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The occurrence of biomineralization products in four lichen species growing on sandstone in western Norway

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Abstract: High performance thin-layer chromatography/thin-layer chromatography, X-ray diffraction, and scanning electron microscopy analysis of thallus and lichen-rock interface samples, were undertaken to characterize biomineralization products in *Fuscidea cyathoides*, *Ochrolechia tartarea*, *Ophioparma ventosa*, and *Pertusaria corallina*, growing on sandstone in western Norway. Whewellite (monohydrate form of Ca oxalate) was found in the thallus of all species, but not in any of the weathering rinds beneath the species. A significantly higher amount of whewellite was detected in the thalli of *F. cyathoides* and *O. ventosa* than in the other two species. There were only a few differences in whewellite occurrence between the thallus edge and centre samples in the four species. HPTLC/TLC and SEM analysis indicate that lichen compounds occur within the rock beneath some of the lichen specimens. Only divaricatic acid was observed within the weathering rind beneath *O. ventosa*. No lichen substances were found in the weathering rind beneath *F. cyathoides* and *P. corallina*, whereas gyrophoric and lecanoric acids were found in the weathering rind beneath *O. tartarea*.

Introduction

The lichen-substratum interface is a site of considerable chemical activity. Lichens produce acids and metal-complexing compounds, either directly, or as an indirect result of biogenic processes. As organic acids may accelerate dissolution of minerals and rocks by proton and ligand attack, the impact of lichens on weathering has been of great interest during the last decade (see Piervittori *et al.* 1994, 1996, 1998; Adamo & Violante 2000; Chen *et al.* 2000). Lichen respiration generates CO_2, which in combination with water forms carbonic acid. The discussion of chemical weathering by lichens has, however, mostly been focused on the role of lichen compounds and of oxalic acid. Laboratory experiments have shown that both lichen compounds (Ascaso *et al.* 1976) and oxalic acid (Jones *et al.* 1980; Wilson *et al.* 1981; Ascaso *et al.* 1982; Welch & Ullman 1993; Stillings *et al.* 1996) may increase the dissolution rate of minerals. As weathering *in vivo* is a complex process involving physical, chemical, and biological processes, it is impossible to distinguish and estimate the explicit role of each process (Bjelland & Thorseth 2002). However, the presence of biomineralization products like oxalate and lichen compound crystals in the lichen-rock interface indicates acid production, and is hence indirect evidence of chemical weathering by lichens.

Some lichen compounds are restricted to, or have their main occurrence in, particular parts of the thallus (Culberson 1969; Tønsberg 1992). Many species have different substances in the cortex and the medulla, and some substances may be restricted to the apothecia or the soralia. In spite of many reports on the spatial distribution of lichen compounds in the thallus, no one has so far presented evidence of their occurrence in the rock beneath epilithic lichens. According to

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Friedmann (1982), some cryptoendolithic lichens produce lichen compounds, but he does not refer to particular species. Literature about lichen compounds in cryptoendolithic lichens is sparse.

Oxalate salts may precipitate extracellularly on the surface of thalli, within the thalli, and at the lichen-rock interfaces. Ranges of metal oxalate precipitates are known to occur within lichens; including calcium oxalate (e.g. Syers *et al.* 1967; Jones *et al.* 1980; Galvan *et al.* 1981; Ascaso *et al.* 1982, 1990; Edwards *et al.* 1992, 1995, 1997; Adamo *et al.* 1993; Johnston & Vestal 1993; Seaward & Edwards 1995; Holder *et al.* 2000; Prieto *et al.* 2000), copper oxalate (Purvis 1984; Chisholm *et al.* 1987), magnesium oxalate (Wilson *et al.* 1980, 1981), manganese oxalate (Wilson & Jones 1984), and iron oxalate (Ascaso *et al.* 1982). There seems to be a direct relationship between the oxalate minerals in saxicolous lichens and the mineralogy and chemistry of the substratum (Purvis 1984). Calcium oxalate hydrates have also been documented on the surface of some epiphytic lichens (Wadsten & Moberg 1985). It is suspected that the lichen absorbs metal ions from run-off to precipitate metal oxalate salts, rather than extracting it directly from its substratum (Czehura 1977; Purvis 1984).

Little is known about the factors affecting oxalate production in lichens, but several studies have indicated that the amount and occurrence of oxalate seem to vary within and between species, and that environmental factors may have an influence (Edwards *et al.* 1995; Holder *et al.* 2000; Prieto *et al.* 2000). Since rates of oxalate production have been shown to be substantially higher in well insolated communities, photosynthetic metabolism is suggested to be involved (Johnston & Vestal 1993; Modenesi *et al.* 1998). In addition, a comparative study of the calcium oxalate content (monohydrate and dihydrate) in *Acarospora* from the Antarctic and from the Mediterranean, showed that the total amount of calcium oxalate produced by the Antarctic species is almost double of that of the Mediterranean, and that significantly more calcium oxalate dihydrate was produced in an arid Antarctic habitat than in a moister Mediterranean location (Holder *et al.* 2000).

Experiments with filamentous fungi on the production of organic acids have, however, showed that as pH rises, oxalic and gluconic acids tend to replace citric acid (Frey 1931; Moyer 1953). Burnett (1976) also confirmed that the release of oxalic acid needs a high initial pH (>6). In the study by Foster (1949), it was suggested that oxalic acid production requires the presence of neutralizing agents such as calcium carbonate. Its presence maintains the pH (buffering capacity) and yields large amounts of oxalic acid, as well as formation of calcium oxalates, whereas the absence of buffering agents never allows accumulation of oxalate even in traces.

Detection of lichen compounds within the rock and differences in amount of oxalate within and between lichen species, growing on the same substratum in the same environmental conditions, would be important for the understanding of chemical weathering effects by lichens. The aim of this study is to compare the occurrence and amount of biomineralization products in the thallus and in the lichen-rock interface of four different crustose species in the same locality.

Material and Methods

Study site and sampling

The study site Vingen is situated on the western coast of Norway in Sogn og Fjordane county at 61°50′N and 05°20′E. The climate is oceanic with a high mean annual temperature (*c.* 7°C) (Aune 1993), mild winters (mean temperature in January *c.* 1·8°C) (Aune 1993) and relatively cool summers (mean temperature in July 12·5°C) (Aune 1993). Annual precipitation is high (*c.* 2500 mm) (Førland 1993). The bedrock in Vingen is an arcosic metasandstone in which quartz (45–55%), plagioclase (15–40%), and potassium feldspar (15–5%) are the dominant minerals. Other minerals present are muscovite (5–10%), Fe-rich chlorite (7–12%), epidote (3–5%), and accessory minerals. The detrital grains are mainly cemented by calcite (5–12%). The arcosic metasandstone has an upper porous weathering rind, the thickness of which shows local variation in the sampling area, from *c.* 5 mm to >20 mm. As no

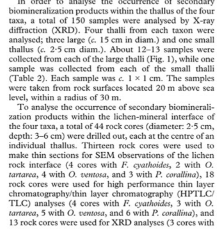

FIG. 1. Sampling method for X-ray diffraction analysis of the thallus. E=thallus edge sample and C=thallus centre sample.

secondary mineral phases are detected, except traces of vermiculite and goethite, the porosity reflects the degree of dissolution of the minerals in the rock. Calcite is absent throughout the weathering rind, while apatite, chlorite, and plagioclase are absent or partly dissolved only in the upper part of the weathering rind. See Bjelland & Thorseth (2002) for a more detailed description of the bedrock.

The lichens used for this study were *Fuscidea cyathoides* (Ach.) V. Wirth and Vězda, *Ochrolechia tartarea* (L.) A. Massal., *Ophioparma ventosa* (L.) Norman, and *Pertusaria corallina* (L.) Arnold.

In order to analyse the occurrence of secondary biomineralization products within the thallus of the four taxa, a total of 150 samples were analysed by X-ray diffraction (XRD). Four thalli from each taxon were analysed; three large (*c.* 15 cm in diam.) and one small thallus (*c.* 2·5 cm diam.). About 12–13 samples were collected from each of the large thalli (Fig. 1), while one sample was collected from each of the small thalli (Table 2). Each sample was *c.* 1 × 1 cm. The samples were taken from rock surfaces located 20 m above sea level, within a radius of 30 m.

To analyse the occurrence of secondary biomineralization products within the lichen-mineral interface of the four taxa, a total of 44 rock cores (diameter: 2·5 cm, depth: 3–6 cm) were drilled out, each at the centre of an individual thallus. Thirteen rock cores were used to make thin sections for SEM observations of the lichen rock interface (4 cores with *F. cyathoides*, 2 with *O. tartarea*, 4 with *O. ventosa*, and 3 with *P. corallina*), 18 rock cores were used for high performance thin layer chromatography/thin layer chromatography (HPTLC/TLC) analyses (4 cores with *F. cyathoides*, 3 with *O. tartarea*, 5 with *O. ventosa*, and 6 with *P. corallina*), and 13 rock cores were used for XRD analyses (3 cores with *F. cyathoides*, 3 with *O. tartarea*, 4 with *O. ventosa*, and 3 with *P. corallina*).

Analytical methods

High performance thin layer chromatography (HPTLC)/ thin layer chromatography analysis (TLC)

The lichen thallus was carefully removed from each core, before the weathering rind was removed by sawing, and crushed by a mortar. Both the lichen thallus and the associated weathering rind were analysed. For major lichen compound identification in *F. cyathoides*, *O. ventosa* and *P. corallina*, HPTLC was carried out in accordance with the method described by Arup *et al.* (1993). The *O. tartarea* samples were examined by TLC (Culberson 1972 and later modifications), as gyrophoric and lecanoric acid were easier to separate by this method. Only the major and chemically well known lichen compounds were studied. This excludes several minor substances [e.g. satellites of fumarprotocetraric acid, confumarprotocetraric and convirensic acid (see Tønsberg 1992; Elix & Yu 1993), decarboxythamnolic acid, which often occurs with thamnolic acid (see Culberson 1969), and the androgyna B unknowns of the *O. androgyna* B/O. *tartarea* species pair (see Tønsberg 1992)].

In order to identify the major lichen compounds by the XRD analysis, reference samples were made of each major lichen compound known to occur in the four selected species. Divaricatic (from *Fuscidea intercincta*), fumarprotocetraric (from *Fuscidea cyathoides*), gyrophoric (from *Lasallia pustulata*), lecanoric (from *Melanelia fuliginosa*), thamnolic (*Pertusaria corallina*), and usnic (*Ramalina polymorpha*) acids were extracted by acetone in amounts large enough to be analysed by XRD. The characteristic reflection of usnic acid (8·6 Å) is also known from the Powder Diffraction File.

X-ray diffraction (XRD)

The thallus, upper, middle, and lower zone of the weathering rind, and fresh unweathered rock of each drill core were ground to powder in an agate mortar and analysed by a Philips PW 1700 diffractometer, using Cu K-alpha radiation, scan range 3–35°2θ, scan step 0·02°2θ, and 1 s per step. The JCPDS PDF (powder diffraction file) database connected to a graphical terminal was used to facilitate mineral identification. To examine for swelling clay minerals the samples were reinvestigated after (a) glycol-treatment and (b) heating to 500°C.

Scanning electron microscopy (SEM)

Rock cores from each of the four taxa were cut in thin sections, impregnated with epoxy resin, polished and coated with carbon. A JEOL scanning electron microscope (JSM-6400), equipped with a Tracor Northern (TN 5600 Series II) EDS (energy dispersive spectroscopy) system and a BSE (backscatter electron) detector, was used. The analyses were performed at an acceleration voltage of 20 kV. To study the amount of biological material within the thalli, samples were stained with Pb citrate, washed, air dried, and re-coated with carbon.

Results

Fuscidea cyathoides

Fumarprotocetraric acid was identified by HPTLC in all thallus samples, but not within any of the rock samples (Table 1). X-ray diffraction analyses of extracted fumarprotocetraric crystals gave a 7·94–8·23 Å reflection. The same peak was found in around 50% of the thallus samples analysed (Fig. 2A), but not in any of the rock samples. Strong reflection at 5·9 indicated the occurrence of whewellite (monohydrate form of Ca oxalate) in the thalli. Whewellite was found in every thallus sample, including the small thallus (100%), but not within any of the weathering rinds. There were no differences in whewellite occurrence between samples from the edge and centre of the thallus (Table 2). Other identified minerals within the thalli were muscovite, albite, quartz, K-feldspar, and goethite, of which goethite is the only secondary phase.

Ochrolechia tartarea

Gyrophoric (major) and lecanoric (submajor) acids were identified by TLC both in the thalli and within the weathered rock beneath the thalli (Table 1). It was not possible to extract large enough amounts of gyrophoric and lecanoric acid crystals for reference samples to determine characteristically XRD peaks. However, in some of the thallus samples analysed (~10%) a peak at 11·5 Å occurred. As this reflection only occurred in *O. tartarea* samples, this could represent gyrophoric acid. Whewellite was found in 20% of thallus samples, but not within any of the weathering rinds. There were no differences in whewellite occurrence between the thallus edge and centre samples (Table 2). Other identified minerals found within the thalli were muscovite, albite, quartz, and K-feldspar.

Ophioparma ventosa

Divaricatic, usnic and thamnolic acids were identified by HPTLC in the thalli (Table 1). Only divaricatic acid was found within the weathered rock beneath the thalli. X-ray diffraction analyses of extracted divaricatic, usnic and thamnolic crystals gave reflections of 12·2–12·83, 8·7–8·9 (and 8·5–8·6), 8·0–8·1 (and 7·5–7·6) Å, respectively. The same peaks were found in the thallus samples analysed (Fig. 2C). While usnic and thamnolic acids were present in all thallus samples, divaricatic acid was only detected in around 40% of the samples. The XRD analyses did not detect any of the lichen compounds in the rock samples. Whewellite was found in most of the thallus samples (63%), but not within any of the weathering rinds. In one of the thalli analysed, only 1 of 13 samples contained oxalate, whereas in the other thalli analysed every sample contained oxalate. There seemed to be slightly more whewellite in the centre of the thallus than at the edge (Table 2). Other identified minerals within the thalli were muscovite, albite, quartz, and K-feldspar (Fig. 3A & B).

The SEM observations showed the occurrence of whewellite crystals (Fig. 3C) and fibrous crystals on hyphae immediately below the lichen thallus (Fig. 3D). The crystals are probably lichen compounds, as EDS or XRD analyses indicated no other secondary mineral phases. Fibrous crystals on hyphae were also observed within the weathering rind beneath *O. ventosa*.

Pertusaria corallina

Thamnolic acid was identified by HPTLC and XRD in the thalli (Fig. 2D), but not within the rock beneath the thalli (Table 1). Whewellite was only found in some of the thallus samples (21%), and not in any of the weathering rinds analysed. There seemed to be no differences in the occurrence of whewellite between the edge and centre of the thallus (Table 2). Other identified minerals within the thalli were muscovite, albite, quartz, K-feldspar, and goethite.

Discussion

The major lichen compounds were not detected in all thallus samples by the XRD analysis. Fumarprotocetraric acid was only

TABLE 1. *The occurrence of lichen products and secondary mineral in the thalli and the lichen rock interfaces of* Fuscidea cyathoides, Ochrolechia tartarea, Ophioparma ventosa, *and* Pertusaria corallina, *and the analytical methods* used for their identification*

Crystal product	d-value Å	*Fuscidea cyathoides* Thallus	*Fuscidea cyathoides* Weathered rock	*Ochrolechia tartarea* Thallus	*Ochrolechia tartarea* Weathered rock	*Ophioparma ventosa* Thallus	*Ophioparma ventosa* Weathered rock	*Pertusaria corallina* Thallus	*Pertusaria corallina* Weathered rock
Divaricatic	12·2–12·83					XRD/HPTLC	HPTLC/SEM?		
Fumarprotocetraric	7·94–8·23	XRD/HPTLC	n.d.						
Gyrophoric	11·5?			XRD?/TLC	TLC				
Lecanoric	11·5?			XRD?/TLC	TLC				
Thamnolic	7·5–7·6 8·0–8·1					XRD/HPTLC	n.d.	XRD/HPTLC	n.d.
Usnic	8·5–8·6 8·7–8·9					XRD/HPTLC	n.d.		
Whewellite	5·9	XRD	n.d.	XRD	n.d.	XRD/SEM	n.d.	XRD	n.d.

*XRD=X-ray diffraction; HPTLC=high performance thin layer chromatography; TLC=thin layer chromatography; n.d.=not detected.

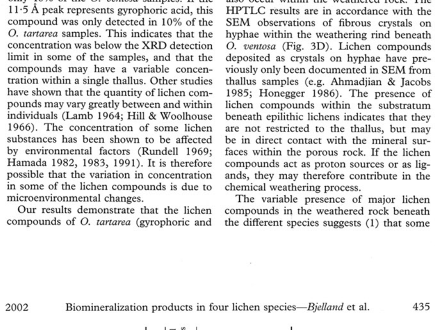

FIG. 2. Representative XRD-spectra of thallus samples A, *Fuscidea cyathoides*; B, *Ochrolechia tartarea*; C, *Ophioparma ventosa*; D, *Pertusaria corallina*. A=albite, M=muscovite, Wh=whewellite, div=divaricatic acid, fpc=fumarprotocetraric acid, gyr=gyrophoric acid, tha=thamnolic acid, usn=usnic acid.

found in 50% of the *Fuscidia cyathoides* samples, while divaricatic acid was found in only 40% of the *O. ventosa* samples. If the 11·5 Å peak represents gyrophoric acid, this compound was only detected in 10% of the *O. tartarea* samples. This indicates that the concentration was below the XRD detection limit in some of the samples, and that the compounds may have a variable concentration within a single thallus. Other studies have shown that the quantity of lichen compounds may vary greatly between and within individuals (Lamb 1964; Hill & Woolhouse 1966). The concentration of some lichen substances has been shown to be affected by environmental factors (Rundell 1969; Hamada 1982, 1983, 1991). It is therefore possible that the variation in concentration in some of the lichen compounds is due to microenvironmental changes.

Our results demonstrate that the lichen compounds of *O. tartarea* (gyrophoric and lecanoric acids) and one of the lichen compounds of *O. ventosa* (divaricatic acid) also occur within the weathered rock. The HPTLC results are in accordance with the SEM observations of fibrous crystals on hyphae within the weathering rind beneath *O. ventosa* (Fig. 3D). Lichen compounds deposited as crystals on hyphae have previously only been documented in SEM from thallus samples (e.g. Ahmadjian & Jacobs 1985; Honegger 1986). The presence of lichen compounds within the substratum beneath epilithic lichens indicates that they are not restricted to the thallus, but may be in direct contact with the mineral surfaces within the porous rock. If the lichen compounds act as proton sources or as ligands, they may therefore contribute in the chemical weathering process.

The variable presence of major lichen compounds in the weathered rock beneath the different species suggests (1) that some

TABLE 2. *XRD analyses of thallus samples from* Fuscidea cyathoides, Ochrolechia tartarea, Ophioparma ventosa *and* Pertusaria corallina

Crystal product	*F. cyathoides* Thallus edge	*F. cyathoides* Thallus centre	*F. cyathoides* Small thallus	*O. tartarea* Thallus edge	*O. tartarea* Thallus centre	*O. tartarea* Small thallus	*O. ventosa* Thallus edge	*O. ventosa* Thallus centre	*O. ventosa* Small thallus	*P. corallina* Thallus edge	*P. corallina* Thallus centre	*P. corallina* Small thallus
Divaricatic							2	14	0			
Fumarproto-cetraric	7	8	1									
Gyrophoric				1?	3?							
Lecanoric				1?	3?							
Thamnolic							12	27	1	12	27	1
Usnic							12	27	0			
Whewellite	13	16	1	2	5	1	7	17	1	6	14	1
n*	13	16	1	11	28	1	12	27	1	12	27	1

*Total number of samples investigated.

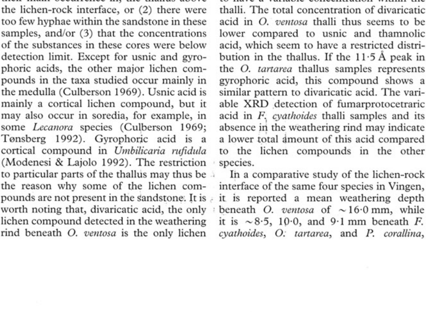

FIG. 3. *Ophioparma ventosa*. A & B, SEM-BSE images of the weathering rind (A, before and B, after staining with Pb citrate); C, SEM images of whewellite (Ca oxalate crystals) in the thallus; D, lichen compound (?) crystals on fungal hyphae.

lichen compounds are restricted to, or have their main occurrence in, the thallus above the lichen-rock interface, or (2) there were too few hyphae within the sandstone in these samples, and/or (3) that the concentrations of the substances in these cores were below detection limit. Except for usnic and gyrophoric acids, the other major lichen compounds in the taxa studied occur mainly in the medulla (Culberson 1969). Usnic acid is mainly a cortical lichen compound, but it may also occur in soredia, for example, in some *Lecanora* species (Culberson 1969; Tønsberg 1992). Gyrophoric acid is a cortical compound in *Umbilicaria rufidula* (Modenesi & Lajolo 1992). The restriction to particular parts of the thallus may thus be the reason why some of the lichen compounds are not present in the sandstone. It is worth noting that, divaricatic acid, the only lichen compound detected in the weathering rind beneath *O. ventosa* is the only lichen compound in this species, which also seems to have a variable concentration within the thalli. The total concentration of divaricatic acid in *O. ventosa* thalli thus seems to be lower compared to usnic and thamnolic acid, which seem to have a restricted distribution in the thallus. If the 11·5 Å peak in the *O. tartarea* thallus samples represents gyrophoric acid, this compound shows a similar pattern to divaricatic acid. The variable XRD detection of fumarprotocetraric acid in *F. cyathoides* thalli samples and its absence in the weathering rind may indicate a lower total amount of this acid compared to the lichen compounds in the other species.

In a comparative study of the lichen-rock interface of the same four species in Vingen, it is reported a mean weathering depth beneath *O. ventosa* of ~16·0 mm, while it is ~8·5, 10·0, and 9·1 mm beneath *F. cyathoides*, *O. tartarea*, and *P. corallina*,

respectively (Bjelland & Thorseth 2002). The same study also reports a larger amount and a deeper penetration of fungal hyphae within the weathering rind beneath *O. ventosa* and *P. corallina* compared to *F. cyathoides* and *O. tartarea*. It is thus possible that the amount of rock material in the *F. cyathoides* samples used in the HPTLC analysis, was too small to allow for the detection of fumarprotocetraric acid crystals within the weathering rind. However, this is unlikely to be the case for the detection of thamnolic acid in the weathering rind beneath *P. corallina* and *O. ventosa*, because these species have a large quantity of fungal hyphae in the weathering rind below the thallus. It seems probable therefore that thamnolic acid is restricted to the thallus above the lichen-rock interface.

Using infrared absorption spectroscopy of lichen material Purvis *et al.* (1987, 1990) have shown that lichen compounds have the ability to complex metal cations from the mineral substratum. Our results do not show any XRD peaks, which might indicate the occurrence of metal-lichen compound complexes. However, as characteristic peaks for metal-lichen compound complexes are not known, their occurrence cannot be excluded.

Oxalic acid is produced in large quantities and by species belonging to all classes of fungi, and may combine with various elements and compounds to form acids and neutral salts (Dutton & Evans 1996). Only one type of metal-oxalate precipitate was found in the samples studied: whewellite, the monohydrate form of Ca oxalate. The calcium source is probably calcite, which occurs as cement in the sandstone. Calcite is very susceptible to chemical weathering, and is dissolved more or less throughout the weathering rind (Bjelland & Thorseth 2002).

The fact that formation of calcium oxalate dihydrate is favoured by cold (<5°C), humid conditions, whilst calcium monohydrate is stable at a higher temperature (5–10°C) and under more acidic conditions (Wiedemann & Bayer 1988), suggests that both minerals could be formed at Vingen. One explanation for the lack of calcium oxalate dihydrate in Vingen could be that the period of low temperature is not long enough. As suggested by Edwards *et al.* (1997), a transformation of dihydrate to monohydrate calcium oxalate mineral could address the need of the species for water storage. However, as the annual precipitation in Vingen is about 2·5 m, water is not expected to be a limiting resource.

Whewellite has been documented in all species, but the content differs between the species, as well as within and between thalli of the same taxon. The whewellite peaks in the XRD spectra are clearly much stronger for *F. cyathoides* and *O. ventosa* than for *O. tartarea* and *P. corallina*, suggesting a higher oxalic acid production of the former species. Differences within and between species in the quantity of oxalate are in accordance with other studies (Edwards *et al.* 1995; Holder *et al.* 2000; Prieto *et al.* 2000).

Our results show no clear correlation between oxalate production and environmental factors. The samples are all from an area with only microenvironmental differences. Similar trends have been observed by Prieto *et al.* (2000), which found that the quantity of oxalic acid secreted was different for three lichen taxa growing on the same substratum under the same environmental conditions. They suggested that calcium toxicity might vary from taxon to taxon. Another proposed explanation is that changes in metabolic processes primarily reflect environmental variations, as for example when oxalate may serve as a source of water in dry sites (Edwards *et al.* 1997). A complicating factor is that the oxalate content varies between thalli of the same taxon within the same area. In one individual *O. ventosa* thallus, only 1 of 13 subsamples contained oxalate, whereas in other thalli analysed every subsample contained oxalate. If the release of oxalic acid in lichens needs a high initial pH, as in non-lichenized fungi (Burnett 1976), then this variation might be due to a low calcite content in the sandstone beneath this thallus, compared to the other samples. The sandstone at Vingen is heterogeneous, and quartz cement is known to

occur occasionally (Bjelland & Thorseth 2002). Further analysis with a better control of the detailed geochemical composition of the substratum beneath each thallus studied and the microenvironmental conditions, for example, light and runoff exposure, sea spray, and other factors related to their microhabitat, are therefore necessary to be able to explain these differences.

Continued fungal growth separates mineral grains and lifts them free from the substratum. This results in accumulation of primary minerals within the lichen thallus (Bjelland & Thorseth 2002). All the species studied have accumulated primary mineral grains inside the thallus. In addition to whewellite, muscovite is the most common mineral within the thallus and is present in more or less every sample, independent of species. This is not surprising, as muscovite is especially susceptible to physical weathering because of its closely spaced and perfect cleavage. However, quartz, K-feldspar, and albite have also been detected in many samples. The origin of most of these minerals is probably the rock surface below the thallus, but a few particles may also be windblown, a phenomenon reported by other authors (Chen *et al.* 2000).

Even if it was not possible to detect oxalate in the weathered rock samples by XRD, one cannot exclude the possibility that it might be present. Due to the large quantity of primary minerals in the rock samples compared to the thallus samples, the concentration of oxalate within the rock may have been too low to be detected by XRD.

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REFERENCES

Adamo, P., Marchetiello, A. & Violante, P. (1993) The weathering of mafic rocks by lichens. *Lichenologist* **25:** 285–297.
Adamo, P. & Violante, P. (2000) Weathering of rocks and neogenesis of minerals associated with lichen activity. *Applied Clay Science* **16:** 229–256.
Ahmadjian, V. & Jacobs, J. B. (1985) Artificial reestablishment of lichens IV. Comparisons between natural and synthetic thalli of *Usnea strigosa*. *Lichenologist* **17:** 149–165.
Arup, U., Ekman, S., Lindblom, L. & Mattsson, J.-E. (1993) High performance thin layer chromatography (HPTLC), an improved technique for screening lichen compounds. *Lichenologist* **25:** 61–71.
Ascaso, C., Galvan, J. & Ortega, C. (1976) The pedogenic action of *Parmelia conspersa*, *Rhizocarpon geographicum*, and *Umbilicaria pustulata*. *Lichenologist* **8:** 151–171.
Ascaso, C., Galvan, J. & Rodrigues-Pascual, C. (1982) The weathering action of saxicolous lichens in maritime Antarctica. *Polar Biology* **11:** 33–39.
Ascaso, C., Sancho, L. G. & Rodriguez-Pascual, C. (1990) The weathering action of saxicolous lichens in maritime Antarctica. *Polar Biology* **11:** 33–39.
Aune, B. (1993) *Temperaturnormaler normalperiode 1961–1990*. Det Norske Meteorologiske Institutt, Oslo: Universitetsforlaget.
Bjelland, T. & Thorseth, I. H. (2002) Comparative studies of the lichen-rock interface of four lichens in Vingen, western Norway. *Chemical Geology* (in press).
Burnett, J. H. (1976) *Fundamentals of Mycology*. London: Edward Arnold.
Chen, J., Blume, H.-P. & Beyer, L. (2000) Weathering of rocks induced by lichen colonization—a review. *Catena* **39:** 121–146.
Chisholm, J. E., Jones, G. C. & Purvis, O. W. (1987) Hydrated copper oxalate, moolooite in lichens. *Mineral Magazine* **51:** 766–803.
Culberson, C. F. (1969) *Chemical and Botanical Guide to Lichen Products*. Chapel Hill: University of North Carolina Press.
Culberson, C. F. (1972) Improved conditions and new data for the identification of lichen products by standardized thin-layer chromatographic method. *Journal of Chromatography* **72:** 113–125.
Czehura, S. J. (1977) A lichen indicator of copper mineralisation, Lights Creek District, Plumas County, California. *Economic Geology* **72:** 796–803.
Dutton, M. V. & Evans, C. S. (1996) Oxalate production by fungi: its role in pathogenicity and ecology in the soil environment. *Canadian Journal of Microbiology* **42:** 881–895.
Edwards, H. G. M., Farwell, D. W., Jenkins, R. & Seaward, M. R. D. (1992) Vibrational Raman spectroscopic studies of calcium oxalate monohydrate and dihydrate in lichen encrustations on renaissance frescoes. *Journal of Raman Spectroscopy* **23:** 185–189.
Edwards, H. G. M., Russel, N. C., Seaward, M. R. D. & Slarke, D. (1995) Lichen biodeterioration under different microclimates: an FT Raman spectroscopic study. *Spectrochimica Acta Part A* **51:** 2091–2100.

Edwards, H. G. M., Russel, N. C. & Seaward, M. R. D. (1997) Calcium oxalate in lichen biodeterioration studied using FT-Raman spectroscopy. *Spectrochimica Acta Part A* **53:** 99–105.
Elix, J. A. & Yu, J. (1993) New lichen β-orcinol depsidones and their congenors. *Journal of the Hattori Botanical Laboratory* **74:** 317–323.
Førland, E. J. (1993) *Nedbørsnormaler normalperiode 1961–1990*. Det Norske Meteorologiske Institutt, Oslo: Universitetsforlaget.
Foster, J. W. (1949) *Chemical Activities of Fungi*. New York: Academic Press.
Frey, A. (1931) Beziehungen zwischen der Wasserstoffionenkonzentration und der Citronensäurebildung durch *Aspergillus niger* und *Citromyces glaber*. *Archiv für Mikrobiologie* **2:** 272–309.
Friedmann, E. I. (1982) Endolithic microorganisms in the Antarctic cold desert. *Science* **215:** 1045–1052.
Galvan, J., Rodrigues, C. & Ascaso, C. (1981) The pedogenetic action of lichens on metamorphic rocks. *Pedobiologia* **21:** 60–73.
Hamada, N. (1982) The effect of temperature on the content of the medullary depsidone salazinic acid in *Ramalina siliquosa*. *Canadian Journal of Botany* **60:** 383–385.
Hamada, N. (1983) The effect of temperature on lichen substances in *Ramalina subbreviuscula* (lichens). *Botanical Magazine, Tokyo* **96:** 121–126.
Hamada, N. (1991) Environmental factors affecting the content of usnic acid in the lichen mycobiont of *Ramalina siliquosa*. *Bryologist* **94:** 57–59.
Hill, D. J. & Woolhouse, H. W. (1966) Aspects of the autecology of *Xanthoria parietina* agg. *Lichenologist* **3:** 207–214.
Holder, J. M., Wynn-Williams, D. D., Rull Perez, F. & Edwards, H. G. M. (2000) Raman spectroscopy of pigments and oxalates *in situ* within epilithic lichens: *Acarospora* from the Antarctic and Mediterranean. *New Phytologist* **145:** 271–280.
Honegger, R. (1986) Ultrastructural studies in lichens. II. Mycobiont and photobiont cell wall surface layers and adhering crystalline lichen products in four Parmeliaceae. *New Phytologist* **103:** 797–808.
Johnston, C. G. & Vestal, J. R. (1993) Biogeochemistry of oxalate in the Antarctic cryptoendolithic lichen-dominated community. *Microbial Ecology* **25:** 305–319.
Jones, D., Wilson, M. J. & Tait, J. M. (1980) Weathering of a basalt by *Pertusaria corallina*. *Lichenologist* **12:** 277–289.
Lamb, I. M. (1964) Antarctic lichens. I. The genera *Usnea*, *Ramalina*, *Himantormia*, *Alectoria*, *Cornicularia*. *British Antarctic Survey Scientific Reports* **38:** 1–34.
Modenesi, P. & Lajolo, L. (1992) Gyrophoric acid in *Umbilicaria rufidula* localized by a new histofluorescent method. *Nova Hedwigia* **54:** 271–276.
Modenesi, P., Piana, M. & Pinna, D. (1998) Surface features in *Parmelia sulcata* (Lichens) thalli growing in shaded or exposed habitats. *Nova Hedwigia* **66:** 535–547.
Moyer, A. J. (1953) Effect of alcohols on the mycological production of citric acid in surface and submerged culture. *Applied Mycology* **1:** 1–7.
Piervittori, R., Salvadori, O. & Laccisaglia, A. (1994) Literature on lichens and biodeterioration of stonework. I. *Lichenologist* **26:** 171–192.
Piervittori, R., Salvadori, O. & Laccisaglia, A. (1996) Literature on lichens and biodeterioration of stonework. II. *Lichenologist* **28:** 471–483.
Piervittori, R., Salvadori, O. & Laccisaglia, A. (1998) Literature on lichens and biodeterioration of stonework. III. *Lichenologist* **30:** 263–277.
Prieto, B., Edwards, H. G. M. & Seaward, M. R. D. (2000) A Fourier Transform-Raman spectroscopic study of lichen strategies on granite monuments. *Geomicrobiology Journal* **17:** 55–60.
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., Elix, J. A., Broomhead, J. A. & Jones, G.C. (1987) The occurrence of copper-norstictic acid in lichens from cupriferous substrata. *Lichenologist* **19:** 193–203.
Purvis, O. W., Elix, J. A. & Gaul, K. L. (1990) The occurrence of copper-psoromic acid in lichens from cupriferous substrata. *Lichenologist* **22:** 345–354.
Rundell, P. W. (1969) Clinal variations in the production of usnic acid in *Cladonia subtenuis* along light gradients. *Bryologist* **72:** 40–44.
Seaward, M. R. D. & Edwards, H. G. M. (1995) Lichen-substratum interface studies, with particular reference to Raman microscopic analysis. 1. Deterioration of works of art by *Dirinia massiliensis* forma *sorediata*. *Cryptogamic Botany* **5:** 282–287.
Stillings, L. L., Drever, J. I., Brantley, S. L., Sun, Y. & Oxburgh, R. (1996) Rates of feldspar dissolution at pH 3–7 with 0–8 mM oxalic acid. *Chemical Geology* **132:** 79–89.
Syers, J. K., Birnie, A. C. & Mitchell, B. D. (1967) The calcium oxalate of some lichens growing on limestone. *Lichenologist* **3:** 409–414.
Tønsberg, T. (1992) The sorediate and isidiate, corticolous, crustose lichens in Norway. *Sommerfeltia* **14:** 1–331.
Wadsten, T. & Moberg, R. (1985) Calcium oxalate hydrates on the surface of lichens. *Lichenologist* **17:** 239–245.
Welch, S. A. & Ullman, W. J. (1993) The effect of organic acids on plagioclase dissolution rates and stoichiometry. *Geochimica et Cosmochimica Acta* **57:** 2725–2736.
Wiedemann, G. & Bayer, G. (1988) Kinetics of the formation of whewellite and weddelite by displacement-reactions. *Journal of Thermal Analysis* **33:** 707–718.
Wilson, M. J., Jones, D. & Russel, J. D. (1980) Glushinskite, a naturally occurring magnesium oxalate. *Mineralogic Magazine* **43:** 837–840.

Wilson, M. J. & Jones, D. (1984) The occurrence and significance of manganese oxalate in *Pertusaria corallina* (lichens). *Pedobiologia* **26:** 373–379.
Wilson, M. J., Jones, D. & McHardy, W. J. (1981) The weathering of serpentinite by *Lecanora atra*. *Lichenologist* **13:** 167–176.

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