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LICHEN WEATHERING ACTIVITIES ON MINERAL AND ROCK SURFACES

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Abstract: The biocorrosion and biodeterioration of limestone and sandstone by epilithic and endolithic lichens was studied using the maceration and the casting-embedding techniques. The investigations revealed alterations on the rock surface, characterized by biocorrosive pitting, etching patterns, imprints of the fruiting bodies, boring channels and mucilaginous etching figures. Moreover, the inside of the rock is penetrated by extensive and compact networks of the lichenized fungal hyphae. These biodeteriorations are positively correlated to the physical and chemical actions of the lichen involved as well as to the nature of the rock.

Introduction

The involvement of lichens in rock weathering has been discussed since the end of the 19. century. Aldready Julien (1883) mentioned the influence of lichens as an organic agent in the deterioration fo stone material. At the turn of the century, particularly Bachmann (1904, 1907, 1911, 1917), Smith (1921) and Fry (1927) provided studies which were concentrating on the mechanical action of lichens. Subsequently more emphasis was placed on the chemical alterations of rocks by lichen compounds (e.g. Schatz, 1962, 1963; Syers, 1969; Iskandar & Syers, 1971; Williams & Rudolph, 1974; Ascaso & Galvan, 1976; Galvan et al., 1981; Ascaso et al., 1982). However, the lichenic weathering on mineral surfaces involves both physical and chemical processes. Of these, the physical mechanism is mainly characterized by hyphae penetration and thallus expansion and contraction, whilst for the chemical action oxalic acid and several other lichenic substances are important. Many of these secondary metabolic products are powerful metal complexing agents leading to a disintegration of the rock surface (Syers & Iscandar, 1973).

Regarding the thallus morphology, crustose lichens which are in direct and intensified contact with the substratum are much more important in the biodeterioration of stone than foliose and fruticose lichens which are only loosey connected with the substrate (Syers & Iscandar, 1973). Furthermore, endolithic lichens although being less conspicuous, are possibly more significant in rock weathering (Krumbein, 1966, 1969; Danin et al., 1982, 1983).

The intention of this paper is to document the phenomenology of the different biocorrosive patterns of lichen-encrusted rocks as these relate to physical and chemical actions.

Material and Methods

Investigating the biodeterioration of epilithic and endolithic lichens on calcareous and siliceous rocks, both the maceration and the casting-embedding technique, were used. The lichenized rocks were macerated with ''Eau De Javelle'' (Schneider, 1973; Gerlach, 1984) and for the casting-embedding procedure the resins ''Epon'' (Golubic et al., 1970) and ''Spurr'' (Spurr, 1969) were applied. The samples were examined by scanning electron microscopy (SEM).

Results and Discussion

The study indicates convincingly different weathering patterns on the surface caused by the lichen investigated, and to what extent the stone is penetrated by individual endolithic hyphae.

Caloplaca heppiana (Müll. Arg.) Zahlbr.
Germany, Jewish cemetry, Rödelsee (Untefranken) 8/86 and Aurich 9/86; lichen on limestone

The activities of the crustose lichen *Caloplaca heppiana* revealed, upon maceration, etching patterns and imprints of the fruiting bodies which were easily distinguishable by the ring-shaped microgrooves as shown in Fig. 1. Besides, the penetration of hyphae into the substratum is indicated by the boring channels (Fig. 2). Longitudinal sections of the embedded samples, the ''casts'', when observed by SEM show the density and number of the endolithic hyphae penetrating the stone (Fig. 3). Stone lamellae perforated by fungal hyphae are documented in Fig. 4.

Acarospora fuscata (Nyl.) Arnold; *Candelariella vitellina* (Hoffm.) Müll. Arg.; *Lecanora grumosa* (Pers.) Röhl.
Germany, Jewish cemetry, Rödelsee (Unterfranken) 8/86; lichens on sandstone

Vertically sectioned sandstone encrusted with the lichens *Acarospora fuscata, Candelariella vitellina* and *Lecanora grumosa* as observed by light microscopy, reveals an extensive compact network of hyphae, which reaches penetration depths of up to 3 mm. At the rock/lichen interface the attacked stone material is inchoherent, evidenced by a notable increase in porosity and a decrease in stability between the structural components leading to a lifting of the surface. This deterioration phenomenon, formerly assumed as abiogenic was called ''swelling''

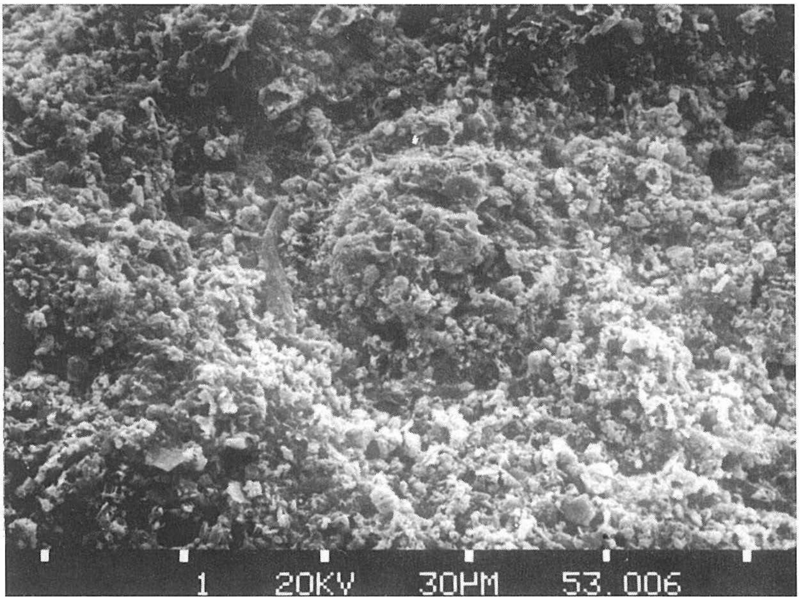

Fig. 1 - x 670. Macerat of *Caloplaca heppiana*. SEM-photo showing a print of an apothecium with and individual hyphae (on the left) penetrating the limestone

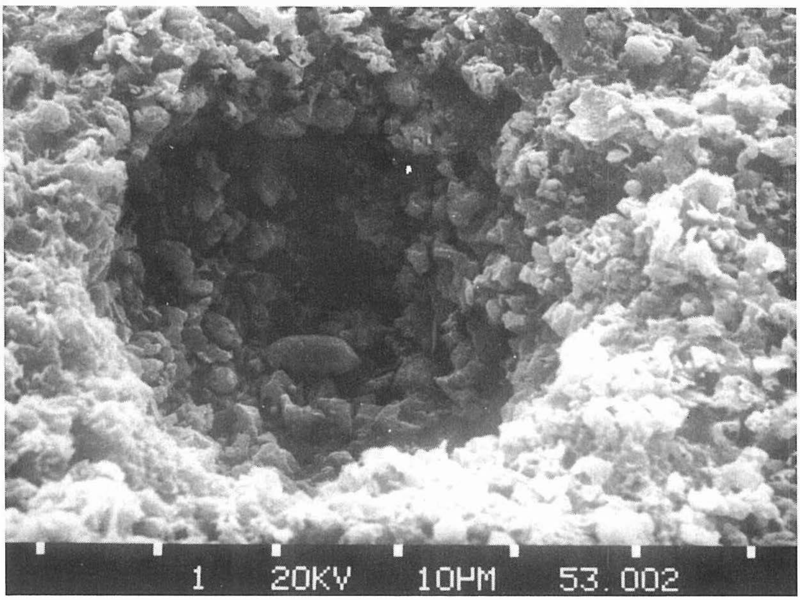

Fig. 2 - x 1700. Detail of Fig. 1; pit with a boring channel as connection to the inside of the stone.

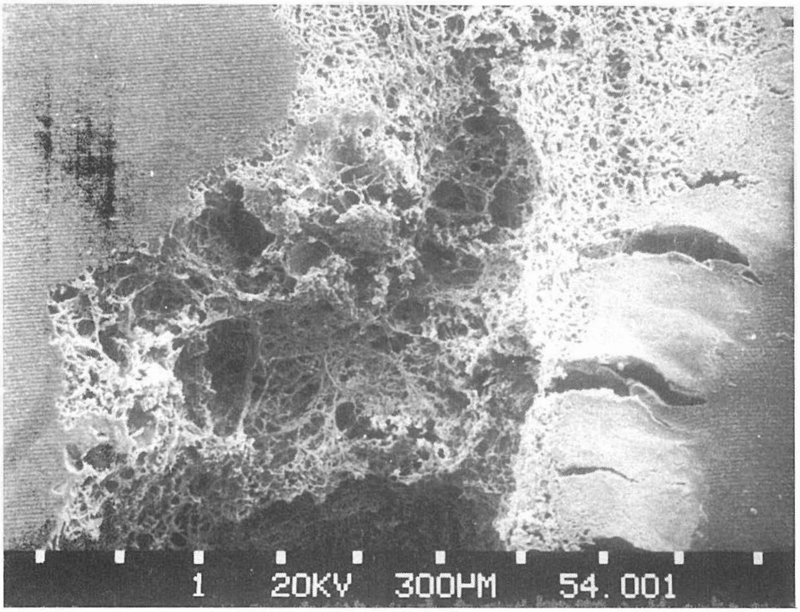

Fig. 3 - x 700. Hyphae of *Caloplaca heppiana*, SEM-photo, cast, showing by partial removal of the rock, how the hyphae penetrate through the stone lamellae.

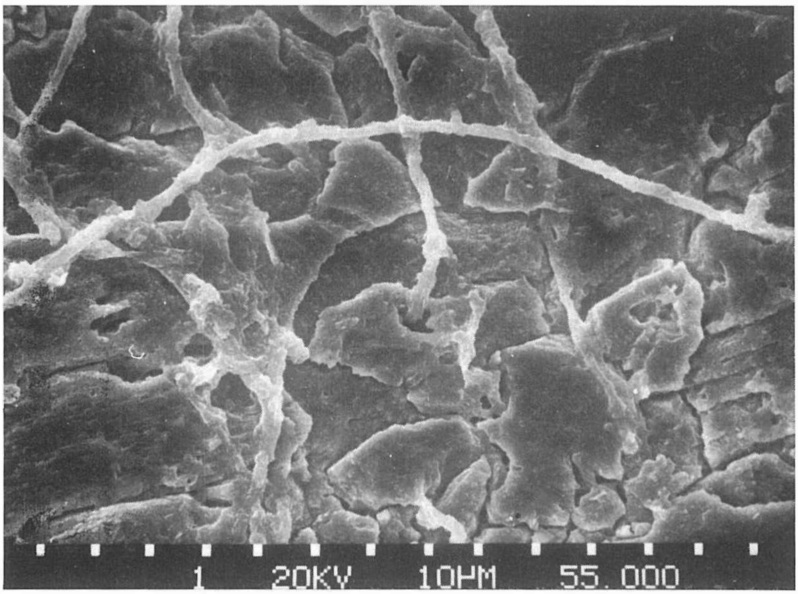

Fig. 4 - x 40. Cross section through the thallus of *Cal•placa heppiana*, SEM-photo, cast. A compact network of endolithic hyphae penetrating the rock.

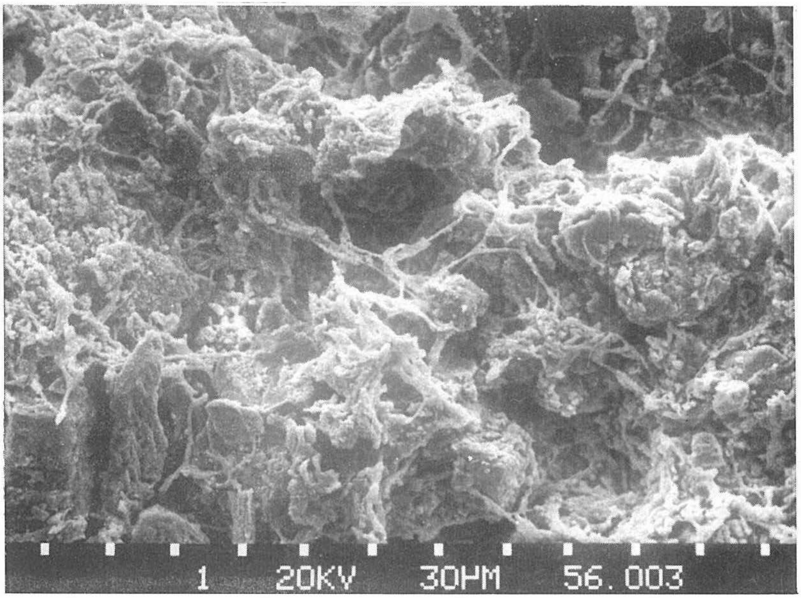

Fig. 5 - x 300. *Candelariella vitellina*, SEM-photo, cast. Rock matrix partially dissolved. The fungal hyphae penetrate the porous and loosened rock material.

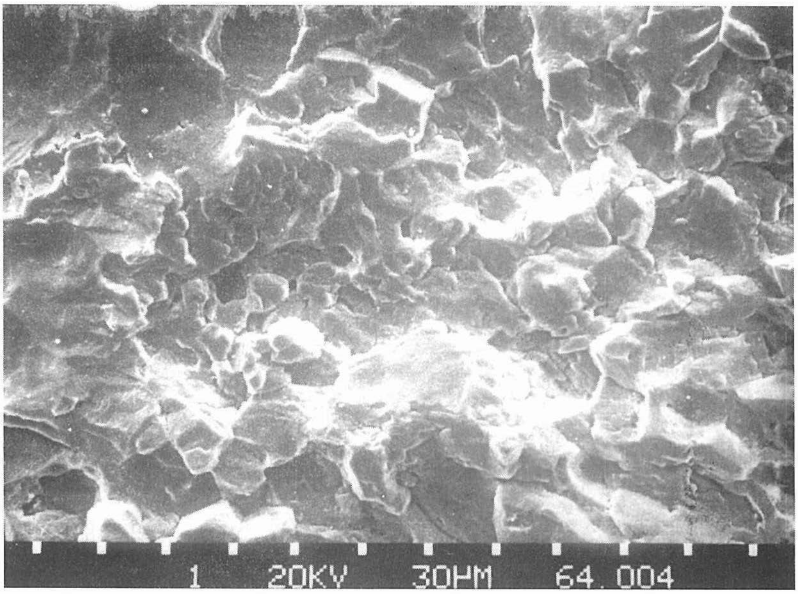

Fig. 6 - x 300. Macerate, SEM-photo. Corroded surface of quartz caused by the activity of *Rhizocarpon geographicum*.

(Torraca, 1980). Such patterns of biogenic initial stages of desquamation are also connected with the lichens *Lecanora polytropa, Lecanora rupicola, Lecanora sulphurea* and *Lecidea fuscoatra*. SEM observations of a cast with *Candelariella vitellina* show mineral fragments intensively incorporated into the lichen mycelium (Fig. 5).

Rhizocarpon geographicum (L.) DC.
Italy, Pozzuoli 8/84; lichen on quartzitic stone.

In general quartzitic rock surfaces are considered as extremely resistant to weathering. The present study demonstrates that, after removal of the lichen, the thallus/stone interface indicates significant etching patterns (Fig. 6). Comparable obsevations have been made by Hallbauer & Jahns (1977) and Jones et al. (1981). Moreover, Jones, Wilson & MacHardy correlated the biocorrosion effect more to the acidic properties rather than to the complexation effects of lichenic compounds.

Lecanora dispersa (Pers.), Sommerf.
Germany, Jewish cemetry Hamburg 9/86 and Oldenburg 4/87; lichens on limestone.

A macerated sample of this calcicole lichen indicates biogenic pits and mucilaginous etching figures on places formerly colonized by apothecia on the surface of the rock (Fig. 7). SEM examinations of the apothecia show the margins of the fruiting bodies properly encrusted with calcium oxalate (Figs. 8, 9). The biomineralisation of Ca-oxalate depends on the substrate and on the lichen involved. Amounts of up to 60 pe cent of the lichen dry weight have been observed (Syers et al. 1967). Depending on the formation conditions Ca-oxalate can occur as "whewellite" mineral, a monohydrate ($Ca_2O_4 . H_2O$), or as "weddellite", a dihydrate (CaC_2O_4). The crystal form of the whewellite is plateled-shaped and that of the wheddellite is bipyramidal (Jones & Wilson, 1986). Besides, a cast of the lichen encrusted stone indicates mucilaginous excretions (Fig. 10).

Pyrenocarpous endolithic lichens
Israel, Negev 8/86; lichen on limestone.

Samples carrying several endolithic pyrenocarpous lichen species are characterized by a typical jigsaw puzzle-like pattern (Danin et al. 1982, 1983). Adjacent colonies of these lichens form micro grooves which are filled up by fungal hyphae of the neighbouring lichens (Fig. 11). SEM observations of macerated samples and casts indicate biopitting and other biocorrosive patterns evidenced by differently developed pits and holes caused by the penetration of individual hyphae and by the activity of the fruiting bodies (Figs. 12, 13). This biodeterioration pattern has already been documented by Krumbein (1969) and later by Danin et al. (1982, 1983). Additionally, chasmolithic lichens colonizing fissures and cracks inside of the rock were documented.

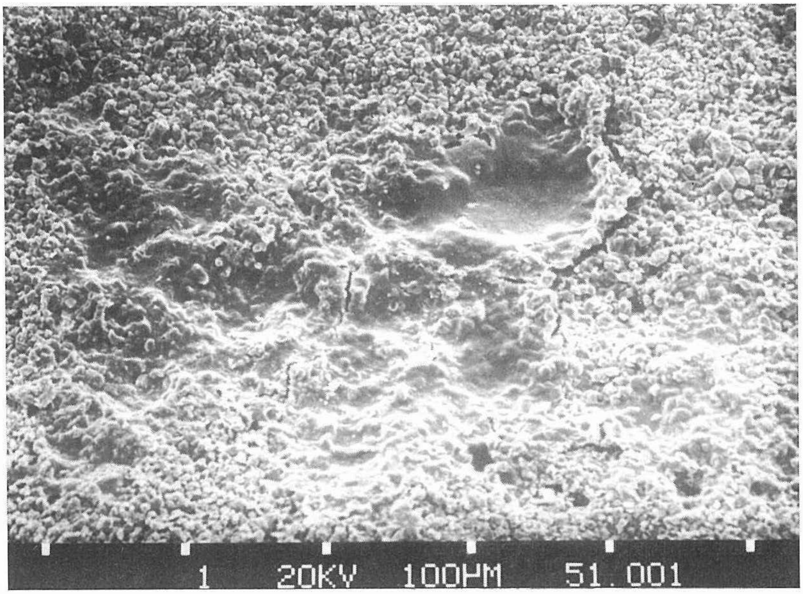

Fig. 7 - x 220. Macerate of *Lecanora dispersa,* SEM-photo, showing mucilaginous etching figures of the apothecia as well as biogenic pits.

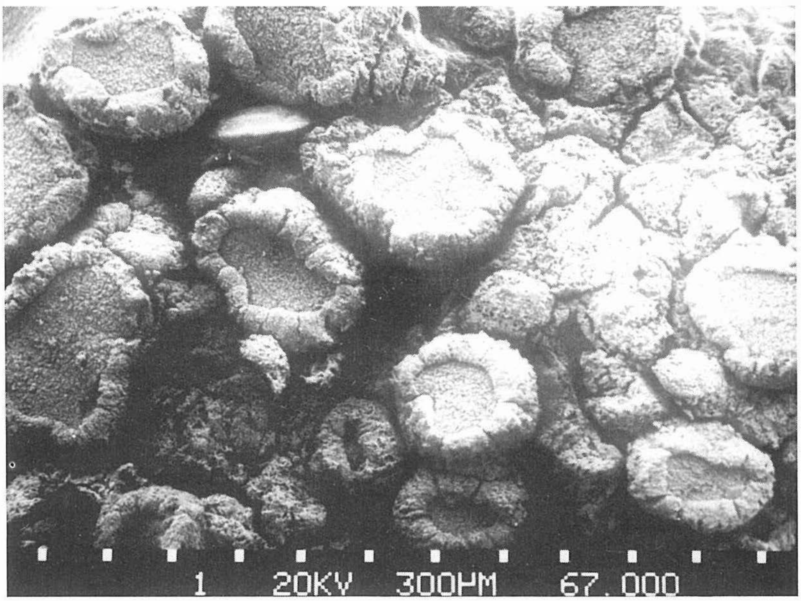

Fig. 8 - x 30. Scanning electron micrograph showing apothecia of *Lecanora dispersa.*

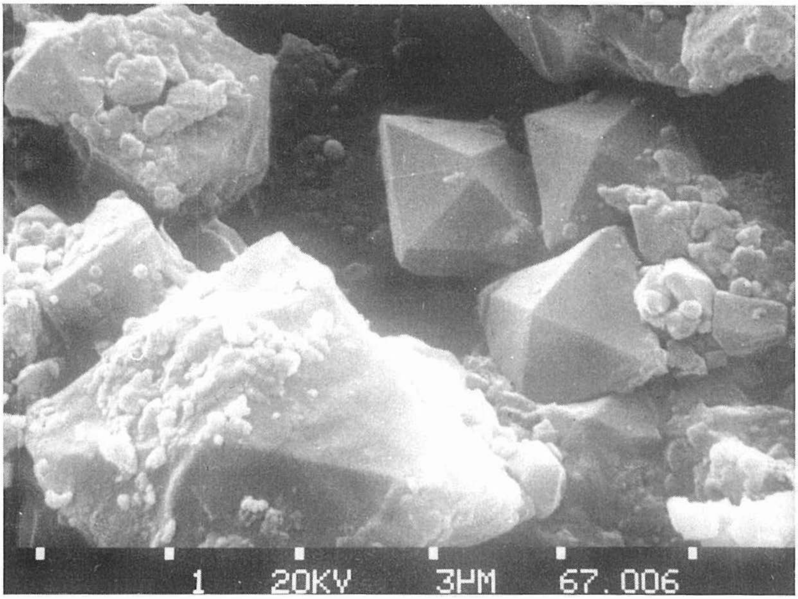

Fig. 9 - x 6600. Detail of Fig. 7. Ca-oxalate crystals with tetragonal symmetry and bipyramidal crystal form (wheddellite) on the margin of the fruiting body of *Lecanora dispersa*.

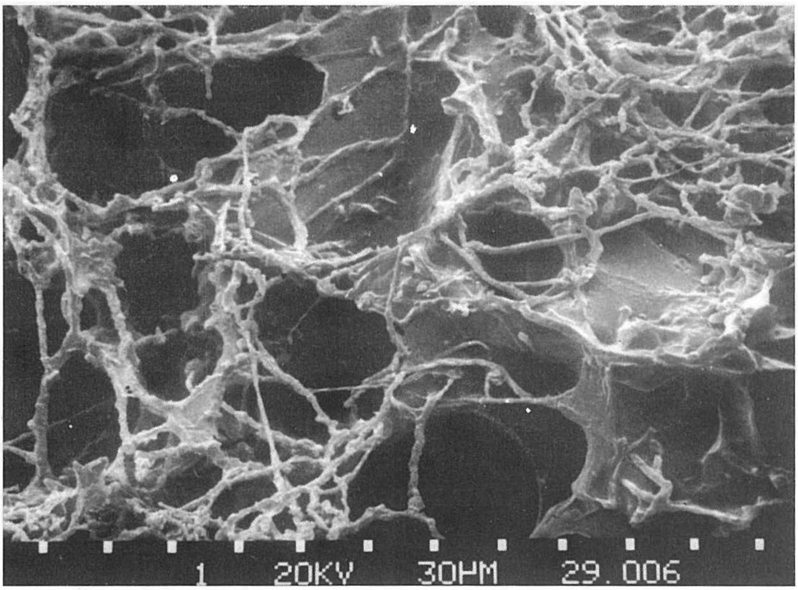

Fig. 10 - x 330. *Lecanora dispersa*, SEM-photo, cast, showing the network of endolithic fungal hyphae and mucilaginous excretions.

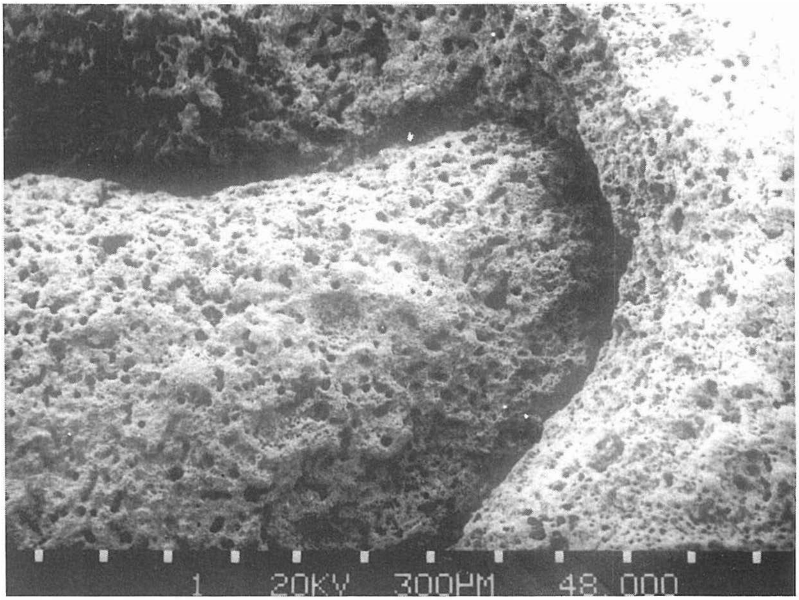

Fig. 11 - x 30. Scanning electron micrograph of a macerated sample showing a micro groove induced by the expansion and contraction of the adjacent lichen thalli as well as biogenic pits.

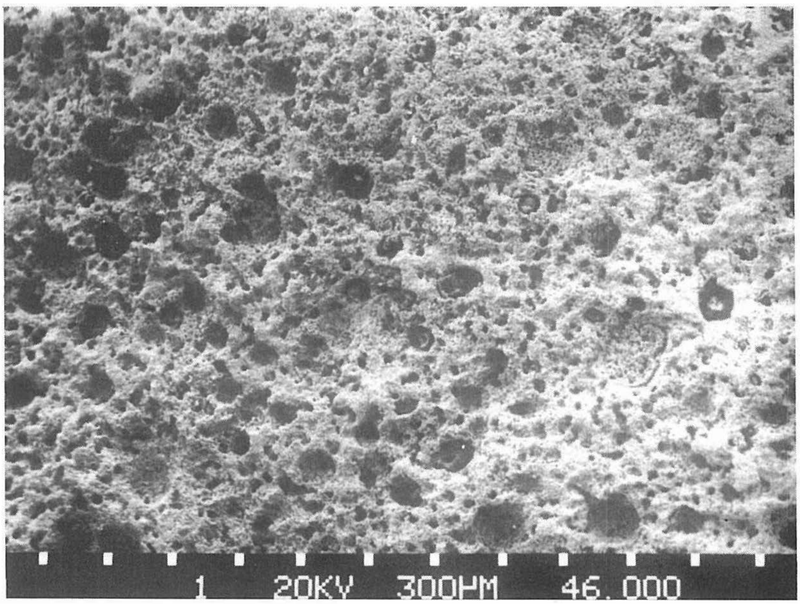

Fig. 12 - x 30. Macerate, SEM-photo, showing the pitting corrosion induced by the activity of endolithic lichens.

The weathering activities caused by epilithic and endolithic lichens were described. These deteriorations of the stones are positively connected to the physical and chemical activity of the lichen involved. Based on its poikilohydric character the thallus is exposed to large and frequent fluctuations in water content creating tensions in the thallus, compared to a pulling strain (Bachmann, 1922, 1923; Fry, 1927; Ried, 1960). These alternating processes along with the microclimate conditions (Jahns & Ott, 1983) as well as the chemical reactions bring about the diruption of rock fragments.

Lichens excrete a variety of secondary metabolic compounds. Many of these substances are powerful metal-complexing agents although differing in their chelating capacity. This fact seems to be correlated rather to the polar groups such as -OH and -COOH than to the water solubility of the compounds. In fact, the presence of the donators in ortho-position favours the formation of soluble complexes which are frequently coloured. On the other hand, oxalic acid, very common in microorganisms and plants is also widespread in lichens being concerned as a significant weathering agent (Zopf, 1907; Smith, 1921). Synthezised by the mycobiont, oxalic acid is excreted, forming hardly soluble calcium oxalate, which is an extracellular deposit (Henssen & Jahns, 1974; Schade, 1970). These calcium oxalates are derived from the dissolution of limestone, marble, dolomite but also by calcium leaching from feldspars and mica. The weathering phenomena brought about at the rock/lichen interface are etching patterns and inhomogenities like desquamation/exfoliant and sanding from the surface of the stone. Biocorrosive activity of mucus produced by the mycobiont must also be taken into consideration. In its dry state, it can produce high adhesion strenghts, leading to a reduction of cohesion and adhesion between the structural components (Fry, 1922, 1927; Eichler, 1986). Besides this, many of these mucilaginous substances are aggressive and active on the surface or degraded by acid producing bacteria (Krumbein, 1973; Krumbein & Schönborn-Krumbein, 1987). Furthermore they act like ''fly-paper'' and particulate aerosol is caught to much larger extent on rocks colonized by epi- and endolithic lichen. These materials in turn can further contribute to biological, chemical and physical destructions on and in rocks of different chemistries and mineralogies.

The extent of rock biocorrosion underneath lichen cover and through endolithic organisms seems to be influenced strongly by the nature of the thallus and its physical and mechanical actions but also by the physical and chemical composition of the rock. Moreover, the ''biomechanical'' deterioration of the stone precedes its biologically or abiogenically initiated chemical decomposition, and biocorrosion precedes abiogenic corrosion processes.

Conclusions

Weathering activities by epilithic and endolithic lichens are positively connected to the thallus expansion and contraction and hyphae penetration as well as to the chelating capacities of the lichen substances and oxalic acid. Furthermore,

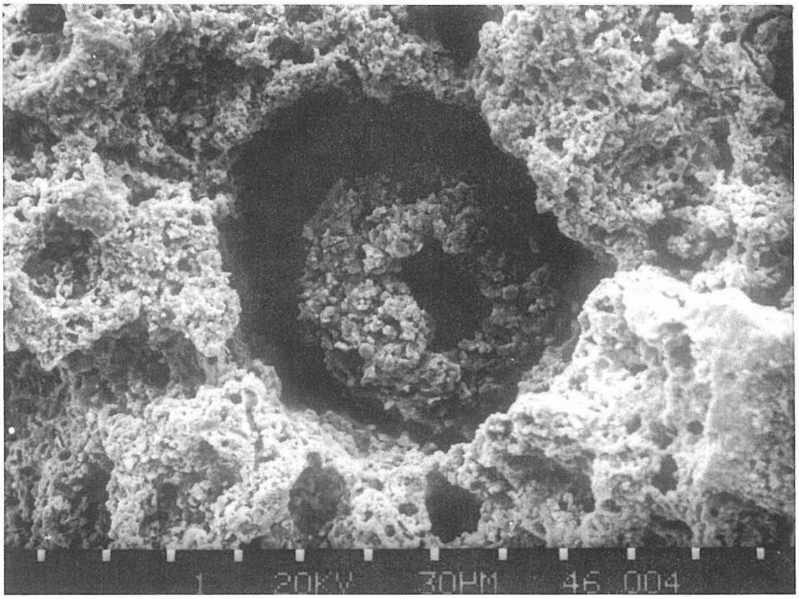

Fig. 13 - x 300. Detail of Fig. 11. Perithecium with crystalline deposit around the pore, pushing through the surface of the stone. Consider the typical pore of this fruiting body.

the intensity of rock weathering is influenced by the lichen tissue and the physical and chemical composition of the rock. Moreover, the macro- and microclimate conditions must also be taken into consideration.

Finally, the overall effect influencing the stone weathering appears in a very complex context. Obviously, one has to be careful in forwarding oversimple chemical, physical or biological theories which do not correlate with the phenomena. Following the investigations presented here, further empirical as well as analytical studies seem to be necessary in order to obtain a better understanding of both abiogenic and biogenic weathering processes although we start to understand some of the complex procedures and processes going on in the field of biogenic action by physical and chemical means and among the chemical means through the action of biogenic inorganic and organic acids or any other aggressive compound.

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