellent drainage, but halloysite precipitated in the subsurface, where the dissolved Si and Al were carried by percolating water. Kaolinite is usually found to dominate the neoformed clay minerals in granitic rocks (e.g., Ascaso and Galvan, 1976; Prieto et al., 1994; Prieto Lamas et al., 1995). However, by treating basalt with organic acids, including oxalic acid at different concentrations, Eick et al. (1996a) found that the reacting solutions are supersaturated with respect to kaolinite, indicating that kaolinite may be a characteristic product of other substrate rocks. Adamo and Violante (1991) reported the weathering of volcanic rocks with dominant mineral leucite by *Stereocaulon vesuvianum*, demonstrating that kaolinite was amongst the most abundant forms of various clay minerals.

Vermiculite, cited as a characteristic product of mica weathering in environments rich in aluminium and in the presence of organic acids (Vicente et al., 1977), has also been identified at the interfaces between lichen thalli and micaceous parts of many rocks such as granite. Usually, it occurs as hydroxyaluminium–vermiculite (Prieto et al., 1994) and biotite–vermiculite intermediates (Pozzuoli et al. 1994; Wierzchos and Ascaso, 1996). The formation of hydroxyaluminium vermiculite is believed to be attributable to a reduction of pH by organic acids secreted by lichens, with consequent substitution of interlayer potassium ions by aluminium hydroxides (Prieto Lamas et al. 1995).

4. Further areas of research

The direct effects of lichens on their mineral substrates, physically and chemically, have been confirmed by the characteristics of the weathered residues and the formation of secondary products. But the mechanisms and kinetics of weathering of rocks induced

by lichens have to be much more defined. And several interesting avenues, namely the effects of lichens in soil-forming processes, the weathering rate promoted by lichens, the involvement of airborne dusts trapped by lichens, the protective roles of lichens against the weathering of mineral substrates appear interesting and opened for further exploration.

4.1. *Involvement of lichens in weathering and preliminary soil-forming processes*

In relation to the weathering of rocks, studies of the lichen colonization to date offer more questions than answers. For example, how can lichens affect their mineral substrates in indirect ways?

It is known that lichen colonization can result in a significant accumulation of organic matter. It was reported that the cryptoendolithic lichen community inhabiting sandstone could accumulate organic carbon from 10 to 100 g · m⁻² even in the Antarctic cold desert (Vestal, 1988). In maritime Antarctica, low loss rates and the absence of grazing allow accumulation of a considerable standing biomass to values reaching nearly 2 kg · m⁻² for *Usnea himantormia* (Kappen, 1993). On one hand, the organic matter and cell excretions enable a heterotrophic bacterial population to thrive, especially around the hyphae or closely associated with them, representing a synergistic effect of the lichen thallus on weathering processes (Ariño et al., 1995). On the other hand, the decomposition of some lichens, especially nitrogen-fixing species, may lead to the production of humic or fulvic acids, which are well known for their ability to form strong complexes with aluminium and iron (Jones and Wilson, 1985). Furthermore, organic matter derived from lichen decomposition, together with detached particles of the substratum, and atmospherically derived dusts trapped by thalli, can all contribute to the development of primitive soils (Seaward, 1997).

As pioneer colonizers, lichens can create a favourable microenvironment by increasing bioavailability of mineral elements and nutrients to successive life-forms that may replace lichens during weathering of rocks and soil development. It has been shown by numerous investigators that there are positive correlations between lichen communities and vascular plant cover, because lichen communities concentrate the two essential resources necessary for plant growth, water and nutrients (e.g., Carcia-Rowe and Saiz-Jimenez, 1991; Harper and Pendleton, 1993). The indirect influences of lichens on weathering and soil-forming processes may also be reflected by animal activities. For examples, Wessels and Wessels (1993) studied the erosion of biogenically weathered Clarens sandstone by lichenophagous bagworm larvae. It was shown that independent quartz grains in Clarens sandstone originating from dissolution of the cementing material by endolithic lichens were then used by the larvae to construct the bags in which they live. It is estimated that the larvae contributed to the removal of 4.4 kg ha year⁻¹ of sandstone in this area. Furthermore, the larvae utilized the lichens as a nutrient source, resulting in about 200 g ha year⁻¹ of organic material in the form of faeces. In the Negev desert Highlands, Shachak et al. (1987) reported an unusual form of herbivory by two snail species feeding on endolithic lichens in the limestone rock. Because these snails must physically disrupt and ingest the rock substrate in order to consume the lichens, the snails were thought to be major agents of rock weathering and

soil formation in this desert. It was estimated that the rates of biotic weathering of rock by snails for the desert ranged from 69.5 to 110.4 g m² per year, and the biotic weathering contributed to the process of soil formation at a rate similar to wind-borne dust deposition.

4.2. Weathering rate of rocks promoted by lichens

Numerous investigations presented above have shown that weathering of rocks and minerals can be promoted by lichen colonization: questions arise concerning the rate of weathering induced by lichens.

According to Nienow and Friedmann (1993), in the Antarctic cold desert the turnover time of the average exfoliation cycle of Beacon sandstone induced by cryptoendolithic lichens is about 10,000 years. It is estimated that the sandstone is exfoliated at 3 mm per century. Fifty years old Hawaiian lava flows, colonized by lichen *Stereocaulon*, already have a weathering crust up to 0.81 mm thick (Jackson and Keller, 1970). Also on Hawaiian basalt flows, Cochran and Berner (1996) studied the promotion of chemical weathering and found that bulk dissolution of plagioclase accounts for most of the weathering observed beneath higher plants on the young basalts. Plagioclase dissolution was also observed on lichen-encrusted flows a few hundred to thousands of years in age. Chemical denudation rates on older flows with higher plants are at minimum 10 times greater than those with only lichens or microbiota in the environments studied (Cochran and Berner, 1996; Berner and Cochran, 1998).

The promotion of weathering rates by lichens depends on many factors, such the effectiveness of different lichen species as weathering agents and the textures and mineralogical constituents of the colonized rocks. It has been suggested by Edwards et al. (1991) that a measure of characteristic production, for instance, of oxalate, on different substrates by various lichen species should be assessed in order to determine spectroscopically a lichen's effectiveness in substratum alteration. Furthermore, as a substrate, a weathered rock appeared more inhabitable for lichens than freshly exposed rock. For example, in a study on Antarctic crustose lichens, Hooker (1980) examined colonization of a dated concrete surface on Signy Island and concluded that for *C. cinericola* it took from 14 to 40 years before colonization occurred. Silva et al. (1997) reported that granitic rocks used in a modern building finished only for 4 years were already showing signs of deterioration caused by lichen colonization. It was concluded that evaluation of deterioration of granitic rocks due to lichen colonization should include an assessment of the state of the parent rock. Therefore, the comparative studies of the colonized and non-colonized rocks at the same sites should be carried out to distinguish the weathering induced by lichens from abiotic weathering mechanisms (Silva et al., 1997). The measurement of an age sequence on moraine ridges was done by McCarroll and Viles (1995) in the Jotunheimen area of southern Norway to illustrate changes in the extent and intensity of weathering by lichen *L. auriculata* over time. A minimum rate of surface lowering of the lichen colonizing rocks was estimated to be 0.0012 mm a⁻¹, 25 to 50 times faster than weathering due to other processes in the same area. As pointed out, the true rate of lichen weathering was likely much higher, since during life of the individual lichens some rock fragments would probably have been removed completely.

4.3. Involvement of airborne dusts

It is well known that lichens are extremely sensitive to air pollution and that many species have the capacity to trap airborne dust particles into their thalli. For example, quartz grains were detected by Adamo and Violante (1991) in the thallus of *S. vesuvianum* growing on a volcanic rock, and this clearly indicates an aeolian origin, as quartz does not occur in the colonized rock. Similar observations have been reported by many other investigators in a variety of rocks, including serpentinite (Wilson et al., 1981), and calcareous rocks (Ascaso et al., 1982). Lichen encrusted on rock surfaces are usually found to contain a considerable portion of aeolian particles (Edwards et al., 1991). This atmospherically derived dust trapped by the thallus may result in accumulation of fine materials, thus contributing to the subsequent formation and development of “primitive” soils (Seaward, 1997).

In the Antarctic cold desert, Weed and Norton (1991) described the formation of thin siliceous crusts on sandstone surfaces. In this process an endolithic lichen community is associated with surface exfoliation that reveals white leached zones and red iron accumulation zones. The “pattern” of lichen community is re-established as organisms grow deeper into the rock, while a siliceous crust forms on the new surface by accumulation and in situ alteration of airborne dust composed of quartz, clays, and Fe oxyhydroxides. Airborne dusts have also been reported to be involved in the biogenetic varnished stains and crusts on a variety of rocks from other diverse parts of the world (e.g., Bell, 1993; Wessels and Büdel, 1995).

Further research on the occurrence of airborne dusts, in terms of weathering induced by lichens, should be conducted, for a better understanding of both the really altered constituents of mineral substrates and the formative processes of primitive soils.

4.4. Protection effects of lichen against weathering process

It has been suggested that, at least in a few cases, lichens may play a role in protection of rocks against weathering, especially in the environments where abiotic weathering processes are much more intense.

First, a dense lichen cover could form a barrier, shielding the substrate rock from external environments and buffering the effects of physical and chemical weathering agents such as wind abrasion, raindrop impact, water flow, temperature variation, salt deposition, and airborne pollution. This assumption has been confirmed by the study conducted by Ariño et al. (1995), who investigated lichen colonization on the flagstones and sandstones used in some historical buildings and revealed that stones without lichen cover showed greater deterioration than those colonized by lichens. It has been concluded that protection presented by lichens can act at both chemical and physical levels. For example, the presence of lichens would affect the rainwater absorption on porous substrates, thus inhibiting dissolution and precipitation processes (Ariño et al., 1995).

Second, the protective effect of lichen could be reflected by the oxalate “patina” frequently found on many monuments and historical buildings, especially on those built in calcareous materials. This oxalate patina, so-called “scialbatura” (meaning to render a monument white) (Del Monte et al., 1987), is composed mainly of biogenetic calcium

oxalate, calcium carbonate and debris of dead thalli of lichens. Due to its hardness and insolubility, the oxalate has been suggested as playing a considerable role in the protection of stones from environmental agents (Ariño et al., 1995), so that these patinas have been misinterpreted as the remaining traces of surface treatment or as the decomposition products of organic material used to protect the buildings (Del Monte et al., 1987; Edwards et al., 1991, 1993; Seaward, 1997).

In view of the fact that lichens do not always accelerate the weathering processes of their mineral substrates, the effects of lichens should include their protective role. In any given environment it seems necessary to determine which species cause physical and chemical weathering, and which are harmless and offer protection from abiotic weathering. Further comparative studies of different habiting environments should be carried out to determine in which environments lichens accelerate or retard weathering processes.

References

- Adamo, P., Violante, P., 1991. Weathering of volcanic rocks from Mt. Vesuvius associated with the lichen *Stereocaulon vesuvianum*. *Pedobiologia* 35, 209–217.
- Ahmadjian, V., 1993. In: *The Lichen Symbiosis*. Wiley, New York, pp. 1–6.
- Ariño, X., Gomez-Bolea, A., Saiz-Jimenez, C., 1997. Lichens on ancient mortars. *Int. Biodeterior. Biodegrad.* 40, 217–224.
- 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. *Sci. Total Environ.* 167, 353–363.
- Ascaso, A., Sancho, L.G., Rodriguez-Pascual, C., 1990. The weathering action of saxicolous lichens in maritime Antarctica. *Polar Biol.* 11, 33–39.
- Ascaso, A., Wierzchos, J., De Los Rios, A., 1995. Cytological investigations of lithobiontic microorganisms in granitic rocks. *Bot. Acta* 108, 474–481.
- Ascaso, C., Galvan, J., 1976. Studies on the pedogenetic action of lichen acids. *Pedobiologia* 16, 321–331.
- Ascaso, C., Galvan, J., Rodriguez-Pascual, C., 1982. The weathering of calcareous rocks by lichens. *Pedobiologia* 24, 219–229.
- Ascaso, C., Wierzchos, J., 1994. Structural aspects of the lichen–rock interface using back-scattered electron imaging. *Bot. Acta* 107, 251–256.
- Bachmann, E., 1890. Die Beziehungen der Kalkflechten zu ihrem Substrat. *Ber. Deutsch. Bot. Ges.* 8, 141–145.
- Barmen, A.K., Varadachari, C., Ghosh, K., 1992. Weathering of silicate minerals by organic acids: I. Nature of cation solubilization. *Geoderma* 53, 45–63.
- Bell, R.A., 1993. Cryptoendolithic algae of hot semiarid lands and deserts. *J. Phycol.* 29, 133–139.
- Berner, R.A., Cochran, M.F., 1998. Plant-induced weathering of Hawaiian basalts. *J. Sediment. Res.* 68, 723–726.
- Berthelin, J., 1983. Microbial weathering processes. In: Krumbein, E. (Ed.), *Microbial Geochemistry*. Blackwell, Oxford, pp. 223–264.
- Beyer, L., Knicker, H., Blume, H.P., Büdter, M., Vogt, B., Schneider, D., 1997. Soil organic matter of suggested spodic horizons in relic ornithogenic soils of coastal continental Antarctica (Casey Station, Wilkes Land) in comparison with that of spodic soil horizons in Germany. *Soil Sci.* 162, 518–527.
- Campbell, I.B., Claridge, G.G.C., 1987. In: *Antarctica: Soils, Weathering Processes and Environment*. Elsevier, Amsterdam, pp. 107–110.
- Carcia-Rowe, J., Saiz-Jimenez, C., 1991. Lichens and bryophytes as agents of deterioration of building material in Spain cathedrals. *Int. Biodeterior.* 28, 151–163.
- Chisholm, J.E., Jones, G.C., Purvis, O.W., 1987. Hydrated copper oxalate, moolootite, in lichens. *Min. Mag.* 51, 715–718.

- Cochran, M.D., Berner, R.A., 1996. Promotion of chemical weathering by higher plants: field observation on Hawaiian basalts. *Chem. Geol.* 132, 71–77.
- Cooke, R.U., Smalley, I.J., 1968. Salt weathering in deserts. *Nature* 220, 1226–1227.
- Cooks, J., Otto, E., 1990. The weathering effects of the Lichen *Lecidea aff. Sarcogynoides* (Koerb) on Magaliesberg Quartzite. *Earth Surf. Processes Landforms* 15, 491–500.
- Crevel, M., 1981. In: *Epilithic Lichen Communities in the Alpine Zone of Southern Norway*. Gantner Verlag K.G., Vaduz, pp. 48–55.
- Culbertson, W.L., 1970. Chemosystematics and ecology of lichen-forming fungi. *Annu. Rev. Ecol. Syst.* 1, 153–170.
- Currie, J.N., Tom, C., 1915. An oxalic acid-producing *Penicillium*. *J. Biol. Chem.* 22, 287–293.
- Del Monte, M., Sabbioni, C., Zappia, G., 1987. The origin of calcium oxalates on historical buildings, monuments and natural outcrops. *Sci. Total Environ.* 67, 17–39.
- Duchauffour, P., 1982. *Pedology, Pedogenesis and Classification* (English Edtn., Trans. T.R. Paton). George Allen and Unwin, London.
- Eckhardt, F.E.W., 1985. Solubilization, transport, and deposition of mineral cations by microorganisms — efficient rock weathering agents. In: Drever, J.I. (Ed.), *The Chemistry of Weathering*. Riedel, New York, pp. 161–173.
- Edwards, H.G.M., Farwell, D.W., Seaward, M.R.D., 1991. Preliminary Raman microscopic analyses of a lichen encrustation involved in the biodeterioration of Renaissance frescoes in central Italy. *Int. Biodeterior.* 27, 1–9.
- Edwards, H.G.M., Farwell, D.W., Seaward, M.R.D., 1993. FT-Raman spectroscopy of *Dirina massiliensis f. soredata* encrustations growing on diverse substrata. *Lichenologist* 29, 83–90.
- Eick, M.J., Grossl, P.R., Golden, D.C., Sparks, D.L., Ming, D.W., 1996a. Dissolution of a lunar simulant as affected by pH and organic anions. *Geoderma* 74, 139–160.
- Eick, M.J., Grossl, P.R., Golden, D.C., Sparks, D.L., Ming, D.W., 1996b. Dissolution kinetics of a lunar glass simulant at 298 K. The effect of pH and organic acids. *Geochim. Cosmochim. Acta* 58, 4259–4279.
- Friedmann, E.I., 1982. Endolithic microorganisms in the Antarctic cold desert. *Science* 215, 1045–1053.
- Friedmann, E.I., 1985. Micro-organisms in the Antarctic desert: a mode for possible life on early Mars. In: Wolfrum, R. (Ed.), *Antarctic Challenge II: Conflicting Interests, Co-operation, Environmental Protection, Economic Development*. Proceeding of Interdisciplinary Symposium. Dunker & Humboldt, Berlin, pp. 445–4550.
- Friedmann, E.I., Roth, W.C., Turner, J.B., 1972. Calcium oxalate crystals in the aragonite-producing green alga *Penicillus* and related genera. *Science* 177, 891–893.
- Friedmann, I.E., Weed, R., 1987. Microbial trace-fossil formation, and abiotic weathering in the Antarctic cold desert. *Science* 236, 703–705.
- Fry, E.J., 1922. Some types of endolithic lichens. *Ann. Bot.* 36, 541–562.
- Fry, E.J., 1924. A suggested explanation of the mechanical action of lythophytic lichens on rocks (shale). *Ann. Bot.* 38, 175–196.
- Fry, E.J., 1927. The mechanical action of crustaceous lichens on substrata of shale, schist, gneiss, limestone and obsidian. *Ann. Bot.* 40, 437–460.
- Galloway, D.J., 1994. Biogeography and ancestry of lichens and other ascomycetes. In: Hawksworth, D.L. (Ed.), *Ascomycet Systematics. Problems and Perspectives in the Nineties*. Plenum, New York, pp. 175–184.
- Galvan, J., Rodriguez, C., Ascaso, C., 1981. The pedogenic action of lichens in metamorphic rocks. *Pedobiologia* 21, 60–73.
- Ganor, J., Lasaga, A.C., 1994. The effects of oxalic acid on kaolinite dissolution rate. *Min. Mag.* 58A, 315–316.
- Golubic, S., Friedmann, E.I., Schneider, J., 1981. The lithobiontic ecological niche, with special reference to microorganisms. *J. Sediment. Petrol.* 51, 475–478.
- Hallbauer, D.K., Jahns, H.M., 1977. Attack of lichens on quartzitic rock surfaces. *Lichenologist* 9, 119–122.
- Harper, K.T., Pendleton, R.L., 1993. Cyanobacteria and cyanolichens: can they enhance availability of essential minerals for higher plants? *Great Basin Nat.* 53, 59–72.
- Harrison, W.J., Thyne, G.D., 1991. Predications of diagenetic reaction in the presence of organic acids. *Geochim. Cosmochim. Acta* 56, 565–586.

- Hawksworth, D.L., 1988. The variety of fungal–algal symbiosis, their evolutionary significance, and the nature of lichens. *Bot. J. Linn. Soc.* 96, 3–20.
- Haynes, F.N., 1964. Lichens. *Viewpoints Biol.* 3, 64–115.
- Henderson, M.E.K., Duff, R.B., 1963. The release of metallic and silicate ions from minerals, rocks, and soils by fungal activity. *J. Soil Sci.* 14, 236–246.
- Hooker, T.N., 1980. Factors affecting the growth of Antarctic crustose lichens. *Br. Antarct. Surv. Bull.* 50, 1–19.
- Iskandar, I.K., Syers, J.K., 1971. Solubility of lichen compounds in water: pedogenetic implications. *Lichenologist* 5, 45–50.
- Iskandar, I.K., Syers, J.K., 1972. Metal-complex formation by lichen compounds. *J. Soil Sci.* 23, 255–265.
- Jacks, G.V., 1953. Organic weathering. *Sci. Prog.* 41, 301–305.
- Jacks, G.V., 1965. The role of organisms in the early stages of soil formation. In: Hallsworth, E.G., Crawford, D.V. (Eds.), *Experimental Pedology*. Butterworth, pp. 219–226.
- 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. *Am. J. Sci.* 269, 446–466.
- Jacquot, R., 1938. Mechanism of oxalic acid production by the Mucedinaea. *Ann. Ferment.* 4, 284–294.
- Johnston, H.W., 1959. The solubilization of “insoluble” phosphates: V. The action of some organic acids on iron and aluminium phosphates. *N. Z. J. Sci.* 2, 215–218.
- Johnston, J.H., Cardile, C.M., 1984. The characterisation of the iron oxide phase in desert varnish from Antarctica using backscattered conversion electron and X-ray Mössbauer spectroscopy. *Chem. Geol.* 45, 73–90.
- Jones, D., Wilson, M.J., 1985. Chemical activity of lichens on mineral surfaces — a review. *Int. Biodeterior.* 21, 99–104.
- Jones, D., Wilson, M.J., McHardy, W.J., 1981. Lichen weathering of rock-forming minerals: application of scanning electron microscopy and microprobe analysis. *J. Microsc.* 124, 95–104.
- Jones, D., Wilson, M.J., Tait, J.M., 1980. Weathering of a basalt by *Pertusaria corellina*. *Lichenologist* 12, 277–289.
- Kappen, L., 1993. Lichens in the Antarctic region. In: Friedmann, E.I. (Ed.), *Antarctic Microbiology*. Wiley-Liss, New York, pp. 433–490.
- Kock, B.C., Sørup, S., Madsen, M.B., Vistisen, L., 1995. Iron-containing weathering products of basalt in a cold, dry climate. *Chem. Geol.* 122, 109–119.
- Larson, D.W., 1987. The absorption and release of water by lichens. In: Peveling, E. (Ed.), *Progress and Problems in Lichenology in the Eighties*. Bibliotheca lichenologica 25 J. Cramer, Berlin, pp. 351–360.
- Lesquibe, F., 1963. Degradation of glucose by oxidation with aqueous acid (HNO₃). *J. Rech. C. N. R. S., Lab. Bellarie* 14, 33–71.
- Liebig, V.J., 1853. Über den Thierschite. *Liebigs Ann. Chem. Pharm.* LXXXVI, 113–115.
- Mast, M.A., Drever, J.I., 1987. The effect of oxalate on the dissolution rates of oligoclase and tremolite. *Geochim. Cosmochim. Acta* 51, 2559–2568.
- McCarroll, D., Viles, H., 1995. Rock-weathering by the lichen *Lecisea auriculata* in an arctic alpine environment. *Earth Surf. Processes Landforms* 20, 199–206.
- Moses, C.A., Smith, B.J., 1993. A note on the role of the lichen *Collema auriforma* in solution basin development on a carboniferous limestone substrate. *Earth Surf. Processes Landforms* 18, 363–368.
- Nienow, J.A., Friedmann, E.I., 1993. Terrestrial lithophytic (rock) communities. In: Friedmann, E.I. (Ed.), *Antarctic Microbiology*. Wiley-Liss, New York, pp. 343–412.
- Nord, F.F., Vitucci, J.C., 1947. The acetate metabolism of certain wood-destroying molds and the mechanism of wood decay. *Arch. Biochem.* 14, 229–241.
- Perez-Llano, G.A., 1994. Lichens: their biological and economical significance. *Bot. Rev.* 10, 2–65.
- Pozzuoli, A., Vielà, E., Franco, E., Ruiz-Amil, A., De la Calee, C., 1994. Weathering of biotite to vermiculite in quaternary lahars from Monti Ernici, central Italy. *Clay Miner.* 27, 175–184.
- Prieto, B., Rivas, T., Silva, B., 1994. Colonization by lichens of granite dolmens in Galicia (NW Spain). *Int. Biodeterior. Biodegrad.* 34, 47–60.
- Prieto, B., Silva, B., Rivas, T., Wierzos, J., Ascaso, C., 1997. Mineralogical transformation and neoformation in granite by the lichens *Tephromela atra* and *Ochrolechia parella*. *Int. Biodeterior. Biodegrad.* 40, 191–199.

- Prieto Lamas, B., Rivas Brae, M.T., Silva Hermo, B.M., 1995. Colonization by lichens of granite churches in Galicia (northwest Spain). *Sci. Total Environ.* 167, 343–351.
- 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., Halls, C., 1996. A review of lichens in metal-enriched environments. *Lichenologist* 28, 671–681.
- Sand, W., 1997. Microbial mechanisms of deterioration of inorganic substrates — a general mechanistic overview. *Int. Biodeterior. Biodegrad.* 40, 183–190.
- Schatz, A., 1963a. Soil microorganisms and soil chelation: the pedogenic action of lichens and lichen acids. *Agric. Food Chem.* 11, 112–118.
- Schatz, A., 1963b. The importance of metal-binding phenomena in the chemistry and microbiology of soil: Part I. The chelating properties of lichens and lichen acids. *Adv. Front. Plant Sci.* 6, 118–134.
- Schatz, A., Cheronis, N.D., Schatz, V., Trelawny, G.S., 1954. Chelation (sequestration) as a biological weathering factor in pedogenesis. *Proc. Pennsylvania Acad. Sci.* 8, 44–51.
- Schatz, V., Schatz, A., Trelawny, G.S., Barth, K., 1956. Significance of lichens as pedogenic (soil-forming) agents. *Proc. Pennsylvania Acad. Sci.* 30, 62–69.
- Schwertmann, U., Fisher, W.R., Papendorf, H., 1968. The influence of organic compounds on the formation of iron oxides. In: *Proc. of 9th Int. Cong. on Soil Sci., Adelaide, Trans.*, 1. pp. 645–655.
- Seaward, M.R.D., 1997. Major impact made by lichens in biodeterioration processes. *Int. Biodeterior. Biodegrad.* 40, 269–273.
- Seaward, M.R.D., Diacobini, C., Giuliani, M.R., Roccardi, A., 1989. The role of lichens in the biodeterioration of ancient monuments with particular reference to Central Italy. *Int. Biodeterior.* 25, 49–55.
- Shachak, M., Jones, C.G., Granot, Y., 1987. Herbivory in rocks and the weathering of a desert. *Science* 236, 1098–1099.
- Shotyk, W., Nesbitt, W.H., 1992. Incongruent and congruent dissolution of plagioclase feldspar: effect of feldspar composition and ligand complexation. *Geoderma* 55, 55–78.
- Siever, R., Woodford, N., 1979. Dissolution kinetics and weathering of mafic minerals. *Geochim. Cosmochim. Acta* 43, 717–724.
- Silva, B., Prieto, B., Rivas, T., Sanchez-Biezma, M.J., Paz, G., Carballal, G., 1997. Rapid biological colonization of a granitic building by lichens. *Int. Biodeterior. Biodegrad.* 40, 263–267.
- Smith, D.C., 1962. The biology of lichen thalli. *Biol. Rev.* 37, 537–570.
- Song, S.K., Huang, P.M., 1988. Dynamics of potassium release from potassium-bearing minerals as influenced by oxalic and citric acids. *Soil Sci. Soc. Am. J.* 52, 383–390.
- Syers, J.K., 1969. Chelating ability of fumarprotocetraric acid and *Parmelia conspersa*. *Plant Soil* 31, 205–208.
- Syers, J.K., Iskandar, I.K., 1973. Pedogenetic significance of lichens. In: Ahmadjian, V., Hale, M.E. (Eds.), *The Lichens*. Academic Press, New York, pp. 225–248.
- Taylor, T.N., Hass, H., Remy, W., Kero, H., 1995. The oldest fossil lichen. *Nature* 378, 244.
- Tsu-Ning Tsao, G., 1963. Production of oxalic acid by a strain of *Agaricus campestris*. *Appl. Microbiol.* 11, 255.
- Urbanus, J.F.L.M., Van en Ende, H., Koch, B., 1978. Calcium oxalate crystals in the wall of *Mucor Mucedo*. *Mycologia* 70, 829–842.
- Varadachari, C., Barman, A.K., Ghosh, K., 1994. Weathering of silicate minerals by organic acids: II. Nature of residual products. *Geoderma* 61, 251–268.
- Vestal, J.R., 1988. Biomass of the cryptoendolithic microbiota from the Antarctic desert. *Appl. Environ. Microbiol.* 54, 957–959.
- Vicente, M.A., Razzaghe, M., Robert, M., 1977. Formation of aluminum hydroxy vermiculite (intergrate) and smectite from mica under acidic conditions. *Clay Miner.* 12, 101–112.
- Vidrich, V., Ceconi, C.A., Ristori, G.G., Fusi, Pi., 1982. Verwitterung toskanischer gesteine unter mitwirkung von flechten. *Zeitschrift Pflanzenernähr. Bodenk.* 145, 384–389.
- Weed, R., Norton, S.A., 1991. Siliceous crusts, quartz rinds and biotic weathering of sandstone in the cold desert of Antarctica. In: *Diversity of Environmental Biogeochemistry*. Berthelin, J. (Ed.), *Developments in Geochemistry* 6 Elsevier, Amsterdam, pp. 327–339.

- Wellman, H.W., Wilson, A.T., 1965. Salt weathering, a neglected geological erosive agent in coastal and arid environments. *Nature* 205, 1097–1098.
- Wessels, D.C.J., Büdel, B., 1995. Epilithic and cryptoendolithic cyanobacteria of Clarens sandstone cliffs in the Golden Gate Highlands National Park, South Africa. *Bot. Acta* 108, 220–226.
- Wessels, D.C.J., Schoeman, B., 1988. Mechanism and rate of weathering of Clarens sandstone by an endolithic lichen. *S. Afr. J. Sci.* 84, 274–277.
- Wessels, D.C.J., Wessels, L.A., 1993. Erosion of biogenetically weathered Clarens sandstone by lichenophagous bagworm larvae (*Lepidoptera; Psychidae*). *Lichenologist* 23, 283–291.
- Wierzchos, J., Ascaso, C., 1994. Application of back-scattered electron imaging to the study of the lichen–rock interface. *J. Microsc.* 175, 54–59.
- Wierzchos, J., Ascaso, C., 1996. Morphological and chemical features of bioweathered granitic biotite induced by lichen activity. *Clays Clay Miner.* 44, 652–657.
- Williams, M.E., Rudolph, E.D., 1974. The role of lichens and associated fungi in the chemical weathering of rock. *Mycologia* 66, 648–660.
- Wilson, M.J., 1995. Interactions between lichens and rocks. *Cryptogam. Bot.* 5, 299–305.
- Wilson, M.J., Jones, D., 1983. Lichen weathering of minerals: implications for pedogenesis. In: Wilson, R.C.L. (Ed.), *Residual Deposits: Surface Related Weathering Processes and Material*. Special Publication of the Geological Society. Blackwell, London, pp. 2–12.
- Wilson, M.J., Jones, D., 1984. The occurrence and significance of manganese oxalate in *Pertusaria corllina* (Lichenes). *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. *Min. Mag.* 43, 837–840.