THE EFFECT OF MINERALIZATION ON LICHEN COMMUNITIES WITH SPECIAL REFERENCE TO CUPRIFEROUS SUBSTRATA

A Thesis submitted for the Diploma of
Imperial College of Science and Technology

by

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November 1985

ABSTRACT

The important interrelationship between copper and iron minerals, pH and other ecological factors in determining the composition of saxicolous lichen communities is surveyed with particular reference to sulphide-rich substrata in central Scandinavia. A new lichen community is described, specifically related to cupriferous substrata at near neutral to slightly basic pH. The taxonomy of its constituent lichens is discussed and species descriptions, nomenclatural studies and reference to ecology, distribution and chemistry are included. Lecidea inops is shown to be a specific indicator for copper throughout its range and a new species Psilolechia leprosa is described.

The greenish coloration in the thalli of certain lichens has been shown to be due to the accumulation of copper; several of these lichens which have been previously described as distinct species or varieties are defined in this study as Cu-rich ecotypes. The complexing within lichens of a metal (copper) by a lichen acid (norstictic acid) has been verified for the first time; this phenomenon explains the unusual coloration observed. It is suggested that other metal-lichen acid complexes will be found. High concentrations of copper of up to 16% dry weight have been recorded in certain species where copper is present as the extracellular oxalate, a compound hitherto unreported in lichens. It is possible that the formation of both oxalates and Cu-lichen acid complexes by lichens are ways in which some lichens are able to tolerate high concentrations of copper.

The probable action of oxalic acid as an agent in rock weathering is briefly discussed and the possible use of lichens as indicators of metalliferous mineralization is reviewed.

ACKNOWLEDGEMENTS

I am indebted to my supervisors, Mr. P. W. James (Botany Department, British Museum (Natural History) [BM (NH)]) for training and advice on the taxonomy and ecology of lichens, and for providing the facilities for the study of botanical collections in the Cryptogamic Herbarium BM (NH), and to Dr. C. Halls [Geology Department, Royal School of Mines (RSM), Imperial College (IC)] for training in geology, for advice on mineralogy and assistance during fieldwork. I am grateful for their encouragement and patience throughout the course of the work and for their constructive reviews of the manuscript of this thesis.

I am also grateful to Dr. A. C. Bishop and Dr. P. Henderson [Mineralogy Department, BM(NH)] for making available facilities to aid in the chemical analysis of various specimens. In particular I should like to thank Dr. J.E. Chisholm for his interpretation of XRD data, Mr. I. A. Somogyi for the laborious task of preparing XRD mounts and taking pictures and Mr. G. C. Jones for performing IR analyses. I also wish to thank Mr. D. Claugher and the SEM unit [BM(NH)] and Mr. D. Giddens (IC) for tuition and assistance during SEM and EPMA sessions respectively. The BM Photographic Unit is thanked for preparing the excellent photographs. Dr. J. A. Elix (Department of Chemistry, Australian National University) is warmly thanked for providing samples of norstictic acid and a synthetic Cu-norstictic acid complex, and for his considerable help in providing further chemical evidence relating to the identification of such a complex in lichens. Assistance from several

lichenologists including Professor Rolf Santesson who introduced me to the lichen flora of Ramundberget and Dr. B. J. Coppins, Dr. O. L. Gilbert, Professor H. Hertel, Mr. E. Timdal and Mr. T. Tønsberg who have drawn my attention to other relevant material, is gratefully acknowledged. The directors and curators of the herbaria: BG, C, E, GZU, H, L, M, O, TUR, UPS and the Montana College of Mineral Science and Technology are thanked for the loan of material.

The management of Grong Gruber A/S and Ing. Arve Haugen are thanked for providing access to the field area at Gjersvik and for generous logistical support. The author gratefully acknowledges receipt of a BM(NH) Centenary Studentship funded by British Petroleum p.l.c., and special thanks are due to Dr. W. J. Syratt for his interest in the project.

Lastly I wish to thank my wife, Diana for her consideration and support.

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CHAPTER 1. LITERATURE REVIEW

1.1. Lichens

1.1.1. Lichens and the role of the substratum

A lichen is an association between a fungus (mycobiont) and one or more algae (photobiont), including either a green alga, blue-green alga (cyanobacterium) or both of these. The resulting structure is of a complex nature, often dissimilar in morphology, physiology and biochemistry from the isolated symbionts. It is well known that the growth of lichens is affected by a wide range of environmental factors including illumination, humidity, exposure, aspect, altitude, temperature, nitrogen enrichment and pH (Barkman 1958, James et al. 1977). All these factors have been used in ecological surveys to explain the distribution of particular lichen species and to define communities. A community is used in this study to describe two or more lichen species growing together in a particular habitat.

The precise role of the substratum in lichen distribution is unknown, although lichens usually show marked preferences for particular types of substratum. Thus lichens may be, for example, characteristic of wood (corticolous), rocks (saxicolous) or soil (terricolous). Corticolous lichens have been most intensively studied, perhaps on account of the relative ease with which they can be collected. Saxicolous lichens have received less attention.

The physical and chemical nature of the substratum are now recognized to be important factors in the distribution of corticolous lichen species (Barkman 1958, Brodo 1973). The important aspects of the substratum in this case are its texture, the availability of water and in addition the availability of nutrients and the pH. There have, however been many observations of corticolous lichen species growing on rocks and other substrata. Such observations suggest that the primary importance of the substratum is the provision of a physical base on which the organism can grow. The literature is relatively lacking in critical comparative studies of the stability, water-holding capacity and microtopography of these different surfaces. Chemical factors, in particular pH, are clearly influential in controlling the distribution of corticolous lichens. These factors are not necessarily derived from the substratum itself. One example of this is the case of the alkaline dust effect on trees in the vicinity of limestone quarries (Gilbert 1976).

The extent to which the rock chemistry, as opposed to the physical nature of the substratum, influences the species composition of lichen communities is not well documented. Since both chemical and physical factors are controlled to a large extent by the mineralogy of the rock, it is necessary to take the petrography as well as the chemical composition of the rock into account.

Räsänen (1953) was able to distinguish six out of ten different rock types, ranging from ultramafic to quartz-rich in the Ala-, Keski- and Ylä-Penikka districts of the Kivalo Hills in

southern Lapland, using differences in their lichen floras. These floras were recognizable on account of the characteristic colour of each. No formal attempt was made to classify these into communities. Easton (1976) in Brooks (1983) found that ten different rock types in Northern Canada were characterized by specific lichen communities. Of particular interest was the association of species such as Lecidea dicksonii (= Tremolecia atrata)* with pyrite and pyrrhotite in gabbroic rocks.

The apparently direct relationship which could be inferred on the basis of these studies is called into question by Wirth (1972) who suggested that rocks can vary qualitatively and quantitatively, in mineralogy and chemical composition, without there being any change in the species composition of the lichen communities growing on them. At SiO_2 contents of 60-95% in siliceous rocks he observes that there is little change in the floras, but at SiO_2 contents below 55% in mafic rocks, the common species typical of siliceous rocks begin to disappear. Wirth noted that the silicate mineralogy of siliceous rocks could vary quite widely without having a significant effect on the lichen flora. Thus he states (transl.) "it is of little consequence in a particular case which relative proportions of plagioclase, orthoclase, hornblende, muscovite, biotite or quartz may be present, or whether one or more of these minerals is completely absent, providing that the grain structure

* Current combinations given in parentheses according to the checklists of Hawksworth et al. (1980), Santesson (1984) or other recent taxonomic literature.

of the rock is the same". However, he is specific on the point that pyritic rocks have a separate and particularly distinctive lichen flora. Wirth's statement may be given an alternative and clearer way: in rocks in the siliceous part of the igneous spectrum, the mafic minerals biotite and amphibole play a relatively minor role in terms of rock composition and the chief variations in mineralogy are caused by differences in the relative proportions of quartz and the constituent feldspars. Wirth's observations on the silicate composition of rocks are a statement of the relative stability of felsic minerals (quartz and alkali feldspars), when compared with the mafic silicates (amphiboles, pyroxenes etc.). In silicate rocks in which calcium, iron and magnesium are subordinate, the lichen flora will not in general be strongly affected by changes in the relative proportions of feldspar and quartz. This is not to say that variation in the silicate mineralogy has no effect on the composition of lichen communities. Both rock chemistry and rock mineralogy are extremely important in determining the species composition of lichen communities (section 1.1.4, a-e).

1.1.2. Rock classification and terminology

One of the major problems in terminology arises from the ambiguity of certain words such as "basic" or "acid" which have different meanings when applied by botanists in a chemical sense and geologists in a petrological sense. It is therefore necessary to discuss the basis on which rocks are classified and to see how these classifications can be used effectively by botanists. The geologist classifies rocks into 3 main categories.

1) The igneous or eruptive rocks formed as a result of crystallization from primary melts within the earth's crust.

2) Sedimentary rocks formed as a result of chemical and physical weathering of these primary rocks and of pre-existing sediments.

3) Metamorphic rocks formed from igneous and sedimentary rocks as a result of deformation, heating and recrystallization within tectonically active zones of the earth's crust.

It is easiest to begin the discussion of mineralogical and chemical clasification of rocks by discussing the principles as they are applied to the eruptive rocks. It is a matter of general observation that igneous rocks which have been crystallized at depth in the earth's crust consist of an intergrowth of well formed, relatively coarse, crystalline grains. For this reason the early classification of these rocks was based on their constituent mineralogy which could be observed in thin section using polarized light. The technique of microscopic petrography has enabled sytematic description and quantification of the mineralogy of rocks to be made. A review of rock classification based on mineralogical principles can be found in Hatch et al. (1972) and Streckeisen (1967, 1976). Igneous rocks which have crystallized at or near the surface in volcanic or sub-volcanic settings are characterized by a very fine or microcrystalline groundmass, the contents of which are often difficult to determine either macroscopically or by the use of the microscope. For this reason it has been found more practical to classify igneous rocks according to their chemical composition

in terms of their constituent elements. The systematic chemical classification of rocks has been dependent to a large extent upon the development of techniques for the analysis of the refractory silicates and oxides. Consequently, chemical classifications are of more recent application (Irvine & Baragar 1971). There is of course a definite relationship between the chemical composition of a rock and its mineralogy. In igneous rocks, this relationship can be expressed by the calculation of a theoretical mineralogy from a given analysis. The ideal mineralogy so calculated is the norm (Cross et al. 1903). In chemical terms it is possible to express the composition of rocks in terms of the nine major oxides SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O and H_2O. Although rock analyses show total silica as SiO_2 this does not mean it occurs as the mineral quartz. Some less siliceous igneous rocks may contain between 45 and 55% SiO_2 but in this case silica is incorporated in the structure of ferromagnesian silicates and feldspars, quartz being absent. The presence or absence of quartz in a rock is regarded by geologists as an important criterion in mineralogical classification and has led to the concept of Acidity and Basicity as applied in a petrological sense. The choice of terms Acid (>66% SiO_2), Intermediate (56-65% SiO_2), Basic (45-55% SiO_2) and Ultrabasic (<45% SiO_2) is based on a misconception and stems from a time when silicates were regarded as 'salts' of various silicic acids and rocks containing an abundance of silica were thus regarded as 'acidic' (Hatch et al. 1972). According to Cross et al. (1903), Abich (1841) considered that since the known feldspar series presented a wide range in silica content and had different specific gravities, it seemed to him certain that there must be a definite relation between the silica content of a given magma and

the feldspar which could crystallize out of it. Consequently, Abich considered it possible to use the different feldspars for the classification of eruptive rocks very much as fossil remains are used in sedimentary rocks. However, this theory is unfortunately untenable, since as pointed out by Hatch et al. (1972), a whole spectrum of feldspars and other minerals is involved, each mineral having a different effect on the total amount of combined silica in the rock. Hatch et al. (1972) recommended that the geological terms Acid, Intermediate, Basic and Ultrabasic should be written with initial capital letters to denote the special meaning with which they have been endowed by petrological usage. This procedure is adopted in the following account, particularly since the terms acid and basic have a wide alternative usage in botanical circles.

The term basic as frequently used by botanists implies high alkalinity or a high pH, typical of $CaCO_3$-rich, calcareous substrata such as limestones. Plants which are confined to basic and particularly Ca-rich substrata where the pH is greater than 6.0, have been termed calcicoles or described as calcicolous species. However, since many so-called calcicoles may be found additionally on other basic substrata with low calcium contents, an alternative nomenclature has been suggested (Ferreira 1963). Ferreira proposed that the noun calciphile (adjective calciphilous) should be used specifically to describe plants restricted to Ca-rich substrata alone, whilst the term basiphile (adjective basiphilous) should be used in a more general sense for those plants which predominate on base-rich substrata where the major cation may be Ca, Mg or Na. The botanical term acidophyte refers to plants characteristic of acidic substrata or those with a low pH,

such as those with a high content of ferrous sulphides (section 1.1.4.c). Siliceous rocks are also Acidic in the petrological sense and the term siliceous is less confusing for botanical purposes.

Ultrabasic rocks are characterized by the absence of quartz and have SiO_2 contents less than 45 wt%. They consist dominantly of ferromagnesian minerals and therefore they are ultramafic in the petrological sense. Dunite, a rock dominantly composed of olivine, $(Fe,Mg)_2SiO_4$ is a typical example. These rocks are consequently rich in Mg but have low contents of Si and Ca; Cr and Ni values are also frequently high. The primary silicate minerals in serpentinites have been altered by metamorphic or supergene hydration; these rocks consist essentially of mixtures of the different serpentine minerals, chrysotile, antigorite and lizardite in different proportions (Hatch et al. 1972). Unfortunately, botanists have rarely differentiated between the different types of Ultrabasisc rocks and often refer to these collectively as serpentines. Thus, only a superficial overview of the lichens associated with Ultrabasic rocks can be given (section 1.1.4.d).

Whilst the bulk chemical content can be useful as a classification for chemical convenience, it is clearly the mineralogy which determines, in the first instance, the elements which will become available to saxicolous lichens. Rock components known to have a pronounced effect on the species composing lichen communities include $CaCO_3$ (section 1.1.4.a), SiO_2 (section 1.1.4.b), Fe (section 1.1.4.c), Mg, Cr and Ni in Ultrabasic rocks (section 1.1.4.d) and Cu (section 1.1.4.e).

1.1.3. Classification of metal ions

Nieboer & Richardson (1980) suggested the term 'heavy metal' be abandoned in favour of a classification based on their binding preferences. The term 'heavy metal' usually has connotations of toxicity and can include light metals of low atomic mass, e.g. Be. For this reason Nieboer and Richardson favour a chemically significant classification. However, it is probably unwise to abolish the use of the term heavy metal since, although scientific accuracy may be gained by avoiding it, something is lost in colloquial communication with the wider public. Nonetheless, Nieboer and Richardson interpret the biochemical basis for metal-ion toxicity which is of fundamental importance to all concerned with toxicity studies. Nieboer and Richardson recognize 2 classes of metals. Class A metals have a preference for metal binding where the preferred sequence of donor atoms in ligands is O>N>S e.g. K^+, Na^+, Mg^{2+} and Ca^{2+}. In contrast, Class B metal ions exhibit the opposite sequence of preference S>N>O e.g. Hg^{2+}, Ag^+, Au^+ and Cu^+. The borderline metal ions form an intermediate group. However, here Class B character increases in the order:

$$Mn^{2+} < Zn^{2+} < Ni^{2+} < Fe^{2+} \simeq Co^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}.$$

In general Class B ions are more toxic than borderline ions which are more toxic than Class A ions, largely due to their efficiency at binding to -SH groups and nitrogen centres at catalytically active sites in enzymes.

1.1.4. Saxicolous lichen communities

Carbonate rocks constitute an easily definable environment

with a well-defined mineralogy dominated by calcite and related magnesium carbonates with the addition of some iron and manganese. The distinctive identity of the communities growing on these substrata and the ease with which the rock type itself is recognized, has led to the fact that they have been reasonably well studied. By contrast, the more subtle problems of classification of the silicate rocks has meant that the level of discrimination used in botanical studies lacks the precision which has been used in the case of the carbonate rocks. Broadly, the lichenologist has not made significant subdivisions of siliceous substrata, although the botanical significance of Ultrabasic rocks has long been appreciated. Attention has been drawn to the specific effects of special components such as sulphides, but much remains to be done to resolve the changes which might arise from variation in sulphide composition and the abundance of base metals.

1.1.4.a Calcareous rocks and related substrata

Calcium in the form of the carbonate, calcite ($CaCO_3$), is generally considered the most important chemical component influencing lichen communities and accounts for the development of the highly distinctive lichen floras occurring on limestones and other calcareous substrata. Lichens present on these rocks in Britain typically include species of *Caloplaca*, *Collema*, *Lecanora* and *Verrucaria*. Certain species within these genera are entirely restricted to these substrata (James *et al.* 1977). It is interesting to note that many of these lichens occur in widely differing climatic environments, emphasizing the importance of the chemical nature of the substratum as a factor controlling lichen

distribution.

Thus Lecidea (= Psora) decipiens, an obligate calcicole, has been recorded from calcareous substrata in desert regions, the arctic, at high altitudes and also from calcareous dunes at coastal sites.

A study of the lichens of the magnesian limestone belt in England showed distinct differences in the lichen communities, as compared with those occurring on the magnesium-free carboniferous limestone (Gilbert 1984). In particular, Gilbert noted the abundance of less exacting calcicoles, including Caloplaca citrina and Lecania erysibe, whereas Caloplaca isidiigera, Lecidella scabra and Lecanora campestris subsp. dolomitica apparently favoured the substrata with high magnesium content.

1.1.4.b Siliceous rocks

Acidic rocks, those with high silica contents (>66% SiO_2), are usually species poor and characterized by species of Fuscidea, Lecidea, Rhizocarpon and Umbilicaria (Wirth 1972, James et al. 1977). These rocks, with the notable exception of those on rocky shores, have received scant attention in the British Isles. In Britain, the siliceous rock communities have been grouped into six broad categories according to habitat: a. shaded, b. exposed, c. nutrient enriched, d. mineral-rich, e. marine and maritime, and f. aquatic (James et al. 1977). Likewise both Wirth (1972) who studied the siliceous lichen communities in central Europe and Creveld (1981) who studied the epilithic lichen flora of Scandinavia,

generally use broad ecological criteria to categorize these communities. The effect of the mineralogy, other than iron (section 1.1.4.c) on lichen communities has received scant attention. Recently, the effect of copper on lichen communities has been noted (section 1.1.4.e).

1.1.4.c Iron-rich rocks

It has long been recognized that certain iron-bearing rocks tend to support a range of predominantly rusty lichen species (e.g. Acharius 1798, Fries 1831). These lichens belong to the community Acarosporetum sinopicae, first recognized by Hilitzer (1923) from the Böhmerwald in Germany and subsequently reported by many workers from central Europe, including Suza (1947), Schade (1932), Poelt & Ullrich (1964) and Wirth (1972). In Scandinavia, these communities have been studied by Creveld (1981) and in Britain are discussed by James et al. (1977). Poelt & Ullrich (1964) introduced the term chalkophile (greek chalkos = ore) to describe those lichens which are more or less restricted to rocks rich in heavy metals, such as slags and ores. However, the elucidation of the precise factors responsible for the development of the Acarosporetum sinopicae has been complicated by the heterogeneous composition of the substrata. In central Europe, where this association has been most intensively studied, the Acarosporetum sinopicae commonly occurs on old slag heaps containing high levels of several elements, including Fe, Zn, Pb, Mn, Cu, and lesser amounts of Sb, Ag and Sn. However, the study of the association on naturally mineralized rocks in the Schwarzwald and Böhmerwald in Germany suggests that the Acarosporetum sinopicae is particularly characteristic of rocks

Table 1. Lichens of the Lecanoretum epanorae and the Acarosporetum sinopicae in central Europe (Adapted from Wirth 1972)

Association	Lecanoretum epanorae		Acarosporetum sinopicae	
Number of localities visited	34		27	
Characteristic and Differential taxa of Lecanoretum epanorae				
C Lecanora epanora	V	53.1		
C Lecanora handelii	II	9.2		
C Coscinodon cribrosus	II	0.9		
D Lepraria spp.	III	3.6		
D Rhizocarpon obscuratum f.	II	0.9		
D Crocynia (=Lepraria) membranacea	II	0.3		
D Aspicilia sp.	II	0.7		
D Umbilicaria hirsuta	I	0.3	1	
Characteristic and Differential taxa of Acarosporetum sinopicae				
C Lecanora subaurea			IV	29.4
D Buellia sororioides (=B. aethalea)			IV	9.3
D Lecanora soralifera			III	2.4
C Acarospora lesdainii f.subochracea			II	2.6
C Lecidea dicksonii (=Tremolecia atrata)			II	3.7
C Lecanora gisleri			II	0.2
C Lecidea silacea			I	7.3
C Acarospora montana			I	0.3
D Stereocaulon nanodes			I	0.3
D Lecanora polytropa	1		IV	2.5
D Lecidea lapicida			II	2.4
D Haplocarpon tumidum (=Huilia tuberculosa)			I	0.3
Characteristic taxa of the alliance				
Acarospora sinopica	IV	7.2	IV	3.1
Bacidia(=Scoliciosporum) umbrina	III	7.7	II	2.6
Rhizocarpon oederi	2		II	1.6
Rhizocarpon furfurosum	2		I	1.1
Rhizocarpon ridescens	1		I	6.6

Explanation of terminology and symbols in Table 1

Association: basic unit of phytosociological classification.
Alliance: phytosociological taxon comprising one or more associations.
Characteristic species: species used in the delimitation of a community.
Differential species: non-characteristic species used in distinguishing closely related communities.
Roman numerals refer to the constancy, the frequency of a species within records of a particular community type, expressed on a 6-category scale:
r (under 1%), I (1-20%), II (21-40%), III (41-60%), IV (61-80%), V (81-100%).
The subsequent number (arabic) refers to the percentage average cover of that taxa in the recorded stands.

Wirth has followed the Braun-Blanquet phytosociological approach to the classification of plant communities. Fuller details of this method are given in Shimwell (1971).

rich in pyrite (FeS_2) (Wirth 1972). The presence of high concentrations of iron pyrite (FeS_2) in the substratum results in the production of sulphuric acid and a consequent decrease in pH, following the oxidative weathering of the sulphides (section 1.2.3.a). Thus the Acarosporetum sinopicae is characteristic of rocks rich in ferrous sulphides which create a low pH environment. Wirth (1972) records pH values of about 3 for the closely allied Lecanoretum epanorae, typical of vertical, dry, shaded surfaces, whereas the Acarosporetum sinopicae is more characteristic of horizontal, sunny and exposed surfaces. These two associations form the alliance Acarosporion sinopicae Wirth ex James et al. 1977, and whilst sharing certain species in common, there are also notable differences (Table 1).

1.1.4.d Ultrabasic rocks

Geologically a distinction can be made between the Ultrabasic rocks which have been subject to serpentinization and those which have not. Because weathering processes invariably produce a thin crust of serpentinitic alteration, botanists in general have not made a distinction between relatively unaltered and serpentinized Ultrabasic rocks. Important mineralogical differences exist and for this reason botanical distinctions can be made and much will depend on the form taken by the iron released from the silicate structure during serpentinization.

These rocks are noticeably different from other rocks in terms of the lichen flora they support (e.g. Räsänen 1953, Ritter-Studnička & Klement 1968, Rune 1953). A general feature of

the lichen floras of these substrata are their paucity, both in terms of numbers of lichen species present and in the cover. Wirth (1972) in central Europe, characterizes the serpentine flora by the absence or scarcity of lichens typical of the more siliceous rocks, e.g. Rhizocarpon geographicum, Acarospora fuscata, Lasallia pustulata, Lecanora rupicola, Parmelia conspersa, and also by the absence of calcicolous species. Furthermore, he recognizes a few species which are apparently restricted to these substrata, including Lecanora serpentinicola, L. dvorakii and Acarospora suzai. Other lichens reach their northernmost distribution on these dark rock surfaces which are composed of refractory ferromagnesian silicates and have a high heat capacity. Examples include Lichinella stipatula, Toninia cinereovirens and Caloplaca rubelliana (Wirth 1972).

There are occasional reports of ochraceous forms of lichens, e.g. Lecidea (= Huilia) macrocarpa f. oxydata occurring on the Bosnian serpentine (Ritter-Studnička & Klement 1968) and Lecidea lapicida f. ochromeliza from the Kivalo Hills, southern Lapland (Räsänen 1953). However, in spite of their concentration of iron and presence of Co, Ni, Cr, these rocks are not apparently characterized by chalkophile lichens restricted to the Acarosporion sinopicae; this is partly due to the higher pH of these surfaces (Wirth 1972) and the general lack of ferrous sulphides.

1.1.4.e Copper-rich rocks

The distinctive green surface coloration produced by the accumulation of copper within lichen thalli has been described

(Czehura 1977, Purvis 1984). This phenomenon is discussed further (section 1.1.7.b). Natural environments in which copper occurs are also in general characterized by an abundance of ferrous sulphides. The most important primary copper mineral is chalcopyrite ($CuFeS_2$) which is generally paragenetically associated with pyrite (FeS_2) and or pyrrhotite ($Fe_{1-x}S$). The oxidation of the ferrous sulphides on exposure to the atmosphere under ambient conditions creates an acid environment and mobilizes copper from the decomposing copper sulphides. The extent to which secondary copper oxidate minerals are fixed in the immediate vicinity of the oxidized rock surfaces will depend on a number of factors, particularly the other minerals in the rock and biological activity of saxicolous lichens and other organisms. Mineralized rocks vary widely in the relative proportions of ferrous sulphides and copper sulphide and it is often difficult to make a simple statement about the relative importance of the copper and iron in the environment of the lichen.

It is notable that there has been no published detailed study listing the species characteristic or present on copper-rich rocks of specific areas. However, there have been a number of studies published on iron-rich rocks (section 1.1.4.c). Wirth (1972), James et al. (1977) and Creveld (1981), in their phytosociological accounts of the lichen floras in central Europe, British Isles and Scandinavia, make no reference to these specialized lichens. However, Vězda (1978) describes several species occurring on predominantly copper-rich rocks at old copper mines at Staré Hory (alt. 600m) and near Špania dolina (alt. 900m) from the Nízke Tatry, Czechoslovakia. Unfortunately, no geological or mineralogical details of the copper mineralization are given.

Lecanora chalcophila was described as a new species, restricted to these copper-rich substrata. Associated species included Lecanora subaurea, Acarospora montana, A. sinopica and Rhizocarpon oederi. As these species are members of the community Acarosporetum sinopicae considered typical of rocks rich in iron sulphides, this community owes its composition as much to the abundance of ferrous sulphides as copper minerals. Of particular importance however, was the discovery of Lecidea inops at these sites, first described from a copper mine (Torskebäckens koppar gruva) in Vaermland County, Sweden by Th. Fries. L. inops colonizes exclusively copper-rich stones or other substrata, including wood subject to copper irrigation, in Czechoslovakia (Vězda 1978), Scandinavia (Santesson 1984) and Britain (see section 4.3.2.c). Vězda (1978) described in addition Huilia musiva var subsquamescens which was the commonest lichen species present on the slag and copper-rich rocks at an old disused mine near Mníšek in the Erz Gebirge of Czechoslovakia. According to Vězda, this Huilia might be a distinct species though further study is needed to confirm this. Stereocaulon vesuvianum var symphycheilodes was also present (type locality of this variety). Other species found in association with copper include Haematomma ventosum var cuprigenum which was described by Poelt (1955) growing on cupriferous substrata in the Großarl, Salzburg and Lecanora vinetorum which thrives on vine supports sprayed with Bordeaux Mixture, [$CuSO_4.5H_2O$ (4): CaO (4): H_2O (50)] (Poelt & Huneck 1968).

1.1.5. Metal uptake in lichens

1.1.5.a Terminology and methodology

The term metal uptake is applied here in a broad sense to describe the inclusion of a metal within the lichen thallus, but not necessarily within the protoplast by any physical or chemical mechanism. Methods of uptake include particulate trapping (section 1.1.6.a), cation exchange (section 1.1.6.b) and precipitation reactions (section 1.1.6.c). The particulate uptake of rock fragments by lichens is possibly the form of metal accumulation which is least dependent upon the physiology and biochemistry of the lichen. Unfortunately, as the phenomenon is so widespread and proportionately significant in terms of mass, conventional bulk chemical analytical techniques, including atomic absorption spectroscopy and plasma emission spectrometry, may fail to detect the lesser concentrations of biologically formed minerals. Thus a major problem of these techniques concerns the satisfactory preparation of material prior to analysis. In most instances, hand dissection of mineral fragments from the lichen thallus under a binocular microscope, followed by washing has been the method employed (e.g. Lange & Ziegler 1963). This will not eliminate all substratum-derived particulate matter from the lichen. Where thallus homogenization and centrifugation has been used (e.g. Le Roy & Koksoy 1962, Czehura 1977), there still remains the possibility of either subsequent contamination of the lichen material or even an actual element loss during sample preparation. Furthermore the techniques used for quantitative analysis of lichen material give no indication of the localization of the elements

concerned within the lichens (section 1.1.8). As a consequence of the unsatisfactory sample preparation and methods of analysis, most analyses of lichen material are of extremely limited value, serving only as a crude indication of the presence of that element in the environment.

1.1.5.b Analyses of lichens collected in the field

The analyses of metal contents in lichens was pioneered by Lounamaa (1956), who investigated the content of trace elements in 16 macrolichens from mainly siliceous rocks, but also from some Ultrabasic rocks, in Finland using spectrographic analysis. These species belonged to the genera Lobaria, Cladonia, Parmelia, Umbilicaria and Cetraria. Lounamaa recorded distinct characteristics in the trace element composition of these lichens, which he attributed to differences in the nature of the substratum. Thus the Cr, Mn, Co and Ni content of lichens taken from Ultrabasic rocks was higher than that of samples from siliceous rocks, which had conversely greater concentrations of Zn, Ga, Y, Zr, Sn and Pb. No appreciable differences in the B, Cu, Mo, Ag and Cd contents were observed. Lounamaa considered the differences in element uptake between the various lichen species to be generally slight. However, Lounamaa observed that Umbilicaria (= Lasallia) pustulata growing on siliceous rocks contained substantially more Zn (10,000 $\mu g g^{-1}$ ashed wt.) than any other lichens which contained, on average, 2800 $\mu g g^{-1}$ Zn ashed wt. The Zn content was closely mirrored by Cd, which in U. pustulata reached concentrations of 30-600 $\mu g\ g^{-1}$, three times as much as in other lichens from siliceous rocks. The Cu content in the majority of samples analysed

ranged from 100-300 $\mu g\ g^{-1}$. Lichens growing on outcrops with rocks containing unusual amounts of copper likewise showed a high content of the element, approximately 10 times above normal. All the Stereocaulon paschale specimens collected from the Orijärvi mining area contained 3000 $\mu g\ g^{-1}$ copper, whereas the content in the samples of the same species from other siliceous rocks varied between 30 and 1000 $\mu g\ g^{-1}$. In conclusion, Lounamaa suggested that lichens were obviously different from other plants with regard to the contents of trace elements which they contain. The majority of the elements studied occurred in lichens in greater concentrations than in any of the leaves, twigs and roots of a range of mosses, ferns, conifers, deciduous trees, shrubs, grasses and herbs. Zn, Cd, Sn and Pb were most strongly concentrated by lichens. Co, Ni, Mo and Ag occurred in lichens in approximately the same amounts as in the other plants from corresponding habitats. Cr, Ga, Y and Zr occurred in general in higher concentrations in lichens than in the other plants but not exceeding the content of the substratum.

It is unfortunate that Lounamaa gives his results in relation to ashed weight as the actual amounts of these elements associated with the living lichen tissues will be only approximately 10% of the ashed weight (assuming the ashed weight to be 10% dry weight). Furthermore, since the macrolichens from similar environments rarely differ in their contents of elements, these concentrations could easily arise through non-selective particulate uptake from the substratum.

A similar study was carried out by Le Roy & Koksoy (1963) who investigated a range of 20 trace elements in the ash of Umbilicaria

hyperborea, Parmelia conspersa, Lecanora rubina (= Rhizoplaca chrysoleuca) and Caloplaca (= Xanthoria) elegans from sandstones of Jurassic and Cretaceous foundations in Denver, Colorado using spectrographic methods. They reported high ash concentrations of Sr, V, Ti and Y, the presence of Be and appreciable amounts of Cu, Cr, Pb, Mo and Zn. Similar criticisms can be applied to this work as that of Lounamaa (1956) as well as for the additional reasons stated (section 1.1.5.a).

Possibly the first detailed investigation of the metal contents of a crustose saxicolous lichen community was carried out by Lange and Ziegler (1963) using chemical methods who examined the Fe and Cu content in several lichens belonging to the Acarosporetum sinopicae growing on Middle Age slag dumps in the Harz Mountains, Germany (section 1.1.4.c). The species studied were Acarospora sinopica, A. smaragdula var. lesdainii f. subochracea, A. montana, Lecanora epanora (= L. subaurea?), Rhizocarpon oederi, Lecidea (= Huilia) macrocarpa, Stereocaulon dactylophyllum and S. vesuvianum. They found that these members of the Acarosporetum sinopicae were capable of accumulating considerable amounts of Fe, on average ranging from 6000–16000 $\mu g\ g^{-1}$ dry weight. This observation explains the rusty appearance of many of these species. The non-rusty Lecanora epanora (= L. subaurea?) contained 5832 $\mu g\ g^{-1}$ Fe dry weight which reflects the concentration of iron within the thallus (section 1.1.8). The high value of 55000 $\mu g\ g^{-1}$ Fe in Acarospora sinopica was found in a specimen growing on slag containing c. 30% Fe in the northern Oker. However, the remarkable ability of Acarospora sinopica to accumulate iron is shown by the specimen collected from the Kahleberg-Sandstone from Rammelsberg

which contained 65000 μg g^{-1} Fe, and the substratum contained 4.5% Fe probably as oxides, Lange and Ziegler also found quantities of copper in A. sinopica, notably 1100 μg g^{-1} Cu from the specimen occurring on the slag and 940 μg g^{-1} Cu in A. sinopica from the Kahleberg-Sandstone. In this latter case, no copper was detectable in the underlying substratum. In contrast Acarospora smaragdula v. lesdainii f. subochracea contained only 60 μg g^{-1} Cu. Lange and Ziegler suggested that the different contents of Cu in the two specimens of these two Acarospora species was evidence of specific differences in their copper uptake. However, the possibility of chance particulate uptake in the sample of A. sinopica cannot be ignored. Evidently more analyses are required and a clarification of the process of metal uptake is needed before it is possible to demonstrate specific differences in metal uptake between species. Furthermore, it is desirable to collect samples as close to one another as possible to minimize environmental variability. Lange and Ziegler additionally analysed Cornicularia (= Coelocaulon) aculeata and Cladonia mitis belonging to the next successional stage. Their discovery of small quantities of both Fe and Cu in these species is not surprising since Cornicularia (= Coelocaulon) aculeata and Cladonia mitis are macrolichens and consequently are not in such intimate contact with the substratum and mineralizing solutions as in the case of the crustose lichens.

Noeske et al. (1970) subsequently investigated polarographically the uptake of the additional elements Pb, Zn, Mn, Sb and Cd by lichens growing on the slags in the Harz region. On the basis of the analysis of single samples they concluded that the lichens belonging to the Acarosporetum sinopicae were

characteristically different with regard to their elemental contents. This suggests that the uptake of elements differs between species. All, however, contained high contents (4875-14409 $\mu g\ g^{-1}$) of iron. Additionally the Cu contents were also considered to be higher in these species, the highest concentration of 590 $\mu g\ g^{-1}$ occurring in Stereocaulon nanodes, but in the same order of magnitude as occurring in phanerogams. Unfortunately, due to the limited sampling, and for similar reasons as explained previously, there seems to be little case to suggest specific differences in metal uptake in these species.

It is now evident that copper can be found in significantly higher concentrations in lichens than in other plants, values around 0.5% dry weight being frequent. Thus, Poelt & Huneck (1968) reported concentrations of 5000 $\mu g\ g^{-1}$ Cu dry weight occurring in Lecanora vinetorum growing on vine supports frequently sprayed with Bordeaux mixture ($CuSO_4.5H_2O$ (4):CaO (4):H_2O (50)) in the Uberetsch area, Austria. Alstrup & Hansen (1977) recorded 4900 $\mu g\ g^{-1}$ Cu in Lecanora polytropa, from a copper-rich rock near Godhavn on Disko Island in West Greenland. On bornite-bearing rocks, from the Lights Creek District, Plumas County, California, Czehura (1977) described 4% copper in the ash of atypical dark green Lecanora cascadensis, approximately 3 times the content of Cu found in associated species collected at the same site. Concentrations of copper, an order of magnitude higher, have now been found by the author in Lecidea lactea (5.3%) and Acarospora rugulosa (5.9%) from cupriferous substrata in Scandinavia (Purvis 1984).

There are a few reports of high contents of zinc occurring in

certain lichens, particularly from calamine-rich soils in Belgium. Lambinon et al. (1964) reported contents of Zn up to 93400 μg g^{-1} dry weight in Diploschistes scruposus var bryophilus (= D. muscorum) from soils bearing 10900 μg g^{-1} Zn. Similarly, Stereocaulon nanodes f. tyroliense was found to contain up to 3300 μg g^{-1} Zn dry weight, on soils containing 700 μg g^{-1} (Maquinay et al. 1961). High levels of lead in Stereocaulon nanodes (2747 μg g^{-1}) growing on slag in the Harz Mountains and also in Cornicularia (= Coelocaulon) aculeata (1740 μg g^{-1}) were also recorded by Noeske et al. (1970).

1.1.6. Mechanisms of metal uptake

1.1.6.a Particulate trapping

This is probably the most frequent way in which metals are accumulated in lichens. In macrolichens the particles are derived chiefly from the atmosphere, especially in polluted regions, a feature which has led to the use of lichens as indicators of heavy metal fall-out from smelters and other industrial sources (e.g. Garty et al. 1977, 1979, Kalevi & Olkkonen 1981, Lawrey & Hale 1981, Nash 1975, Nieboer et al. 1972, 1982, Seaward 1973, Schutte 1977). The important scale of particulate trapping from the atmosphere is emphasized by the observation that 5g dry weight samples of Cladonia rangiferina that had been thoroughly washed following collection from within 70m of a uranium mine ventilation shaft, had an ash content of the order of 300 mg. In contrast, comparable specimens collected 430m away yielded only 40 mg of ash (Richardson & Nieboer 1980). Additionally, mineral and rock

fragments from the substratum are likely to be incorporated within the lichen thallus, due to degradation of the surface as growth proceeds. This will occur particularly in the case of crustose lichens, which intimately overgrow their substrata.

1.1.6.b Cation exchange

Tuominen (1967) was able to remove significant amounts of Ca^{2+} from Cladonia alpestris in dilute $SrCl_2$ ($2.5x10^{-4}M$) leading to a significant reduction in the pH of the solution. This observation suggested that the thallus functions as a cation exchanger or some kind of chelator, which is buffered to moderately acidic conditions. Brown & Slingsby (1972) were able to remove nearly all of the accumulated Pb^{2+} from Cladonia rangiferina in 1N HCl or 0.1M Cu^{2+}. There are many other observations demonstrating that a range of cations can displace previously bound elements from lichen thalli in precisely stoichiometric proportions such that a divalent cation will displace a single divalent atom or two monovalent atoms (e.g. Brown & Beckett 1984, Nieboer et al. 1978, Puckett et al. 1973, Tuominen & Jaakkola 1973). In general, the uptake of metal ions by lichens is largely extracellular, passive and rapid (Richardson & Nieboer 1980). Thus the presence of metabolic inhibitors caused no significant decrease in metal uptake in Umbilicaria muhlenbergii. In fact, dead thalli were found to accumulate nickel to a greater extent than live thalli (Nieboer et al. 1976).

However, elements differ in their affinity for the available binding sites (Brown & Beckett 1984). Competition experiments (e.g.

Beckett & Brown 1983) demonstrate preference for lichen extracellular exchange sites in the sequence monovalent class A (e.g. K^+, Na^+) < divalent class A (e.g. Mg^{2+}, Ca^{2+}) < borderline divalent (e.g. Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}) < divalent class B (e.g. Cu^{2+}) (Brown & Beckett 1984). As shown by Nieboer & Richardson (1980), the ligand preferences for class A elements were O>N>S and for class B elements the reverse. A discussion of the explanation and biological relevance of class A and class B elements is given (section 1.1.3).

1.1.6.c Precipitation of salts

The precipitation of salts from solution, either within or on the surface of lichens, is a phenomenon which has rarely been considered to explain metal uptake in lichens (e.g. Jones et al. 1981). Indeed in many review articles there is no reference to this phenomenon in lichens, e.g. Brown 1976, Tuominen & Jaakkola 1973, Rao et al. 1977 and Nieboer et al. 1978.

Evidently this process would occur primarily in crustose lichens which have received less systematic study and the lack of reference to this phenomenon is perhaps not surprising. Crustose lichens will be irrigated by mineralizing solutions to a greater extent than foliose or fruticose species, which are less intimately bound to the substratum.

In the case of ochraceous or rusty forms of lichens Weber (1962) suggested these could arise from the absorption of iron salts from the rock, followed by their oxidation and precipitation

upon the surface of the lichen thallus. Lichen fungi produce oxalic acid, accounting for the formation of a number of essentially insoluble oxalate precipitates, now known to occur widely in lichens (section 1.1.8). These precipitates, however, are usually considered to form at the rock / lichen interface, or within the lichen thallus and to precipitate as a result of the direct breakdown of a number of minerals in contact with the lichen thallus (e.g. labradorite: Jones et al. 1980, manganese ore: Jones et al. 1981, Wilson & Jones 1984, serpentinite: Wilson et al. 1981). However, copper oxalate has recently been discovered in Lecidea lactea occurring on quartz irrigated by copper-rich solutions (Purvis 1984, see appendix). Thus, although cation availability is evidently of importance in oxalate formation, a direct contact between the lichen and the mineralization is unnecessary.

Also of interest is the recent discovery of the basic lead carbonate, hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], isolated from thalli of Stereocaulon vesuvianum, collected on a stone of siliceous limestone in the ruins of a flue from the former C.B. lead-smelting mill in Langthwaite, North West Yorkshire (Jones et al. 1982). This phenomenon is discussed further (sections 1.1.8, 1.1.10).

1.1.7. Effects of metals on morphology

Lichens behave as two organisms thrown together in adversity (James, pers. comm.). In fact it is only during regimes of fluctuating humidy and low nutrient supply, that a successful recombination of a photobiont and mycobiont has been achieved in

the laboratory (e.g. Ahmadjian & Heikkilä 1970). In axenic culture lichen fungi form a featureless mass, bearing no resemblance to the lichen form. It is now apparent from the studies on lichen morphotypes (James & Henssen 1976), that in certain circumstances a green alga or blue-green alga may combine with the same fungus, to form two morphologically, anatomically, chemically and ecologically distinct lichens. This demonstrates that even in those lichens where there is a complex structure derived from an apparently dominant fungal partner (80-98% thallus volume) it is the presence and subsequent interaction of the phycobiont with a particular mycobiont that plays a vital role in determining the phenotypic expression of the fungal partner (James & Henssen 1976).

Superimposed upon alga-fungus interactions which play an important role in lichen morphology, are the influential factors of the environment. Environmental factors which commonly cause modifications in lichen structure include exposure, water supply, altitude, grazing by invertebrates, SO_2 pollution and the chemistry of the substratum. Weber (1962) suggests three main ways in which lichens can be environmentally modified:

a) inhibition or stimulation of growth

b) destruction of accomplished growth

c) accumulation or diminution of substratum materials, pigments or other metabolites, in or upon the surface of the thallus.

In view of the plastic response of lichen species to these features it is hardly surprising that many superfluous lichen names have been created. For instance, Weber (1968) reduced some 80 species of Acarospora subgen. Xanthothallia to 2 species, after concluding that they were merely morphological variants induced by changes in

substrata. However, subsequent work has shown that while the basis of this observation was correct, some 20 species can now justifiably be recognized (P. W. James, pers. comm.). Evidently, both a sound knowledge of lichen taxonomy and careful observation of lichen material in the field, is fundamental to a correct understanding of the variability of a species and delimitation of further taxa.

1.1.7.a 'Oxydated' thalli

Perhaps the most striking and well known modifications occurring in lichens are in those ochraceous forms of usually white or grey crustose lichens. The association of these rust-coloured lichens with certain iron-rich rocks has long been recognized (e.g. Acharius 1798). Moreover, it is now generally considered that the ochraceous colour is due to a deposition of hydrated ferric oxide upon the lichen surface (section 1.1.8) though few lichens have actually been analysed. Thus Weber (1962) considers the ochraceous thallus to be merely a matter of absorption of iron salts from the rock, followed by their oxidation and precipitation upon the surface of the lichen thallus. Such lichens have been termed 'oxydated' (Weber 1962).

A large number of lichens are known to have ochraceous forms including Aspicilia aquatica, A. polychroma, Acarospora amphibola, A. smaragdula, A. murorum, Huilia macrocarpa, H. tuberculosa, Hymenelia lacustris, Lecidea lapicida, L. lithophila, L. lactea and occasionally the ascocarps of Rhizocarpon obscuratum (James 1973, Weber 1962). In addition the rusty Aspicilia (= Bellemerea)

diamarta is now considered to be a form of Aspicilia (= Bellemerea) cinereorufescens; the former name takes priority (Clauzade & Roux 1984). Many of the lichens mentioned above have been given form or varietal status in taxonomic studies e.g. ochracea, oxydata, ferrosa, ochromeliza and ferruginea (Weber 1962). However, as such lichens are environmental modifications, the choice of the words form or variety to describe these taxa should be avoided, since a taxonomic rank is implied by their usage. Alternatively, these lichens might be referred to as iron-rich states or ecotypes.

In addition to these ochraceous states of lichens, there are a number of lichens which are often considered to be permanently rusty including Acarospora sinopica, Lecidea silacea, Rhizocarpon oederi, Tremolecia atrata (James 1973) and Lecidea atrofulva (Hertel 1975). However, the last three species are occasionally non-rusty, particularly in shady situations and presumably on rocks with either a low iron content or where iron is not available.

According to Magnusson (1929) the ochraceous nature of a lichen alone is insufficient evidence to justify the creation of a distinct lichen species. Thus a rusty lichen may only be regarded as a distinct species if other significant taxonomic characters are present separating the rusty taxon from other species. Although Magnusson (1929) considers that the specific rank of Acarospora sinopica must at all events be looked on as settled, the possibility that it is a modification of A. smaragdula cannot be entirely discounted (section 5.3).

1.1.7.b Thallus modifications in response to copper mineralization

There are several reports of stunted macrolichens occurring on cupriferous substrata e.g. Stummerer (1970) describes poor growth of Cladonia verticillata (= C. cervicornis subsp. verticellata) on soil with 1.34% copper in the Bundesland, Salzburg, Austria. Unusual forms of crustose lichens occurring on cupriferous substrata have been described as varieties. Thus Poelt (1955) described Haematomma ventosum var cuprigenum consisting of reduced, more or less convex, scattered areoles from cupriferous substrata in the Großarl, Salzburg, Austria. It is now also known from similar rocks in Scandinavia (Santesson 1984). Poelt (1955) at the same site also observed Aspicilia (= Bellemerea) alpina var sulphurata which he considered to represent a genetic modification of A. alpina, typified by its colour as well as by its smaller, dispersed thallus. However, in 1978 Santesson collected similar material at Ramundberget, Härjedalen, Sweden. He recognized the significance of the yellow-green colour as being due to the incorporation of copper from the rocks on which it was growing. This material was distributed to various herbaria by Vězda, Lich. Sel. Exs. No. 1549.

Interestingly, the first reports of copper-stained lichen thalli appears to have been made by a geologist (Wild 1968) who reported Lecanora galactiniza and Hypotrachyna (= Parmelia) lecanoracea stained blue with copper salts from outcrops with ferruginous gossan containing visible malachite at the surface at Copper Queen, Umniati River, 95km WSW of Sinoia, Rhodesia. A second geologist, Czehura (1977), discovered dark green examples of

Lecanora cascadensis at Lights Creek District, N. California, growing on rocks containing blebs of disseminated bornite and other copper minerals. Other species in the community remained uncoloured. Alstrup & Hansen (1977) reported dark green Lecanora polytropa from copper-bearing rocks on Disko Island, Greenland. However, this coloration was not recognized to be due to the accumulation of copper salts.

It is now well established that a range of usually grey lichens can become greenish-yellow and additionally unusually verrucose or folded when growing on certain copper-rich rocks (Purvis 1984, see appendix). Previously, this unusual coloration has resulted in the description of modifications as distinct species. It is now recognized (Purvis 1984) that Lecidea theiodes is a modification of Lecidea lactea caused by the growth on copper-rich rocks. Similarly Acarospora isortoqensis and A. undata have been recognized to be modifications of A. smaragdula (Purvis et al. 1985, see appendix).

1.1.7.c Thallus modifications caused by other elements

Macrolichens often become distorted when growing in mineral-rich areas. On zinc-rich calamine soils from Belgium, Lambinon et al. (1964) reported distortions of growth in some Cladonia species in direct proportion to the zinc content of the thallus. Thus Cladonia cornutoradiata (= C. subulata) had darkened granular-squamulose podetia which were swollen and contorted. The state of development of podetia in Stereocaulon nanodes f. tyroliense was related to the zinc content of the substratum, high

concentrations supressing podetial growth. Goyal & Seaward (1982a) suggested that Peltigera canina (= P.membranacea?) and P.rufescens in metal-polluted environments are modified by a decrease in thallus size, rhizinal length, dense rhizinal growth, profusely branched veins and hypertrophy of the medulla. However, as stated by Beckett and Brown (1983), these morphological variations could equally well be caused by water conditions in the environment. Alternatively the degree of exposure could also be important.

Certain lichens may be pruinose, a feature which is often of taxonomic importance. Weber (1962) analysed samples of pruina from a number of lichens, including Acarospora strigata, Lecidea crenata, Lecanora muralis var albopulverulenta and Lecidea (= Psora) rubiformis, and found the pruina to consist, in most instances, of calcium oxalate. However, Weber recognized that pruinosity is not a reliable taxonomic character and that any species of Acarospora will tend to produce pruinose and non-pruinose phases according to the availability of calcium.

1.1.8. Sites and type of metal deposition

There are four main ways in which the location of metals in lichens has been studied.

1. Optical microscopy is used employing polarized light in the transmitted mode in combination with specific staining techniques. In the reflected mode specimens have been inspected in order to determine the presence of crystalline precipitates within lichens. In addition, lichen material has been ashed and studied

microscopically.

2. Electron beam methods in which the scanning electron microscope (SEM) is used in conjunction with electron probe microanalysis (EPMA) to provide plant analyses and maps of element distribution and also to determine cathodoluminescence.

3. By homogenization of lichen thalli followed by centrifugation in order to separate the various components. Isolation of the algal and fungal components in this way has been followed by chemical analysis using atomic absorption spectroscopy (AA) and X-ray fluorescence (XRF).

4. Procedures involving elution of the thalli in which elements present in extracellular sites are displaced into solution in the laboratory in the presence of ions with high affinities for those sites.

Electron beam methods are particularly versatile, they are non-destructive and the physical relationships of lichen thalli and mineral precipitates can be examined in a more natural state. It is possible to identify a range of elements and to determine their precise location within the thallus.

There are few systematic studies in which the precise identity and location of elements within lichen thalli have been described. Lange & Ziegler (1963) made a careful study of the distribution of Fe^{2+} and Fe^{3+} in members of the Acarosporetum sinopicae from the Harz Mountains, Germany, using potassium

ferrocyanide and potassium ferricyanide. The localization of iron within these species was found to be variable and apparently characteristic for each species. In three lichens, Acarospora sinopica, A. smaragdula v. lesdainii f. subochracea and Rhizocarpon oederi, iron was deposited as a crust on the thallus surface. Lange and Ziegler noted the similarity between the localization of iron in both Acarospora sinopica and A. smargdula v. lesdainii f. subochracea. In both species the whole of the upper surface is encrusted in a brown layer ranging from 15 to 30 μm in thickness which is of an irregular, granular nature. Lange and Ziegler suggested that the thickness of the crust in Acarospora smaragdula v. lesdainii f. subochracea was strongly dependent upon the environment, in contrast to the crust of more constant thickness in A. sinopica. In these species the crust was also observed to cover the young apothecia. A blue-black reaction of the crust in potassium ferrocyanide and virtually no reaction with potassium ferricyanide, demonstrated that this layer consisted mainly of Fe^{3+}. Lange and Ziegler considered that this layer was secreted from the cortical layer situated immediately below. Support for this idea was provided by their observation that cells in the upper part of the cortex contained appreciable amounts of Fe^{2+} and some Fe^{3+}. Iron was apparently absent in a large part of the cortex above the algal layer in both species. However, both species contained large concentrations of Fe^{3+} within the hypothallus in direct contact with the underlying substratum. Of particular interest was the discovery that although the medulla and algal layer in both species contained no soluble iron, these areas were shown to be Fe^{3+}-rich subsequent to ashing of the lichen sections. Furthermore, in both the non-rusty lichen species,

Acarospora montana and Lecanora subaurea the iron was also shown to occur in a 'masked' form, particularly in the cortical area. These observations led Lange and Ziegler to suggest that the iron was complexed, possibly in organic form (see page 39).

In an extension of the work of Lange & Ziegler (1963), Noeske et al. (1970) studied the localization of Fe, Zn and Cu in cross-sections of the thallus of Acarospora smaragdula v. lesdainii f. subochracea using the electron microprobe. Both Fe and Cu were present as a crust on the thallus surface. Zn was generally present throughout the thallus. As the crust also contained S, Si, P and O_2, it was assumed that the Fe and Cu would occur as the sulphate, silicate and phosphate. However, no X-ray powder diffraction, infrared spectroscopy or other diagnostic techniques were carried out to confirm this supposition. This observation, in my opinion, appears most unlikely, particularly since in other lichens, the ochraceous crust, as in e.g. Acarospora sinopica, have been found to contain ferric oxide (Weber 1962) and Lecidea dicksonii (= Tremolecia atrata) encrusting biotite-chlorite-schist from Ben Lawers, Perthshire, Scotland, contained aluminium-containing goethite by electron diffraction (Jones et al. 1981).

Jones et al. (1982) using EPMA and X-ray powder diffraction, demonstrated the presence of metallic lead oxides and hydrocerussite in Stereocaulon vesuvianum (section 1.1.6.c, 1.1.10). A further study with EPMA is that of Lawrey (1977) who examined Cladonia cristatella from a coal-strip mining area in Ohio. He concluded that in this species there was a greater concentration of Fe in or on the algae, than in the rest of the

lichen tissues. However, Richardson & Nieboer (1980) suggested that the mycobiont could still be responsible for the larger part of the binding of Fe by virtue of the larger mass of fungal tissue present as compared with the alga. Garty et al. (1979) also used SEM and TEM energy dispersive X-ray analytical systems to study the localization of heavy metals and other elements accumulated in Caloplaca aurantia. The presence of mineral particles was demonstrated to be located within the medulla including weddellite, quartz, calcite, magnetite and alkaline amphibole. Studies on the location of Ca, K, Mg and P were also carried out using an electron microprobe to analyse the different anatomical tissues of ten foliose and fruticose lichens (Asta & Garrec 1980). In fungal tissues, the hyphae with thick walls were found to be richest in Ca while the medullary tissue is poor in all these elements. Abundant K was observed in the algal layer and the presence of Mg and P was detected. Another study, using the X-ray microanalytical facility of the SEM in conjunction with cathodoluminescence, was carried out by Mathey & Hoder (1978). Four fluorescent lichens (Lecanora-, Buellia, Laurera and Trypethelium sp) were examined. Clorinated xanthones were localized by cathodoluminescence and calcium oxalate crystals were identified using EPMA. Of particular note was the discovery of abundant large, crystals rich in Mg and Mn located in the walls of the perithecia of Laurera megasperma. As this specimen (BM!) is growing on wood these inclusions are presumably airborne particulates though this is not specified in the paper.

Dissection and centrifugation of lichen thalli led Goyal & Seaward (1981) to suggest that Fe, Mn and Pb were accumulated maximally by rhizinae in a number of terricolous Peltigera sp.,

wheras the phycobiont was found to accumulate the highest concentrations of Cu, Ni and Zn. However, the greater capacity of the phycobiont to accumulate these elements is not of overwhelming significance because of the smaller contribution of the algal symbiont to the total thallus weight.

Perhaps the biggest research effort has been made by physiologists in the attempt to locate the specific sites to which cations bind as a result of the process of ion-exchange. Evidence to date indicates that metal ions are bound to extracellular carboxylic acid or hydroxycarboxylic acid functional groups (Richardson & Nieboer 1980). It is unlikely that uronic acid polymers, which are probably of major importance in bryophytes, will be involved, as there are no reliable reports of their occurrence in lichens (Brown & Beckett 1984). Richardson & Nieboer (1980) suggest that the carboxylic acid groups in lichens, to which metal ions bind reversibly, are not those of oxalic acid or those of lichen acids. Evidence to support this conclusion was provided by Brown (1976) who discovered that acetone treated Cladina rangiformis retains its cation binding capacity; both lichen acids and oxalic acid would be removed by this organic solvent. However, whilst this may be the case for ion-exchange in the laboratory it is evident that a range of extracellular metal oxalate precipitates can form within crustose lichen thalli in the field. These oxalates tend to be formed at the rock-lichen interface within the medulla and include calcium oxalate, both weddellite and whewellite (e.g. Erdman et al. 1977, Syers et al. 1967, Ascaso et al. 1982, Schade 1970), magnesium oxalate (Wilson et al. 1980, 1981), manganese oxalate (Jones et al. 1981, Wilson & Jones 1984) and copper oxalate

(Purvis 1984). Additionally, the formation of large amounts of ferric oxalate at the interface between Caloplaca callopisma and dolomite rock and lesser quantities of the same in the rock-lichen interface of Diploschistes ocellatus has been reported, from Arrebata Capas, Spain (Ascaso et al. 1982).

The possibility of complexing of Fe^{3+} in an organic form by members of the Acarosporetum sinopicae has been considered [(Lange & Ziegler 1963), see page 36]. It is now recognized that soluble metal complexes can form when lichen compounds are allowed to react with suspensions of minerals and rocks (Iskandar & Syers 1971, 1972, Ascaso & Galvan 1976, Ascaso et al. 1976). This demonstrates that lichen compounds are to some extent soluble in water, largely due to the presence of polar groups such as *-OH, -CHO* and *-COOH* (Syers & Iskandar 1973). The possibility of complexing of metal ions with lichen acids by members of the Acarosporetum sinopicae has been considered (Huneck 1966). However, whilst no such complexes have yet been found in field studies (Jones et al. 1980), some tentative evidence suggests that complexing of Cu by norstictic acid within lichen thalli might occur (Purvis et al. 1985, see appendix).

1.1.9. Effect of metals on lichen metabolism

It is not known whether all the elements required for normal growth by the majority of higher plants are essential to lichens (Nieboer et al. 1978). These essential elements include H, B, C, O, Na, Mg, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn and Mo (Evans & Sorger 1966). However, levels of elements Cu, Fe, Zn, Mn, Mo, P and N

observed in lichens from non-polluted habitats are ofen comparable to those characteristic for higher plants ie. 6, 1000, 20, 50, 0.1, 2000 and 15,000 $\mu g\ g^{-1}$ dry tissue (Nieboer et al. 1978).

Little is known of the maximum concentrations of individual metals tolerated by lichens. Nash (1975) reported a 90% decrease in the lichen species richness and abundance in lichen communities near a zinc factory. However, SO_2 pollution could also be implemented in this decline. Diminution in both the number of species and the coverage along transects towards smelters has been noted (e.g. Nieboer et al. 1972, Seaward 1973). Seaward (1974) noted that dead thalli subjected to drip from a zinc galvanized wire were richer in Zn, Fe and Pb compared to lichens above the wire and suggested zinc was the major toxic element. A similar observation was also made by Garty et al. (1979) in the case of Caloplaca citrina.

There are few reports giving the thresholds of tolerance of lichens to particular toxic metals. Rao et al. (1977) suggest that when accumulation occurs in Hypogymnia physodes over a long period of time, the threshold tolerance levels may be 718-918 $\mu g\ g^{-1}$ for Pb, 210-405 $\mu g\ g^{-1}$ for Cu, 168-233 $\mu g\ g^{-1}$ for Zn and 5 $\mu g\ g^{-1}$ for Cd. Unfortunately, no indication of the form in which these elements occur is given. From data given (section 1.1.5.b) it is evident that far higher concentrations of these elements can occur in other lichens without any detectable adverse effects. In the absence of the identity of the form of toxic elements, such data is of limited value for comparative purposes.

The incubation of lichen thalli with excess levels of toxic metals causes the release of cellular K^+ which is considered a useful parameter by physiologists in assessing loss of cellular integrity (Puckett 1976, Nieboer et al. 1978, Burton et al. 1981). This parameter has also been used for monitoring SO_2 stress (Puckett et al. 1977, Nieboer et al. 1978, 1979, Richardson et al. 1979). Likewise, both photosynthesis and to a lesser extent respiration are adversely affected by a range of toxic elements and have been used to monitor toxic effects. In general, it appears that photosynthesis is more sensitive than respiration to class B elements with Hg and Ag being most toxic (Puckett 1976). Class B elements, as a result of their preference for N_2 and S centres in biological systems (section 1.1.3) have been found on several occasions by Nieboer, Richardson, Puckett and co-workers to be most toxic. Thus Nieboer et al. (1978) found that only concentrated solutions of Ni^{2+}, Pb^{2+}, Co^{2+} and Cd^{2+} induced release of cellular K^+ while even very dilute solutions ($\geqslant 2\times10^{-4}$ M) of Cu^{2+}, Hg^{2+} and Ag^+ were effective in doing so. Richardson et al. (1979) investigated the role of metal ion binding in modifying the toxic effects of SO_2 on the lichen Umbilicaria muhlenbergii . Uptake of class A ions (Ca^{2+}) resulted in protection against damage due to SO_2 exposure. However uptake of borderline ions (eg Cu^{2+}) particularly with a capacity to penetrate cells was deleterious in terms of $^{14}CO_2$ fixation.

It appears from studies on photosynthesis that lichens containing a cyanobacterial photobiont are significantly more sensitive to Zn, Cd and Cu (Brown & Beckett 1983).

1.1.10. Tolerance mechanisms

Lange & Ziegler (1963) suggested three ways in which lichens could tolerate the toxic effects of elements;

a) Unspecified cytoplasmic resistance of lichenized fungi and algae to metal cations.

b) Some kind of immobilization of the ions in a chelated form within the cytoplasm of the symbionts.

c) Active and/or passive transport of the ions to regions external to the plasma and cell wall and localization in the form of insoluble salts on the surface of the thallus.

Since specimens of Acarospora sinopica, A. smaragdula f. subochracea and Rhizocarpon oederi were frequently observed to have large amounts of Fe in intercellular spaces and as a coating on their outer surfaces, Lange and Ziegler considered explanation c) to be the most plausible. This is further supported by the discovery of insoluble oxalates within lichens. Magnesium oxalate dihydrate has been found within Lecanora atra growing on a substratum of magnesium silicate minerals (serpentinite) (Wilson et al. 1981). Since this salt is insoluble and isomorphous with the dihydrated oxalates of Ni, Co, Fe, Zn and Mn, these authors suggested that the incorporation of heavy metal ions into magnesium oxalate provided a possible detoxification mechanism to protect the lichen from these cations. Evidence of manganese, iron and nickel substitution was provided by electron probe microanalysis. However, it is now evident that oxalates of a range of elements can form directly as a result of precipitation by reaction with oxalic acid during lichen growth. Purvis (1984, see appendix) reports the occurrence of copper oxalate in several lichens from Scandinavia,

which offers further evidence in support of the view that insoluble oxalate formation is a mechanism to protect lichens from the effects of these toxic cations.

Another example of a compound which could be formed as a result of an inactivation process is the case of hydrocerussite occurring in Stereocaulon vesuvianum subjected to Pb-rich flue dusts (sections 1.1.6.c., 1.1.8). Jones et al. (1982) suggested that the lead was presumably inactivated by the hyphae of the mycobiont, but were unable to specify an exact reaction.

The presence of certain morphological features has occasionally been offered as evidence for possible tolerance mechanisms. Thus Goyal & Seaward (1982b) suggested that metal accumulation within the rhizinae of Peltigera reduced the amounts of metals available for translocation to the phycobiont and medullary zone. In other instances tolerance has been induced to Zn in Peltigera by brief initial exposures to Zn (Beckett & Brown 1983). These authors found that Peltigera spp. collected from uncontaminated sites are sensitive to the addition of heavy metals in the laboratory whereas material collected from contaminated sites is more resistant.

1.1.11. Uses as indicators of metal deposits

Le Roy & Koksoy (1963) suggested that lichens, because of their longevity, could have sufficient time to concentrate many elements (section 1.1.5.b) from the bedrock that the more rapidly growing seasonal plants would be unable to absorb. Consequently

their use as possible indicators of metal deposits was suggested. This approach is of a biogeochemical nature where the elemental content of the organism is used as an indication of mineralization. However, it is evident that geobotanical factors have been considered equally important. Czehura (1977), during a geochemical survey of the Lights Creek District, was able to distinguish 1000 $\mu g\ g^{-1}$ and greater than 2000 $\mu g\ g^{-1}$ copper anomalies on the basis of the lichen colour (sections 1.1.5.b, 1.1.7.b). On the basis of this work, Czehura suggested that the examination of herbarium lichen collections could be a useful means of locating other mineralized sites.

An interesting example of unconscious biogeochemical prospecting by the use of lichens is provided by Tomassini et al. (1976) who discovered high copper levels in lichens aroud Contwoyto Lake in NW. Territories, Canada. At a later date, a mining company independently discovered a copper ore deposit in the area (Brooks 1983).

Easton (1976), according to Brooks (1983), concluded that lichens were of much more use for geobotanical prospecting than for biogeochemical work owing to their limited ability to sample beneath the surface layer of the substratum. Lichens do not have a root system, however they are able to accumulate elements directly from mineral-rich solutions which may have come from depth. This of course depends on the topography and hydrology of the site of growth. Easton further suggested that because lichens give a characteristic colour to specific rocks they should provide a ready method of identification of such rocks at a distance and might even

be visible from aerial photographs or satellite imagery.

The suggestion of Dahl (Rosenkvist 1950) that hydrophilous lichens might experience a decrease in growth rate when irrigated by copper-rich water is relevant, but difficult to quantify for exploration purposes. The rate of lichen growth is affected by so many factors that it seems unlikely that this could be correlated with specific elements during field surveys.

According to Viktorov (1956) Lecidea (= Psora) decipiens and Collema minor are used as indicators of gypsum in desert areas of the Soviet Union.

1.2. Microorganisms, algae and fungi

1.2.1. Algae

The following account is based on the review by Whitton (1984) and basic text of Darley (1982), unless otherwise stated.

The capacity of algae to take up heavy metals from the water producing an internal concentration greater than in their surrounding medium has been shown for many species. It has been suggested that the analysis of algae could prove useful in geobotanical surveys. For instance, collections of Lemanea australis from Manipur State, India were found to contain detectable levels of Ag, in contrast to other analyses for Ag made on Indian plants. However, many species are senstitve to several elements, including copper. Thus excessive algal growth in

freshwater systems is frequently controlled by an algicide such as copper sulphate, applied at a rate of 0.2-2 mg l^{-1}. Unfortunately, the fate of the copper and its influence on the alga is rarely recorded, though photosynthesis may be significantly affected at copper levels as low as 5-10 µg l^{-1}. Blue-green algae are especially susceptible to copper toxicity, primarily because of the inhibition of nitrogen fixation. Alkaline pH and high organic carbon levels in the water may detoxify Cu, so that it is not only an ineffective algicide, but it may actually stimulate growth. Thus Richardson & Nieboer (1980) report that Mierle & Stokes (1976) established that the presence of Ca^{2+} in Cu^{2+} exposures reduced the K^{+} loss by the green alga Scenedesmus. Copper based antifouling paint has been use as a means of reducing fouling by marine algae. However, in several species, including Ectocarpus siliculosus, both copper-tolerant and copper-sensitive strains have been isolated (Russell & Morris 1970). It seems likely that copper exclusion by the tolerant strains is due to properties of the cell membrane, rather than to extracellular binding of copper. Differences in metal resistance within a single species almost certainly reflect actual genetic differences. A copper-tolerant strain of Chlorella was found by Foster (1977) to tolerate up to 1 mg l^{-1} Cu, whereas at copper concentrations of as little as 0.05 µg l^{-1} non-tolerant strains experienced a decrease in growth rate and died at 0.3 µg l^{-1} Cu. The appearance of giant cells up to 20 times the normal volume was taken to reflect an uncoupling of growth from cell division. Non-tolerant strains accumulated 5-10 times more metal at comparable external copper concentrations than did the tolerant strains. Since growth rate, lag period and yield of both tolerant and non-tolerant strains were identical as a function of

the amount of cellular Cu, Foster suggested that copper exclusion is likely to be the only mechanism of tolerance in the alga.

Whilst it would clearly be useful to be able to comment on the metal compositon of a water body simply by observing its flora, there are apparently no algae which are dependent on water with a specific 'heavy metal' content. However, the absence of sensitive species may prove to be a more useful indication of heavy metal enrichment than the mere presence of resistant ones.

1.2.2. Fungi

It is well known that fungi are sensitive to a range of metals, including in particular copper and mercury, a feature which has led to the widespread use of copper and mercury based compounds to control fungal infections of plants, timber etc. However, certain species have been shown to possess a remarkable degree of resistance to these elements. For instance, Acontium velatum can grow in a 4% copper sulphate solution at pH 0 (Antonovics et al. 1971). Penicillium ochro-chloron has been described as a species characterized by an unusual tolerance for copper, since it has been isolated from copper solutions and from tentage and fabrics treated with copper fungicides, in a number of geographically distinct localities (Stokes & Lindsay 1979). Since growth is actually stimulated by copper at low levels, Stokes and Lindsay suggest that the species requires more copper than is provided at normal micronutrient levels. Penicillium ochro-chloron was isolated by these authors from a copper-plating solution containing 25% $CuSO_4$ (63,612.5 $\mu g\ g^{-1}$) and 7% H_2SO_4. Other species have developed

resistant strains including Physalophora obtusa. The spores of this species taken from orchards sprayed with Bordeaux mixture are more resistant to copper than spores of the same species from unsprayed orchards (Taylor 1953). Unfortunately, the mechanisms of tolerance are by no means well understood, though sulphur, oxalates, calcium and pH are implicated in certain species. Somers (1960) examined the toxicity effects on fungal conidia of a number of metal salts. His results suggest that there is a common, non-specific toxic effect caused by most metal cations; this can be related to the strength of the covalent binding to the surface ionogenic groups (e.g. imidazole, carboxyl, phosphate or sulphydryl) present outside the cell protoplast. Somers (1963) reported that copper uptake was reduced by the presence of calcium chloride in Neurospora crassa. It was assumed that Ca can compete with Cu for the available binding sites on the spores, thereby leading to a decrease in toxicity. Somers suggested that copper uptake was an ion exchange reaction and passive in character. Similarly Chester (1965) concluded that calcium exerted a protective action against copper poisoning in yeasts.

The lowering of pH from an initial value of 4.5 to 4.0 in a copper sensitive strain and from 4.5 to 3.2 in a copper tolerant strain, reduced the toxic effect of a medium containing 4mM Cu in Aureobasidium pullulans (Gadd & Griffiths 1980). At pH 4.5 the copper-tolerant strains took up less copper than did the sensitive strain. The lowering of pH below this level decreased copper uptake in both strains. Variations of the uptake of copper according to variations in pH and the metabolism of different fungal strains were suggested to be the reasons for the differing sensitivities

observed. Ross (1975) suggested that at low pH's a decrease in copper toxicity could arise through the binding of H^+ to cation-acceptor sites on the cell surface with consequent exclusion of copper.

The importance of sulphur is shown in copper-tolerant strains of Saccharomyces cerevisiae (Antonovics et al. 1971). Here hydrogen sulphide appears to be released as a by-product of an over-active cysteine pathway. When tolerant strains are cultured with copper, the hydrogen sulphide combines with copper and copper sulphide is deposited in and around the cell wall. Other sulphur compounds have now been inferred to be important in acquiring tolerance. For instance, thiosalts added in vitro, to reduce the toxic effects of heavy metals, can form thiosalt-metal complexes (Wainwright & Grayston 1983). Thiosalts ae also produced in vivo by Thiobacilli, heterotrophic sulphur oxidizing bacteria and some fungi. Sulphur and toxic base metals frequently occur together in the same environment. Consequently, Wainwright & Grayston (1983) suggested that those organisms capable of oxidizing sulphur would tend to develop under these conditions. Alternatively, non-sulphur oxidizing fungi might also benefit from the protection provided by thiosulphate produced by other organisms. It seems likely therefore that the metabolic interrelationships between the various organisms present in the environment may be of considerable importance in determining the toxic effects of particular elements.

Ross (1975) emphasizes how the combination of copper with organic chelating agents can modify the toxic effects on fungi. Complexes with amino acids are much less toxic to Candida utilis

than free Cu^{2+} at pH values around 7. At low pH the stability of the chelate may be lessened so that some copper ions are released. Four fungal species viz, Aspergillus niger, Penicillium spinulosum, Verticillium psalliotae and Poria placenta caused the formation of copper oxalate when grown in a medium containing copper sulphate (20mM Cu). However,the extent to which the production of the crystalline oxalate is indicative of tolerance in these fungi remains uncertain (Murphy & Levy 1983).

1.2.3. Microorganisms

The two important autotrophs in mineralized environments are Thiobacillus oxidans and T. ferrooxidans. The only unequivocally proven bacterium utilizing the oxidation of iron as the basis for autotrophic growth is Thiobacillus ferrooxidans (Nealson 1982). In contrast, T. thiooxidans utilizes the oxidation of sulphur as the basis of its metabolism. Both organisms grow well in acidic environments and act as catalysts in the breakdown of pyrite and associated sulphides in the supergene environment (section 1.2.3.a). The optimum condition of growth for both T. thiooxidans and T. ferrooxidans occurs at pH 3; these species have consequently been termed acidophiles (Harrison 1984). As a result of iron oxidation, T. ferrooxidans produces soluble ferric iron that precipitates when it reaches an area of high pH as $Fe(OH)_3$, by reaction with water. In contrast, T. thiooxidans oxidizes sulphur producing sulphuric acid.

Other bacteria oxidize iron under conditions of neutral pH (Nealson 1982). Unfortunately, it has not been possible to

demonstrate unequivocally that their growth is autotrophic, or even that oxidation is enzymatic. As indicated by Nealson, this is no doubt partly due to the fact that ferrous iron (Fe^{2+}), the geochemically mobile form, oxidizes spontaneously to ferric iron in the presence of even small amounts of molecular oxygen and is no longer soluble. This leads to precipitation of one of a variety of hydrated ferric oxides. These bacteria which have long been recognized for their ability to deposit iron hydroxide or manganese oxide in structures outside their cells are commonly known as 'iron-manganese bacteria' and include Gallionella, Sphaerotilus, Leptothrix and Clonothrix (Ghiorse 1984). As a rule, metal oxide deposits are found outside the cell envelope. Bacteria produce a variety of extracellular polymers consisting of acidic polysaccharides, proteins or polysaccharide-protein-lipid complexes that may or may not form distinct structures outside the cell wall. Thus under neutral or slightly acidic conditions any bacterium that produces acidic extracellular polymers will adsorb positively charged iron hydroxides non-specifically when these are present in the environment (Ghiorse 1984).

Under the ambient conditions at the earth's surface, the occurrence of populations of Thiobacillus thiooxidans and T. ferrooxidans is ubiquitous. Consequently, the process of oxidation of ferrous sulphides and the release of other associated metals into solution e.g. copper and zinc is driven forward by the metabolism of these organisms (section 1.2.3.a). It is also reasonable to expect that iron bacteria may play some role in the fixation of ferric oxides within or on lichen thalli.

1.2.3.a Bacterial influence of the oxidation of sulphides

The oxidation appears to consist of chemical as well as biological processes. The reactions governing oxidation of both pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2) are basically similar.

The following sequence has been proposed for the oxidation of pyrite (Freney & Williams 1983). The first step in the oxidation is non-biological and ferrous sulphate is formed (equation 1)

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1)$$

This reaction is then followed by bacterial oxidation of ferrous sulphate, a reaction which is normally carried out by T. ferrooxidans (equation 2)

$$4FeSO_4 + O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (2)$$

Subsequently, ferric sulphate is reduced and pyrite is oxidized by what appears to be a strictly chemical reaction (equation 3)

$$Fe_2(SO_4)_3 + FeS_2 \longrightarrow 3FeSO_4 + 2S \qquad (3)$$

Elemental sulphur so produced may then be oxidized by T. thiooxidans (equation 4) and the acidity generated favours the continuation of the process

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \qquad (4)$$

The main difference between the oxidation of pyrrhotite and pyrite is the very much greater resistance of the latter to attack by atmospheric oxygen.

Since ferric sulphate is a powerful oxidant, other sulphides including chalcopyrite can be oxidized to form sulphuric acid along with soluble copper (equation 5)

$$CuFeS_2 + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 \longrightarrow CuSO_4 + 5FeSO_4 + 2H_2SO_4 \quad (5)$$

1.3. Bryophytes

1.3.1. Metals as a factor in bryophyte distribution

Mosses indicative of deposits containing metals, other than copper, have not been studied in detail. Aerobryopsis longissima is reported to be an indicator of chromium in New Caledonia and Weissia controversa v. densifolia is associated with lead rich soils in England (Richardson 1981).

A number of mosses, usually belonging to the genera Mielichhoferia and Merceya, are so often associated with copper-rich rocks that they have been termed 'copper-mosses'. However, there has been much debate as to the precise conditions responsible for their growth in particular habitats. Mårtensson & Berggren (1954) were the first to record high levels of copper and also a low pH in soil underlying Mielichhoferia spp. at Torne Lappmark. In contrast, Wilkins (1977) suggests that in Britain at

least, copper is not an important factor in controlling the distribution of 'copper mosses' and that the latter term is therefore misleading. Certainly copper mosses do not incorporate much of the copper from the environment in their tissues, which contain a much lower copper content than the substratum and in this respect are no different from other bryophytes (Shacklette 1967, Coker 1971, Wilkins 1977). Schatz (1955) suggested the term 'sulphur moss' might be more suitable, since some of these mosses have been found around sulphur springs (eg Persson 1948) where copper was presumably absent. Furthermore, Schatz suggested that sulphur could be used in a photosynthetic capacity as a reductant donor in photosynthesis. However, as some Merceya sp. have been reported from copper-covered rooves in the absence of sulphur enrichment, this explanation is also unlikely (Brown 1982). In view of this evidence it seems likely that copper mosses are simply rather poor at competing with other pioneer mosses but can tolerate both acidity and copper ions (Richardson 1981). Physiological studies lend support to this conclusion; a 5×10^{-3} mM $CuSO_4$ solution was found to be toxic to Mnium undulatum wheras Mielichhoferia elongata can withstand 0.1 M Cu^{2+} (Url 1956). One possible explanation for the tolerance of copper mosses to copper has been suggested by Richardson (1981). He suggests that calcium, which has been discovered in high concentrations (6600 ppm dry wt) in Mielichhoferia elongata (Coker 1971), could stabilize cell membranes. Cetainly, this element has been shown to provide protection against SO_2 stress in the lichen Umbilicaria muhlenbergii (Nieboer et al. 1979).

Clearly the presence of a copper moss in an area is by no

means an infallible indication of copper mineralization. However, Persson (1956) investigated copper mosses in herbaria and analysed the associated soil for copper. The suggestion was made that this method could be useful for locating copper deposits, however no new orebody has been discovered as a result of this survey.

1.3.2. Accumulation of metals in bryophytes

Very little has been written about the mineral nutrition of bryophytes in saxicolous habitats (Brown 1982). According to Brown, elements may be concentrated by passive physico-chemical processes or alternatively by biological incorporation in the cell through a selectively permeable membrane. This situation is similar to that occurring in lichens, however there appears to be no obviously rusty or otherwise minerally coloured mosses. Whilst calcium oxalate has been found in mosses (Lowenstam 1981) it occurs intracellularly as in the case of higher plants. In certain instances, the presence of calcium oxalate has been used as a character for taxonomic discrimination. Touw (1971) considers the most striking feature of Hypnodendron colensoi to be the crystals in the costal cells of what is probably calcium oxalate. These have been found in all specimens of H. colensoi but not in any other species of Hypnodendron. It seems that mineral precipitates which appear to be widespread in lichens are not a special feature of mosses.

According to Shacklette (1965) the content of an element in a bryophyte is generally related to the amount contained in the supporting substratum, only if the substratum has an anomalously

high content of that element. Thus the highest concentrations of most elements in bryophytes are found in those samples that are collected from substrata that also have a large content of the same elements. This assumption presupposes a dominance in elemental uptake from the substratum as compared with that from the ambient water or atmosphere. However, in polluted areas it is now widely recognized that uptake of airborne particulates from a range of industrial activities can assume primary importance.

There are many reports of concentrations of a range of elements occurring in mosses, reputedly derived from the substratum. Stummerer (1970) observed 0.739% dry wt. copper in Pohlia sp. irrigated by copper-rich water in a stream near Salzburg. Likewise Brooks (1973) found elevated copper contents in three species of bryophytes from Coppermine Island, New Zealand. He suggested that in that area bryophytes showed promise for use in mineral exploration, particularly as one of them, Fisidens rigidulus had been previously used in uranium exploration in the South Island. Boyle (1977) reported up to 2.4% Cu dry wt. in Pohlia nutans growing near a spring in a cupriferous bog at Sackville, New Brunswick, Canada where the amount of copper concentrated was found to be proportional to the degree of chlorosis. According to Brooks (1983) this is the highest copper level ever recorded for any plant, though this has now been superseded by values of c. 5 wt.% found in lichens from cupriferous substrata in Scandinavia (Purvis 1984). Furthermore, it is very doubtful if the Pohlia nutans was alive at these high contents of copper. Interestingly, the so-called "copper mosses" (section 1.3.1) do not concentrate copper to any significant extent.

Unfortunately, attempts have rarely been made to identify the site and the chemical state of the metal concerned. Lee et al. (1984) found the hydrated zinc silicate, hemimorphite $Zn_4Si_2O_7(OH)_2.H_2O$ in a number of mosses in blanket bogs, fed by Zn, Pb and Cd-rich spring water in the Yukon. However, this mineral precipitate forms only within the decaying moss layers and it is not possible to demonstrate that it is dependent on the metabolic activity of the living plant.

1.3.3. Modifications in response to metal stress

There is some evidence to suggest that mosses, as in the case of lichens and higher plants, may adapt physiologically to metal-rich environments. Thus Brown & House (1978) compared the copper resistance of 2 populations of the hepatic Solenostoma crenulatum from a copper mine at Ramsley, North Devon and a lead mine spoil tip at Priddy, Somerset. Incubation in copper solutions showed that copper uptake was very similar in the 2 populations. However, greater potassium leakage, indicative of membrane damage and inhibition of photosynthesis occurred in the lead mine populations supplied with copper, than in the populations from the copper mine. Consequently it was suggested that the copper mine population is a copper-tolerant ecotype. Potassium loss was a specific response to copper and was not caused by low pH, osmotic shock or cation-induced damage. Moreover the lead population, although it probably survived in elevated concentrations of lead, did not show tolerance to copper in the presence of lead, indicating that similar uptake does not imply similar tolerance. However, these results do not indicate whether the tolerance is

genotypic or substratum-induced.

Briggs (1972) studied population differentiation in Marchantia polymorpha subjected to various levels of lead pollution. M.polymorpha is relatively common in moist shady streets in the centre of Glasgow where it typically undergoes asexual reproduction. Briggs demonstrated that clones of gemmae in cities tolerated $PbNO_3$-rich agar (400ppm) wheras those from uncontaminated areas were not tolerant. This observation led Briggs to suggest that lead tolerant genotypes have a selective advantage in city regions. It is interesting to compare this observation with the case of the lichens Stereocaulon nanodes and S.pileatum. It has been suggested (e.g. James 1973) that the known affinity of these lichens for lead may explain why these species are increasing in towns, especially on walls adjacent to roads polluted by car exhausts. For instance, the writer has observed S.pileatum growing on the top of a brick wall near Fulham Road, South Kensington, London. A study similar to that of Jones et al. (1982) (section 1.1.6.c, 1.1.8 and 1.1.10), is required to determine whether the formation of insoluble lead compounds by some detoxification mechanism is a particular feature of these species, which could explain their tolerance to lead in the environment.

Coombes & Lepp (1974) observed morphological changes in copper- and zinc-stressed Funaria hygrometrica and Marchantia polymorpha and suggested these changes could be possible tolerance mechanisms. Funaria develops "capsule cells" and "brood cells" when subjected to high doses of copper and zinc respectively, thereby decreasing the surface area of the protonema in contact with the

copper and zinc. In copper-stressed Marchantia, a buffering zone of outer dead cells may immobilize copper within their walls, thus preventing toxic concentrations from reaching the inner cells. Copper levels above 8ppm resulted in the cessation of protonemal growth and inhibition of spore germination in Funaria and much reduced growth of gemmalings in Marchantia.

1.4. Vascular Plants

1.4.1. Plant communities of metal-rich rocks

A large number of plant communities characteristic of metalliferous soils in both Europe and elsewhere have been described and are reviewed by Ernst (1974). Individual plant species may be more or less confined to soils rich in particular elements and can thus be designated indicators for these elements in geobotanical surveys. Alternatively, plants may undergo changes in morphology such as stunting or changes in flower colour in mineralized terrains. Lambinon & Auquier (1964) proposed a classification for indicator plants in which metallophytes are taxa restricted to metal contaminated soils, either locally (local metallophytes) or throughout the distribution of that plant (absolute metallophytes). Although the area of contamination is frequently recognizable by a flora different from that in surrounding areas, the extent to which metal concentration and type of metal are important in determining the distribution of these plants has been little studied (Antonvics et al. 1971). In addition the taxonomic status of many of these indicator plants is far from resolved. It is a common error in taxonomy to be influenced by a

specialized environment and to describe new species on the basis of phenotypic rather than genotypic variation.

Viscaria (= Lychnis) alpina , a distinctive species known as the kisplant (ore-plant) in Scandinavia, is often very abundant on soils of low pH with high copper contents, and in sulphide-rich terrains (e.g. Vogt 1942, Vogt & Braadlie 1942). For this reason it has been widely used as an indicator of copper deposits, as in the case of the LKAB Viscaria Gruva at Kiruna, Northern Sweden. This provides an example of the practical use of indicator plants in prospecting. No rock exposures with mineralization were visible, though copper-rich water was seeping out of the ground (Svenska Dagbladet 20.8.1981). However, Lynchnis alpina is by no means restricted to specifically copper-rich environments and has been identified by Rune (1953) as typical also of Ultrabasic rocks in Sweden, where he described the Lychnis alpina - Arenaria norvegica association. Whilst Minuartia verna may also be present in the community on cupriferous substrata, it is also found over old lead workings in Wales and Northern England (Brooks 1983). It is interesting to note that in Scandinavia Minuartia verna occurs only at Odda, Hordaland, Norway (Lid 1979) where zinc ore is processed in large amounts. According to Nordhagen (1930) this species was introduced with fluorspar sent from Matlock in Derbyshire, England, in the early part of this century.

Elsewhere in Europe, particularly in Belgium, a specialized "galmei" flora occurs on calamine-rich soils with high levels of zinc. This flora has been termed the Violetum calaminariae on account of the presence of the "zinc violet" Viola calaminaria

(2n=52) (Schwickerath 1931). However, the taxonomic status of this species is uncertain and has been discussed by Heimans (1960). Its closest relative appears to be Viola tricolor subsp. alpestris (2n=62) (Viola tricolor subsp. alpina) and could represent a tetraploid of this species having been formed by a process similar to catastrophic selection involving drastic chromosomal adjustments of a specifically adapted type, leading to reproductive isolation (Antonovics et al. 1971). It is interesting to note that Schwickerath (1931) considers that the influence of $ZnCO_3$ and ZnS in soils on the vegetation depends on the occurrence of $CaCO_3$. A Ca:Zn ratio of 1 is considered optimum for the development of "galmei" floras, wheras with the higher contents of calcium the solubility of zinc decreases so that a typical calcareous flora develops.

Ultrabasic rocks have characteristically impoverished floras on account of their high magnesium, nickel and chromium contents, whilst calcium and nutrient levels are correspondingly low. Cerastium arcticum subsp. edmonstonii is almost restricted to the dunite debris on the keen of Hamar on Shetland (Proctor and Woodell 1971).

In central Africa, Duvigneaud & Denaeyer de Smet (1963) found at least 26 species or sub-species endemic to the copper outcrops of Katanga. Duvigneaud considered Becium homblei amongst the "cuprophytes", species characterized by a tendency to accumulate copper in soils lightly enriched with that metal and which can serve as a botanical indicator for copper. For some time, B.homblei was believed to be endemic to cupriferous ground in Rhodesia, where

it was thought to be a physiological ecotype which required high copper for healthy growth (Howard-Williams 1970, 1972). However, he has shown that B.homblei is fairly widespread in Zambia and Rhodesia in non-metalliferous areas. The anomalous distribution of B.homblei in central Africa has been considered to be due to biotype depletion brought about initially by a climatic change which resulted in a decrease in the competitive ability of the species at the limits of its range of distribution.

In the United States very characteristic floras are found on seleniferous soils. Here Astragalus species have been used as indicators of uranium deposits with high selenium contents (Cannon 1957, 1960).

1.4.2. Origin of indicator plants

There has been much controversy over the origin of indicator plants. Stebbins (1942), in discussing the interpretation of disjunct distribution, distinguished 2 types:- "palaeo-endemics" which are species of formerly wide distribution that are now confined to particular areas; and "neo-endemics" which are species that have originated recently in a given area in response to peculiar environmental conditions. Since many metallophytes have close relatives which may not be reproductively isolated and because of the recent artificial creation of many metalliferous sites added to the activity of man in the disseminating of plant species, Antonovics et al. (1971) favour the neo-endemic hypothesis. Infact heavy metal tolerance in plants is considered by these authors to be a better example of evolution in action than

industrial melanism in moths. This aspect of natural selection has been demonstrated in more than 30 plant species (Taylor & Crowder 1984). In pioneer studies by Bradshaw (1952) populations of Agrostis tenuis tolerant to lead and zinc were found occurring on mine spoil at Goginan, near Aberystwyth, Wales, while only 3 plants out of a sample of 60 from a pastureland some 100 yards away showed any tolerance. Generally speaking, tolerance is acquired for specific metals and tolerance to one metal does not confer tolerance to any other (Gregory & Bradshaw 1965), though resistance to several metals may develop within a given race if the soil contains a mixture of metals (Jowett 1958, Hogan & Rauser 1979). However, in contrast, Taylor & Crowder (1984) demonstrated that multiple tolerance can be inherent in Typha latifolia and need not require selection for, and amplification of, existing low frequency adaptive traits.

A palaeo-endemic hypothesis to explain the occurrence of certain plants in metal-rich environments is favoured by Ernst (1974). Evidence to support this conclusion is provided by pollen records of Armeria maritima and Minuartia verna which, since the twelfth century, have grown in a copper-rich turf at Dolfrwynog in Wales (Ernst 1969). According to Ernst Minuartia verna, Thlaspi alpestre and Armeria maritima are the only certain glacial relicts, whilst metal tolerant forms of the other plants could be formed by mutations from more widespread specis. However, since no vascular plant is known that has an inherent or constitutional resistance to heavy metals throughout its distribution, the problem of the evolution of tolerance in these palaeo-endemic species still requires an explanation.

1.4.3. Vascular Plant Analyses

There are several reports of unusually high concentrations of trace elements occurring in plants colonizing metalliferous sites. Brooks (1983) considered such plants as "hyperaccumulators" if they have the ability to concentrate certain trace elements to a degree well in excess of that in the substratum. Examples quoted on a dry weight basis include *Alyssum masmenaeum* with 2.43% nickel, *Aeolanthus biformifolius* with 1.37% copper, *Pearsonia metallifera* with 0.77% chromium, *Haumaniastrum robertii* with 1.02% cobalt, *Thlaspi rotundifolium* ssp. *cepaeifolium* with 0.79% lead, *Epilobium angustifolium* with 0.1% molybdenum, *Astragalus pattersoni* with 4.6% selenium, *Uncinia leptostachya* with 0.13% uranium and *Thlaspi calaminare* with 4% zinc. However, not all plants colonizing sites with high metal contents accumulate such high amounts of particular metals, as in the case of the Australian "copper flower", *Polycarpaea spirostylis* (Brooks 1983). Accumulation of a particular element is dependent both upon its concentration and form in which the element occurs. Thus Brooks & Crooks (1980) noted complete exclusion for lead in *Lychnis alpina* until *c.* 3000 ppm Pb in the soil, when there was an exponential increase in Pb content. The plant ceased to grow in solutions with greater than 1% of Pb. Partial exclusion was also noted for copper and zinc. The mechanism of metal uptake may occasionally be attributed to a specific biochemical process, as in the case of *Phacelia sericea*. This species has an ability to accumulate considerably more gold than other plants (Girling *et al.* 1979). *P. sericea* is cyanogenic and can liberate free cyanide into the soil with the resultant

dissolution of gold. The gold-cyanide complex is readily absorbed by the plant and translocated to the leaves where gold is concentrated. Other factors which may influence element contents in plants include variation of soil pH, the competitive effect of other elements and the organic content of the soil. Jarvis (1981) recognizes the variation of soil pH as causing one of the most marked changes in the contents of many trace elements in plants. This may act either through its effects on the mobility of the element in soils, or by affecting its absorption by roots. A decrease in metal uptake by plants has occasionally been observed in the presence of certain elements, particularly calcium which may be preferentially absorbed. Thus Wilkins (1957) discovered that calcium ameliorated the toxic effects of lead on Festuca ovina, the effect of being independent of the anion combination in which it was supplied. Another compound which may moderate toxicity includes aluminium alum which was found to promote seedling growth on copper tailings from copper mines in the upper peninsula of Michigan (Erbisch 1974).

The content of organic matter in the soil is also of extreme importance since stable complexes are formed with metal ions, so making them largely unavailable for uptake by plants. For instance, a larch-black spruce forest occurs on the Tantramar copper swamp in SE. New Brunswick where copper is present up to 7% dry weight of peat (Dykeman and de Sousa 1966). It is interesting to note that Stone & Timmer (1975) failed to confirm the exceptionally high copper contents previously reported by Beschel (1959) in the vegetation at the Tantramar Copper Swamp. Wide discrepancies between plant analyses may occur in the literature, no doubt partly

due to different methods of sample preparation and analysis. It is unfortunate that attempts are rarely made to discover the chemical state and location of the elements in the plant. This information is essential if the role of high elemental accumulation by the plant or contamination during sampling and analysis is to be assessed. This information, moreover, can be of considerable value in discovering the part played by the plant in the fixation of the metal.

It is now evident that accumulator plants can fix high concentrations of some inorganic ions and low molecular weight organo-metallic compounds as well as high molecular weight metal containing biopolymers (Peterson 1983). Amongst the low molecular weight compounds seleno-amino acids, nickel organic acids e.g. complexes of malic, malonic and citric acids, chromium-organic acids including the trioxalatochromate (III) ion, gold cyanide, copper proline, zinc malate and fluoroacetate have been detected (Peterson 1983). However, there is no evidence to suggest that these compounds are essential to the biochemistry of the plant. Amongst the high molecular weight compounds a metallothionein has been isolated from the roots of Agrostis gigantea tolerant to excess copper (Rauser & Curvetto 1980). This low molecular weight protein has high contents of half-cystinyl residues (up to 33%) which can bind metals Zn, Cu, Cd, Hg or Ag in mercaptide complexes. Since metallothioneins have an important function in metal metabolism in animals and are usually in low concentration, but increase with increasing exposure to a metal, Rauser and Curvetto suggested that these unusual proteins may also have a role in the metal metabolism of plants. Mathys (1977) assumes that malate

production is a major factor in the evolution of zinc resistance in herbage plants. Malate may act as a complexing agent for zinc within the plasma, whereas oxalate and mustard oils may function as terminal acceptors of large amounts of zinc.

1.4.4. Vascular plants and mineral exploration

The Russian geologist Karpinsky (1841) was one of the first to recognize that different plant associations exist on different geological substrata and that their distribution might be used to characterize the geology of the area concerned. His work led to the science of indicator geobotany, much used in the Soviet Union (Brooks 1983). Kovalevskii (1979) argues that biogeochemical prospecting in Russia using perennial plants with deep root systems, is one of the most economical methods of discovering deeply buried mineral deposits. Ore-bodies buried under a cover of allochthonous or autochthonous loose debris 30m or more thick can be discovered. Often the recorded concentrations of metals in plants which are considered of significant importance are low. Thus Cannon (1957) suggests values of >1 ppm uranium in the ash of branch tips can be regarded as a favourable indication for further exploration.

Alternatively, the analysis of herbarium specimens of plants known to preferentially colonize metalliferous sites has been undertaken. Brooks et al. (1979) examined over 700 herbarium specimens of Melandrium dioicum and Lychnis alpina from throughout Fennoscandia for Cu, Pb and Ni contents. Anomalous levels of these heavy metals identified the major copper mining districts of Norway

and Sweden, as well as several major Ultrabasic regions in Fennoscandia. The highest value of copper recorded in this survey occurred in L. alpina from Røros, Norway with 280 μg g^{-1} Cu.

The existence of a partial or total exclusion mechanism in plants is one of the biggest obstacles to biogeochemical prospecting (Brooks 1983). In the course of time, some elements such as nickel and uranium have acquired the reputation of being "easy" for biogeochemical prospecting, whereas elements such as Cu and Zn were considered to be "difficult". For example Marmo (1953) noted the following: During biogeochemical investigations in Finland, even comparatively small copper, zinc, nickel and molybdenum contents are distinctly reflected by the corresponding metal content both in the ground water and in the plants growing on the rocks in question. From observations made by botanists, the concentration of copper in plants does not increase linearly, but after reaching some value separately determined for each plant, the increase of the copper content of the plant will no longer reflect increasing contents in the underlying rock. Marmo suggests that the method should be used to complement geophysical methods of prospecting for ores e.g. if strong electric or magnetic anomalies from some region have been observed, but no knowledge of the character of the underlying ore minerals exists, biochemical methods can be very useful. This depends upon the fact that, in Finland, pyrrhotite and graphite will often produce strong geophysical anomalies. For the prospector these minerals are of no value and therefore it is important for him to know if minerals of the more valuable metals, copper, zinc or nickel are also present. Here biogeochemical methods are evidently useful. A number of types

of mineralization do not have strong geophysical signatures. It is in these cases, particularly when the cover is relatively thick, that biogeochemical prospecting can be applied with great effect.

CHAPTER 2. AIMS OF THE RESEARCH PROJECT

The aims of the research project have been to make an integrated study of saxicolous lichen communities and their substrata, laying emphasis upon environments with high concentrations of copper and iron sulphides. The specific objectives have been as follows;

1. To describe the lichen communities characteristic of certain copper-bearing rocks at several sites in Scandinavia and one site in Britain.

2. To discover if specific assemblages of minerals present at the sites give rise to characteristic lichen communities and to define indicator species, specific to these particular mineralogical environments.

3. To assess the importance of pH and other ecological factors in controlling the development of the lichen communities examined.

4. To investigate the effect of copper mineralization on the individual lichen species growing within a community in a given mineralogical environment. An important aspect has been to investigate the extent to which lichen species differ in their response to the mineralization. For instance, it is possible that certain lichens may preferentially accumulate copper or other elements, whilst adjacent lichen species may not. Alternatively, it is conceivable that certain lichens may undergo changes in morphology induced by the chemical stress imposed by the copper mineralization.

5. To identify, as far as possible, the type and location of unusually high concentrations of elements and compounds,

particularly those of copper, which occur within certain lichens growing on cupriferous substrata. It has been important to distinguish the process of physical incorporation of rock and mineral fragments from the substratum, from processes of chemical or biochemical precipitation within lichen thalli. The nature of the interaction between lichen growth and mineral decomposition in the substratum has also been considered.

6. To suggest mechanisms by which lichens can tolerate the high levels of copper found in the substratum and to assess the limits of tolerance for copper by particular lichen species.

7. To establish some general principles governing the relationship between saxicolous crustose lichens and the substrata on which they grow and to assess the use of lichens as indicators of mineralization.

2.1. Projections and methodology

The survey of the literature outlined in Chapter 1 shows that the relationship between saxicolous, crustose lichens and the rocks on which they grow is poorly understood, although there have been important studies of lichens as agents in rock weathering (section 1.1.6.c). There have been a number of problems which have made progress in this field of research difficult. Firstly, the problems of taxonomy of saxicolous crustose lichens are in themselves considerable and in order to provide an adequate mineralogical and chemical account of the rocks, the disciplines of geology, geochemistry and petrography, have to be employed. To properly understand the relationships which exist between a saxicolous lichen and the underlying rocks, a multidisciplinary approach is

required and a balance between the combination necessary for the botany and geology has rarely been achieved. In addition, ecological and biochemical aspects should also be taken into account. In the last decade, non-destructive electron beam analytical methods have reached a level of sophistication which enables a detailed chemical and structural analysis of the lichen thallus and its adjacent substratum. For this reason, SEM and EPMA are techniques which have been of great use in the present study. Working from the basis of a training in botany with special knowledge of lichens, the investigator during the course of the study has employed standard geological techniques, notably the petrographic examination of rocks in polarized light and the chemical analysis of rocks. It has obviously been of the greatest importance to be able to identify the primary and secondary metal-bearing minerals in the mineralized sites which have been studied. In the first instance, the research was initiated by making detailed collections from chosen sites in the field, taking into account all the factors of ecology and rock composition which could affect the physiology and the biochemistry of the lichen communities. The area open for research is a large one and it has been necessary to limit the scope in terms of the type and number of the sites studied. Careful taxonomy and a detailed study in the field have formed the basis of the research. Because chemical factors originating from the mineralogy may modify the growth and alter the morphology of particular species, saxicolous, crustose lichens pose many taxonomic problems (section 1.1.7). For this reason, an essential part of the research has involved the comparative study of herbarium material. Taxonomic research is additionally complicated because the identification of lichens as

reported in the literature must often be checked. This is particularly the case where saxicolous lichens growing in metal-rich habitats are concerned because they are often found to show anomalous, fragmentary forms (section 1.1.7). The ability to recognize phenotypic variation, as opposed to simply genotypic variation, is of fundamental importance. It is evident that insufficient attention has been given in previous taxonomic studies to environmental factors which influence either lichen growth, morphology and thallus growth (section 1.1.7).

2.2. Fieldwork

At most of the sites investigated a detailed ecological analysis of the lichen communities was carried out, paying particular attention to altitude, aspect, exposure, slope, the type of substratum e.g. pebble or rock boulder and the distribution of lichens on the substratum. A broad assessment of the moisture regime was made at individual sites. Additionally, the presence of bird-droppings and the possible influence of leachates from soil was noted. In view of the often wet weather, it was usually possible to obtain pH measurements of rain water in direct contact with the rock surface. The measurement of pH was made using Whatman narrow range pH indicator paper. Rain water was allowed to remain on the rock surface for several minutes where possible, to allow some degree of equilibrium between the water and mineral phases to be reached. Although this is considered a relatively crude technique, repeated trials in the same environment gave an accuracy to within one unit of pH, which was considered adequate for the present study.

Lichens from each site were collected with care and a succinct description of the precise situation of each species was made. Notes were made on the abundance of the species at particular sites. Furthermore, a photographic record of most sites was made, including close-ups of specific communities. Representative rock samples, about fist-sized were collected at several sites where there were obvious differences in the composition of the lichen communities. Underlying fresh rock samples, with relatively unweathered minerals, were collected where possible. This procedure was often laborious, involving perhaps the complete destruction of a boulder where there was a high concentration of sulphide, particularly when this was weathered pyrrhotite.

2.3. The phytosociological approach adopted in the present study

There are several review articles which discuss the various approaches to the study of plant communities (e.g. Barkman 1958, Shimwell 1971, James et al. 1977). In the present study, the method of James et al. (1977) has been adopted. Since a continuum of plant communities exist, James et al. (1977) suggest that phytosociology should aim to define those major noda which are related to clearly recognizable ecological and environmental parameters. These authors suggest a two stage approach involving 1. an initial selection of the communities based on the species present and 2. a subjective attempt to correlate the presence of these communities with environmental factors, in so far as these can be determined in the field. In the present study, however, an objective attempt has been made to identify those factors which are responsible for the

development of the striking communities occurring on certain copper-rich rocks. The analysis of the stands of vegetation is expressed in the form of relevé tables, where the frequency of the individual lichens is recorded by the Domin scale. Inclination, aspect, altitude and other factors of the site are also included. The angles of inclination are measured from the horizontal, vertical = 90^{o} .

2.4. Lichen identification

2.4.1. Light microscopy

Observation and measurement of external features were made using a Wild binocular microscope with variable magnifications (x6 to x50). Sections of lichen material were made by hand with a razor blade. Sections were usually mounted in water or lactophenol cotton blue. Internal anatomical features were studied using a Leitz Dialux 20 microscope, employing transmitted light. 10% KOH (abbreviated as 'K' in the text) was routinely used to intensify specific pigments in the epithecium and elsewhere. KOH was used in addition to detect norstictic acid. Lugol's I_2 solution (1g I_2 and 2g KI in 300ml distilled water H_2O) was used to check for amyloid compounds. Calcium hypochlorite solution (C) and paraphenylene-diamine (Pd) dissolved in ethanol were also used to check for specific lichen acids and pigments.

2.4.2. Thin-layer chromatography (TLC)

The TLC techniques employed are those described by Walker &

James (1980). During routine analysis, only 2 of the 3 basic solvent systems were utilized, notably HEF and TDA. For difficult situations, special combinations of solvents were used, including TA and EA; the latter system was used to separate gyrophoric from lecanoric acid. Two dimensional chromatography was also employed (Culberson & Johnson 1976, Wilkins & James 1979). Approximately 1000 lichen identifications were carried out during the course of this study using TLC. The technique was of great use for the identification of sterile taxa and of material in a fragmentary state.

2.4.3. Texts and herbaria consulted

There is no existing text describing the entire Scandinavian lichen flora, though 'Lavflora' (Krog et al. 1980) and 'Lavar' (Moberg & Holmåsen 1982) were used in the identification of the macrolichens. Additionally, the checklist of the lichens of Norway and Sweden (Santesson 1984) proved invaluable in establishing whether or not species occur in Scandinavia and in providing literature references. The annotated keys in "The Lichens of Torne Lappmark" (Magnusson 1952) were useful in the identification of many crustose lichens. Frequent reference was also made to "Lichenographia Fennica IV" (Vainio 1934) and the standard lichen texts, Ozenda & Clauzade (1970), Poelt (1969), Poelt & Vězda (1977, 1981) and Wirth (1980). There is a series of more specialized papers on particular genera which have been consulted, including, importantly, those on Lecidea by Hertel and co-workers which are listed in the bibliography.

Wherever possible, lichen collections were compared with named material, referred to the BM collections; frequently type material was consulted. Additionally, a month was spent in Scandinavian herbaria investigating the collections made by Magnusson (Uppsala), Vainio (Turku) and Nylander (Helsinki). Additional loans of material were obtained from Bergen (BG), Copenhagen (C), Edinburgh (E), Graz (GZU), Helsinki (H), Leiden (L), Munich (M), Oslo (O), Turku (TUR), Uppsala (UPS) and the Montana College of Mineral Science and Technology, Butte, Montana.

2.5. Rock classification

Certain problems arise in providing a definitive classification of the deformed and metamorphosed rocks, which form the principal substrata of the sites with copper and iron sulphides, chosen for the present study. Igneous rocks can be classified by normative calculation, based on their chemical composition determined by analysis (see Irvine & Baragar 1971); alternatively they can be classified making use of the proportions of mineral constituents of which they are composed, i.e. their modal composition (Streckeisen 1967). The determination of the mode by microscopic examination is extremely difficult in the case of fine-grained, volcanic rocks and is further complicated when such rocks are subject to deformation, recrystallization and remobilization of their constituents during metamorphism. A classification based simply on a chemical norm is also unsatisfactory because this disregards the variation introduced by differential mobility during the metamorphic process (Hill 1980). When gross variation in mineralogy occurs on the scale of cm to dm,

then the problems of sampling representative material are so great, that it is not meaningful to classify the rock, except in terms of describing its mineral constituents and commenting on the chemical composition, in relation to the broad grouping of rocks within which the site is located. These limitations having been recognized, it is still appropriate to give a name to the rock on the basis of its silica and major oxide content, providing that petrographic examination does not indicate massive metamorphic redistribution.

At an early stage in the study, it became apparent that certain accessory minerals, notably Fe and Cu sulphides and their associated oxidation products, exerted a profound effect on the lichen communities. It was thus generally found to be more important to identify the mineralogy of the rock, than to name the rock according to accepted petrological classification, although it was relatively easy to make a statement of the general grouping within which the particular substrata belonged. Partial chemical analyses were carried out on a range of representative samples from the sites investigated, employing inductively coupled plasma emission spectrometry (ICP).

2.5.1. Preparation of samples for chemical analysis

Rock samples (normally 1kg) were first crushed to -0.5cm in a jaw crusher. The sample was split and a fifth split of c. 30g was crushed to -200 mesh (-75 μm) using an agate tema. 5g aliquots weighed to 5 decimal places were then heated in a porcelain crucible for 24 hours at 950°C and the loss on ignition (L.O.I.)

determined. L.O.I., in this case, consists primarily of lost H_2O, CO_2 and SO_2. Because of the abundance of ferrous sulphides, carbonates and hydrous minerals in many of the samples, L.O.I.'s were high, up to 10 wt %. Additional problems arose because of oxidation of ferrous to ferric iron during ignition, in which a gain of O_2 occurs and then it was difficult to separate gains from losses during the ignition process. The ignition process was undertaken to oxidize and break down, as far as possible, the sulphide material present, which can react with platinum and consequently cause damage to the platinum crucibles used during the fusion process.

2.5.2. Fusion procedure

0.1g of each sample, 0.750g $LiBO_2$ and 0.5g $LiNO_3.3H_2O$ were mixed in platinum crucibles and heated slowly over a meker burner for 5 minutes. After cooling, these were then fused in a muffle furnace at 1000°C for 30 minutes. Finally, the melt was dissolved in 25ml 2N HNO_3 and dissolved with 70ml H_2O using a magnetic stirrer and the solution was then diluted to 250ml in a volumetric flask. Analysis of these prepared solutions was carried out using inductively coupled plasma emission spectrometry (ICP). Standardization of the results obtained was made using blanks. However, as no satisfactory copper standard was available and some of the rocks contained high contents of this element (to 10%) the results are, in certain cases, not calibrated and totals are therefore high. For the purposes of the present survey, these discrepancies do not alter the conclusions which would otherwise be obtained from ideal totals.

2.5.3. Petrography

Both thin sections and polished thin sections were prepared from many of the rock samples and minerals were identified using standard techniques of petrological microscopy employing both transmitted and reflected polarized light. Standard texts including Optical Mineralogy (Kerr 1977) and the Atlas of Rock-Forming Minerals in Thin Section (Mackenzie & Guilford 1980) were used to identify transparent minerals in thin section. Features such as colour in plane-polarized light, cleavage angles, birefringence, vibration direction and optic sign were determined where necessary. Since the majority of the rocks studied have been subjected to greenschist facies metamorphism, a fairly restricted assemblage of minerals was encountered and these were mostly readily identified after some practice. However, quartz and albite proved difficult to identify when present in a microcrystalline groundmass, though in these circumstances, the evidence provided by chemical analysis helped in resolving this problem. Opaque minerals were studied in reflected light and the text Ore Microscopy and Ore Petrography (Craig & Vaughan 1981) consulted for their identification. Attention was paid to the state of preservation of various minerals and the possibility of particular elements being made available to the lichens during oxidative breakdown of sulphides, in particular.

2.6. Chemical analysis of lichen material

A large number of lichens were analysed qualitatively using the SEM in the microanalytical mode. In general, for routine analysis, a geol 733 SEM with a Link system energy dispersive X-ray

spectrometer was used. For high resolution micrography a Hitachi field emission S-800 SEM was used. Additionally, a limited amount of high resolution analytical work was carried out on a Hitachi S-530 SEM with a Kevex energy dispersive X-ray spectrometer.

Sample preparation was relatively uncomplicated, involving controlled fracturing of lichen and substratum, initiated by using a razor blade. Samples were then sputter-coated with gold/palladium. Spot analyses, X-ray mapping for individual elements and electron images in the back-scattered mode were all used to investigate compositional variations in the lichen thallus. Selected specimens were dissolved in solution and analysed by plasma emission spectrometry. In these cases, a careful examination was made and visible rock fragments were carefully removed from the lichen thalli using a binocular microscope. However, as has been stated, chemical analysis made in this way must be interpreted with caution (section 1.1.5.a). Confirmation of the identity of several compounds was obtained by using X-ray powder diffraction and infra red spectroscopy.

2.7. Choice of sites

A restricted number of sites have been selected for study, since it was believed that a detailed ecological investigation in a small area was likely to be more profitable than a less thorough investigation of a large number of localities. However, a number of similar metal-rich sites have been investigated, in order to be able to make some generalizations about the lichen communities of mineralized rocks.

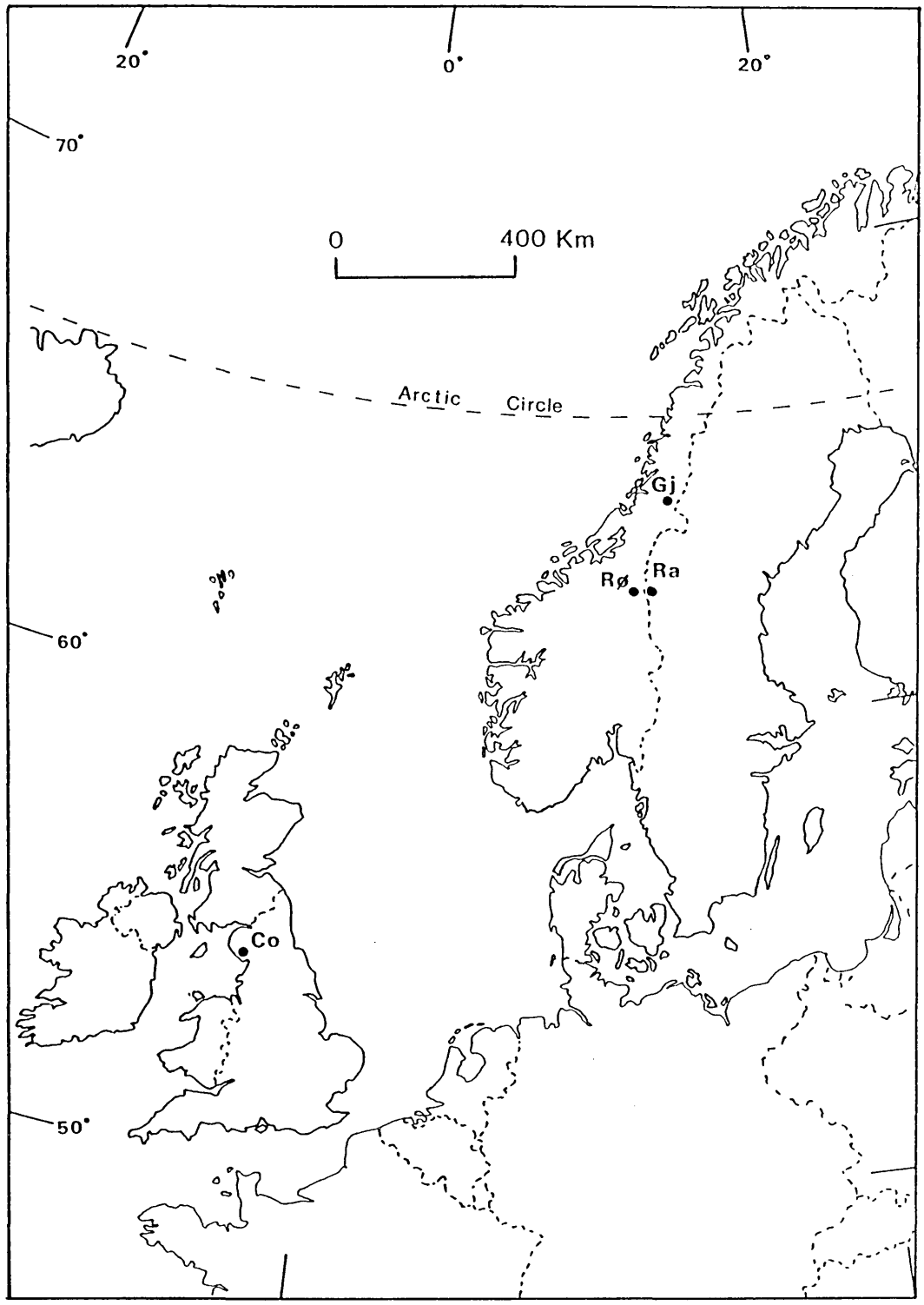


Fig. 1. Map showing localities studied in Scandinavia and Britain, Co=Coniston, Gj=Gjersvik, Ra=Ramundberget and Rø=Røros.

The main sites studied occur in the central part of the Caledonides in central Scandinavia (Fig. 1). The Grong area in Nord Trøndelag County was chosen for a reconnaissance during July and August 1982, primarily since it is a region of contrasting geology and of considerable economic importance (section 2.8). An additional important factor was that the area had been geologically investigated by Halls and others, over a period of some 10 years. The Grong area has been little studied by lichenologists. This is particularly so in the case of the crustose, saxicolous lichens; neither an ecological survey of the lichen flora of this area, nor a comprehensive list of species exists. Ahlner (1948) reported several epiphytic macrolichens from the area. Additionally, a survey of the macrolichens has been undertaken in the Børgefjell National Park, Nordland (Tønsberg, unpubl.). Magnusson collected several lichens in the neighbouring county Jämtland in Sweden (hb. Uppsala!), though he has not published on the flora in this area. Santesson (1975) produced a preliminary checklist of lichens for this county, which then numbered c. 870 species. However, the number of lichens now known from Jämtland is considerably greater (Santesson pers. comm.). Degelius (1982) provided an account of the distribution and habitat ecology of lichens on the Island of Vega in Nordland, where he recorded 668 species. From these examples of work carried out in neighbouring regions, it was evident that the lichen flora in the Grong area would, in all probability, be similarly rich.

Surveys of saxicolous lichens were also carried out at abandoned copper mines in the vicinity of Røros, Sør Trøndelag,

Norway, the oldest copper mining district in Scandinavia and at Ramundberget, Härjedalen County, Sweden (Fig. 1). The lichens at the Ramundberget site are currently being investigated by Professor Rolf Santesson.

In addition, one cupriferous locality has been studied in Britain. During a brief visit by the British Lichen Society to Coniston Copper Mines, Westmoreland, England in October 1983, Lecanora handelii was recorded. This species has been recognized as a characteristic constituent of the association Lecanoretum epanorae V. Wirth, ex P. James et al. (1977), which is found on vertical surfaces in dry, shaded environments rich in sulphides. This had not been found previously in the British Isles. Because of the special interest of the site a further two day visit was made to study the area in more detail.

The choice of particular sites for study at the various localities was not random, but they were chosen carefully to enable both the study of the influence of mineralogical and ecological factors on the lichen communities. The time spent at each site has been recorded to give some indication of the relative detail of the field study and collection in each case. It is, however, inevitable in the Scandinavian mountain terrain that bad weather limited the study in some cases.

A general classification of the sites is as follows:

1. Rock outcrop bearing sulphide minerals showing colour zonation of lichen communities on Litlfjellet, Røyrvik, Nord Trøndelag, Norway (section 3.2).

2. Disused copper mine with a wide range of habitats at Gjersvik, Nord Trøndelag, Norway (section 4.2).

3. Magnetite-rich siliceous boulder on Annlifjellet, west of Gjersvik, Nord Trøndelag, Norway (section 3.3).

4. Disused copper mines with dumps and copper-contaminated soils at Muggruva, Storvartsgruva, Kvintushögda and Olav's gruva in the vicinity of Røros, Sør Trøndelag, Norway (section 4.6).

5. Disused copper mines at Norrgruvorna, Glimsjön and Gammalgruvan near Ramundberget, Härjedalen, Sweden (section 4.4).

6. Bonsor ore-dressing floor walls, Simon's Nick, Black Scar Workings above Levers Water and a mine dump above Coniston Youth Hostel at Coniston Copper Mines, Westmoreland, England (section 4.3).

2.8. Geology of the investigated areas

The belt of metamorphosed Lower Palaeozoic rocks, chiefly of Ordovician age, within which the important stratiform pyritic copper- and zinc-bearing orebodies of the Scandinavian Caledonides are located, extends over 1500 km from Rogaland in southwestern Noway to Nord Troms (Halls et al. 1977). In the central Norwegian Caledonides, there are several stratiform base-metal deposits including Gjersvik, Skorovas, Joma (Nord Trøndelag), Løkken, Røros (Sør Trøndelag) and also Stekenjokk and Ramundberget in the geographically adjacent area of Jämtland, Sweden. The stratiform ores in all these regions lie within rocks of the Köli Nappe Complex which is the upper structural unit of the Seve-Köli Nappe Complex (Oftedahl 1958). Central Scandinavia is an area of considerable economic importance. Mining for copper and zinc is

currently in progress at Joma, Stekenjokk, Løkken and Røros and has only recently terminated at Skorovas. The mineralogy of the worked ores is dominated by pyrite and, or, pyrrhotite in combination with chalcopyrite and sphalerite and occasionally galena as the economically important constituents (Oftedahl 1980).

Sites in three of these areas have been studied in the present survey, the main ones being at Gjersvik and Røros. A less detailed survey was also made at Ramundberget.

2.8.1. Gjersvik

The Gjersvik area consists of low-grade metamorphosed rocks overlain in the west by the higher grade Helgeland Nappe Complex. The low-grade sequence is divided into three groups, the Gjersvik, the Limingen and the Røyrvik Groups. The greenstones and felsic rocks in the Gjersvik Group are of tholeiitic affinity and are thought to represent part of a lower or middle island arc complex which was affected by sea floor weathering after deposition (Lutro 1979). It has long been recognized that the Gjersvik greenstones are composed of a sequence of Basic to Acid rocks, including basalts, andesites and keratophyres of distinctly spilitic affinity (Oftedahl 1958). It seems likely that the spilitic character of these rocks is the result of metasomatism, which accompanied the sea-floor metamorphosis of the volcanic rocks during Lower Ordovician times. In particular, metasomatic alteration has enhanced the Na_2O content of the rocks (Halls *et al.* 1977). Parorogenic movements, possibly in Middle Ordovician time, led to erosion of the Gjersvik Group and the formation of a polymict

conglomerate marking the basal unit of the Limingen Group (Halls et al. 1977, Lutro 1979). The Røyrvik Group consists of phyllites, often bituminous, associated with quartzites and some green schists.

The Gjersvik deposit, first discovered in 1909 (Oftedahl 1958), has been exploited, but not brought into production. It contains 4 mill. tons of copper-bearing sulphides (Oftedahl 1980). The rocks at the major site investigated during the survey, in the vicinity of the outcropping ore body at Gjersvik belong to the Gjersvik Group, which have been metamorphosed in lower-middle greenschist facies and have been subjected to several phases of deformation. According to Lutro (1979), the Bjørkvatnet Formation constitutes the eastern part of the Gjersvik group, consisting of an approximately 3km-thick sequence of metavolcanic and meta-intrusive rocks. The dominating rock types within the formation are massive to variably schistose, volcanic greenstones which were deposited either as pillow lavas or as massive flows. A dark greenstone is the most extensive which is fine-grained, massive to slightly schistose, composed of the greenschist facies minerals notably albite, actinolite, epidote and chlorite, locally with stilpnomelane, calcite and pyrite and other sulphides, mainly pyrrhotite and chalcopyrite. Veins and lenses consisting of epidote with some quartz or calcite are widespread in this rock-type. On Litlfjellet, Halls et al. (1977) record that here an even darker greenstone occurs which is stilpnomelane-rich.

2.8.2. Røros

The Trondheim region is the largest and most important copper district in Norway. Copper has been mined in the region for 300 years and the area is still an important copper district in which discoveries are being made and considerable exploration is presently being carried out. The Røros Kobberverk was founded in 1664 and, until its closure in 1977, was the oldest operating mining company in Norway (Bugge 1978). The Røros district is situated in the eastern part of the Trondheim region. Numerous pyritic orebodies occur in the metavolcanics of the Hersjø formation, including the Løkken, Tverrfjellet, Killingdal, Hersjø and Geitryggen deposits, but most of the classical copper deposits of the area, notably Kongen, Sextus, Mugg, Menna, Kjøli and Leirgruvebakken deposits are confined to sedimentary strata lower down in the succession, usually occurring in metagreywacke. Other common metasedimentary sequences (phyllite, black schist, quartzite) are mostly barren. Pyrite is the dominant iron sulphide in the Hersjø metavolcanics, pyrrhotite breccia ores being more prominent in the sedimentary rocks (Rui 1980). In the eastern mining field situated 10km northeast of Røros at about 900km above sea level, a group of once important, but now exhausted mines occur in the Røros schists (calcareous mica schists) of the Røros formation, underneath the Hestkletten meta-gabbro. Hestkletten and Christianus Quintus mines occur just below the gabbro and Storwartz, the most important mine, and Kronprins Olav in the same horizon lie 60-80m below the metagabbro. The northern mining field is situated 10-15km NW. of Røros. Here the mines including Mugg mine (1717-1919) occur in meta-greywacke and mica schist with

intercalations of greenschist of the Røsjø formation (Bugge 1978).

2.8.3. Ramundberget

The stratabound sulphide/oxide deposit of Ramundberget lies tectonically in the lower part of the Seve sequence within the Seve-Köli Nappe Complex, which here overlies the Särv Nappe. Host rock to the ore is a tholeiitic metabasalt, metamorphosed to greenschist facies. The size of the Ramundberget deposit has been estimated at probably less than one million tonnes and more than 50000 tonnes, with an average grade of approximately 0.9% Cu. The sulphide occurs disseminated to massive as layers, with the massive layers of magnetite within the greenschist or the epidotite. Essential minerals in the greenschist include actinolite, albite, epidote and chlorite; accessory minerals include quartz, biotite, white mica, apatite, leucoxene, magnetite, ilmenite, sphene and calcite. On the basis of hydrous mineral assemblages and calcite it is probable that H_2O and CO_2 have been introduced to the rock pile (Hill 1980).

2.8.4. Coniston

Historically, the Coniston region was the major source of copper in the Lake District. Of the entire output 75% came from the Coniston group of veins which included, in particular, the rich Bonsor and Paddy End Veins. The main mining area lies on the slopes of the Old Man of Coniston (c. 800m) and adjacent hills. There is historical evidence of mining activity for the last 2000 years which reached a peak in the late 19th century ceasing in 1942 (Shaw

1970) accompanied by the gradual dereliction of the associated buildings. Subsequently some slate mining has also occurred in the vicinity.

The copper mineralization in the area takes the form of epigenetic infillings predominantly of normal faults, but also along tear faults and in joints. Host rocks for the Coniston deposits are the Borrowdale Volcanic Series of Ordovician age. Chalcopyrite, pyrite and arsenopyrite are the dominant ore minerals; locally, oxidation of the copper minerals has occurred, giving rise to azurite and malachite (Stanley 1979). Natural surface exposures of ore-rich veins are poor and mine dumps and the derelict Bonsor ore-dressing floor walls are the major sites where ore material is located and special lichen habitats exist.

CHAPTER 3. THE INFLUENCE OF IRON SULPHIDE MINERALIZATION ON LICHEN COMMUNITIES

3.1. Introduction

Two contrasting sites, both with high contents of iron, in the vicinity of Gjersvik, Nord Trøndelag, Norway have been chosen for study. The site at Litlfjellet (section 3.2) has, locally, high contents of the sulphides pyrite (FeS_2) and pyrrhotite (FeS_{1-x}), wheras the site at Annlifjellet (section 3.3) has high contents of the oxide, magnetite (Fe_3O_4). The importance of iron and pH as factors influencing both the composition and colour of these lichen communities, is discussed. A discussion of the current knowledge of the relationships between lichens and iron-rich rocks is presented in sections 1.1.4.c and 1.1.7.a.

3.2. Litlfjellet site

3.2.1. Site description

The site is located c. 2.75km N. of Gjersvika (13°25' E., 64°53' N.), Nord Trøndelag, Norway, c. 250m NW. of the western shore of the eastern Pertjörnin lake on the mountain Litlfjellet, map NGO 1:50000, sheet number 1924 IV Røyrvik, UTM: VM 257964, altitude 625m.

The Litlfjellet site studied during 7-10 August 1982 and 23-24 August 1983 is an irregular ice-worn rock outcrop facing ESE.

in typical vidda terrain (Plate 1). Its most noticeable feature is the sequence of seven distinctive, more or less horizontal bands. These bands are obviously coloured rusty red-brown, grey or yellow-green as a result of weathering and lichen growth (Plates 1 and 2). The outcrop studied covers an area of about 200m^2 and dips 42° ESE. at maximum inclination. The distinctive colour sequence observed at this site raises certain questions.

1. Are similar colour zones characterized by
   a) similar lithologies?
   b) similar lichen communities?
2. What similarities, if any, exist between the lichen communities in the different zones?

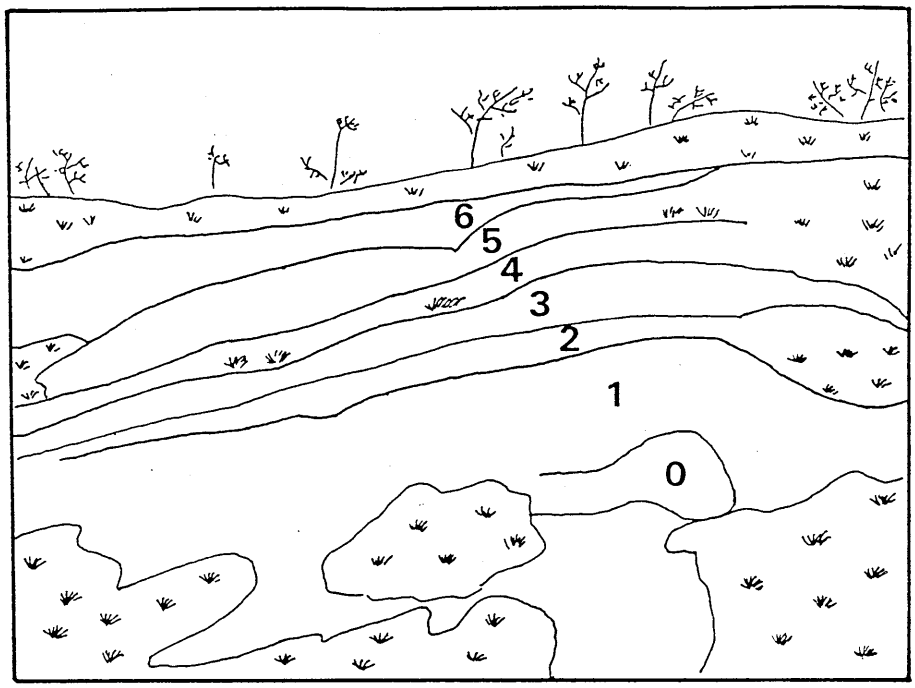
By investigation, it was hoped to assess the importance of the rock mineralogy as a factor influencing the composition of the lichen communities and surface colour of particular lichens.

3.2.2 Local vegetation

At an altitude of 625m, the vegetation at this site is essentially sub-alpine in character and in the immediate vicinity of the outcrop stunted Betula pubescens, scattered Juniperus communis and more frequently Betula nana, Salix lanata and S. herbacea occur. Associated herbaceous plants also abundant include Empetrum hermaphroditum, Vaccinium myrtillus, V. uliginosum, Viola palustris, Trientalis europaeus and Lycopodium selago. Macrolichens are here also frequent associates, including Baeomyces roseus, Cetraria islandica, Cladonia bellidiflora, C. coccifera, C. pleurota, C. rangiferina, C. uncialis, Ochrolechia frigida and O.

PLATE 1.

A. General view of Litlfjellet site looking WNW., 7 August 1982. Note the contrasting colour bands. Zones studied are shown in diagram below.



B. View looking E. from zone 6 of Litlfjellet site. Note oxide-encrusted surface supporting a range of ferruginous species.



A

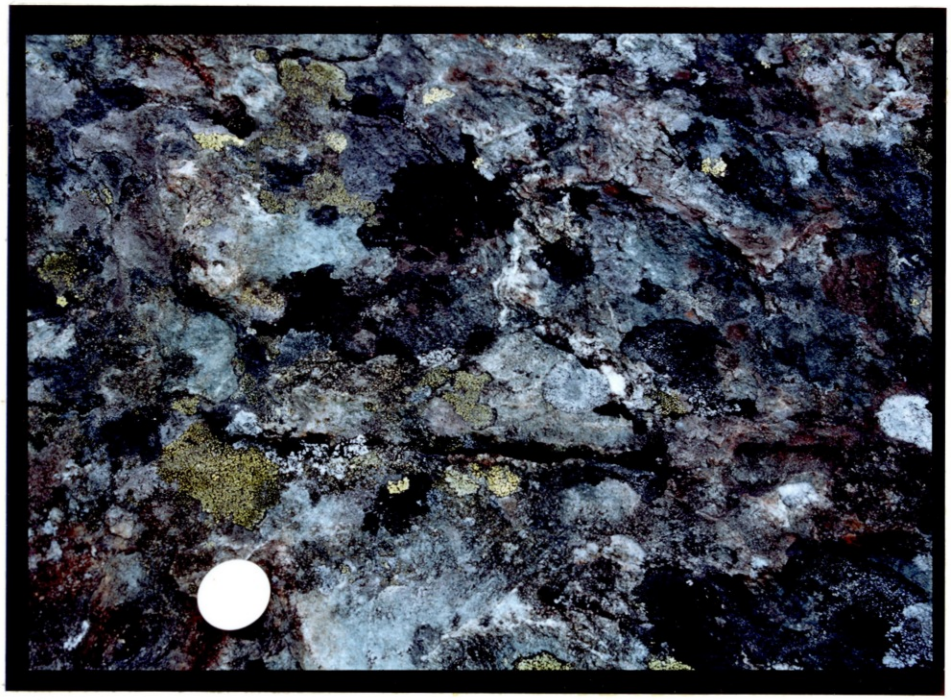


B

PLATE 2.

A. Close-up of lichen community occurring in zone 5 of Litlfjellet site comprising a range of species, mainly belonging to the genera Aspicilia, Huilia, Lecidea and Rhizocarpon.

B. Close-up of lichen community occurring in zone 3 of Litlfjellet site showing an extensive development of Rhizocarpon geographicum. Scale : 5kr coin, c. 30mm diam.



A



B

Table 2. Lichens occurring at Litlfjellet site

	Zone						
	0	1	2	3	4	5	6
Acarospora sinopica	o	vr	a	r	a	–	a
Aspicilia alpina	r	–	–	o	–	a	–
cinerea	–	f	–	–	–	a	–
complanata	–	f	o	o	–	–	–
subsorediza	o	r	o	o	o	r	o
sp. (norstictic acid)	o	r	–	f	o	–	–
Caloplaca magni-filii	–	–	–	–	–	r	–
stillicidiorum	–	–	–	–	–	r	–
Cetraria commixta	–	r	–	–	–	–	–
Huilia cf. contraponenda	a	–	–	–	–	–	–
flavocaerulescens	–	–	–	–	–	f	–
macrocarpa	–	–	–	la	–	–	f
cf. melinodes (stictic acid)	–	–	a	–	a	–	la
cf. musiva	f	a	–	f	–	–	–
panaeola	–	–	–	–	–	a	r
tuberculosa	f	a	o	f	–	a	o
Ionaspis cyanocarpa	–	f	r	–	o	–	–
epulotica	f	f	o	o	–	–	o
Lecanora badia	–	f	–	–	–	a	–
intricata	–	–	–	r	–	f	–
leptacina	–	–	–	–	–	r	–
polytropa	o	f	o	f	o	f	r
subaurea	f	–	–	–	a	–	–
Lecidea atrofulva	–	–	–	–	–	vr	o
caesioatra	–	r	–	–	–	r	–
confluens	–	–	–	–	–	a	–
griseoatra	o	–	o	a	–	f	o
lactea	–	–	o	o	–	a	a
lapicida	–	–	f	–	–	f	a
lithophila	–	f	–	–	–	a	r
nigroleprosa	–	–	–	r	–	–	–
paupercula	–	–	–	–	–	r	–
silacea	f	–	a	–	a	–	a
swartzioidea	–	–	–	–	–	f	–
umbonella	o	f	–	–	a	f	r
vorticosa	–	o	–	–	f	–	o
Lecidella stigmatea	–	–	–	–	–	a	–

Table 2 continued:

	Zone						
	0	1	2	3	4	5	6
Lepraria neglecta	–	f	–	–	–	f	–
Ochrolechia geminipara	–	–	–	–	–	r	–
Pertusaria oculata	–	–	–	–	–	r	–
Porocyphus sp.	–	–	r	–	o	–	a
Pseudephebe pubescens	–	–	–	–	–	o	o
Psora demissa	–	o	–	–	–	–	–
Pyrenopsis granatina	–	–	–	–	–	r	–
Rhizocarpon alpicola	–	–	–	a	–	o	–
badioatrum	r	–	–	–	–	a	–
cinereonigrum	–	–	–	–	–	r	–
geographicum	r	o	o	a	o	f	a
sp. (gyrose discs)	–	–	–	–	r	r	–
hochstetteri	f	f	f	o	f	r	a
jemtlandicum	–	–	–	o	–	–	f
lavatum	a	a	–	–	–	–	r
polycarpum	–	–	r	r	–	–	–
Sporastatia polyspora	–	–	f	a	f	–	–
Stereocaulon dactylophyllum	–	–	–	–	–	–	f
evolutum	–	o	–	–	–	f	–
spathuliferum	–	o	–	–	–	–	–
vesuvianum	r	a	o	–	–	–	a
Tremolecia atrata	f	–	a	o	a	vr	a
Umbilicaria cylindrica	–	–	–	–	–	–	f
hyperborea	–	–	–	–	–	–	o
polyphylla	–	–	–	f	–	–	–

Legend

a – abundant
la – locally abundant
f – frequent
o – occasional
r – rare
vr – very rare

geminipara.

However, the lichen flora of the rock outcrop is predominantly crustose, foliose and fruticose species being largely absent. Some 60 lichens were observed on the outcrop and are listed in Table 2.

3.2.3. Lichen flora of outcrop

3.2.3.a Zone 0

The smallest zone in extent (c. 3x2m) situated at the bottom right hand side of the outcrop (Plate 1), dipping c. 40° ESE. This area has a partially ferruginous surface. Lichens are inconspicuous in this zone, though some 19 species were recorded, albeit in an often depauperate and stressed form. The most frequent lichens present are Rhizocarpon lavatum, often with rusty pruinose discs and occasionally ferruginous thalli, Huilia cf. contraponenda, Huilia cf. musiva usually abundantly fertile but also occasionally sorediate and H. tuberculosa. The discovery of Lecanora subaurea growing at this site was of considerable interest. The first Norwegian record of this species was that of Tønsberg in 1981 who found it growing on a discarded horseshoe in Nordland. The other lichens present in this zone known to be characteristic of rocks rich in certain iron minerals, include Lecidea silacea, Tremolecia atrata and Acarospora sinopica.

3.2.3.b Zone 1

This characteristically grey zone (Plate 1) of approximately 2x10m in extent, dipping 22-42° ESE. is characterized by 26 species. Virtually all the species occurring in the previous zone (see above) are also found here. However, Lecidea silacea is absent and Acarospora sinopica is very rare. Lecanora subaurea, also common to Zone 0 was not found in this zone.

The most frequent species present include Aspicilia cinerea, A. complanata, Huilia tuberculosa, H. cf. musiva, Ionaspis cyanocarpa, I. epulotica, Lecanora badia, L. polytropa, Lecidea lithophila, L. vorticosa, Lepraria neglecta, Rhizocarpon hochstetteri and R. lavatum. This last named grows particularly well in this zone, reaching up to 30cm in diameter and frequently has a rusty coloration, similar to the same species in zone 0. Stereocaulon vesuvianum is abundant and S. evolutum and S. spathuliferum occur occasionally, particularly along cracks and fissures in the rock surface. Rhizocarpon geographicum also occurs occasionally, Cetraria commixta rarely.

A notable feature of this zone is the presence of numerous, more or less unoxidized, cubic crystals of iron pyrite (FeS_2), exposed on the rock surface. No lichens were recorded on these.

3.2.3.c Zone 2

Nineteen lichen species were recorded from this narrow band c. 45cmx10m, dipping c. 24° ESE. The surface is characteristically

ferruginous (Plate 1) and the lichen cover rarely exceeds 50%. The dominant lichen species are rust-coloured and include Acarospora sinopica, Lecidea silacea, Tremolecia atrata and ochraceous states of Lecidea lapicida and Huilia cf. melinodes (stictic acid). Non-ferruginous species, Rhizocarpon hochstetteri and Sporastatia polyspora are frequent whilst Aspicilia subsorediza, Lecidea griseoatra, Rhizocarpon geographicum and Stereocaulon vesuvianum are occasional and usually poorly developed.

3.2.3.d Zone 3

A striking assemblage of large, yellow-green Rhizocarpon species, including both R. geographicum and R. alpicola is particularly noteworthy in this zone (Plate 2B), which is c. 1mx10m in extent, dipping 14-40° ESE. Other abundant lichens include Aspicilia sp. (norstictic acid), Huilia cf. macrocarpa (ochraceous), H. cf. musiva, H. tuberculosa, Lecanora polytropa, Lecidea griseoatra, Sporastatia polyspora and Umbilicaria polyphylla. Small thalli, c. 2 cm diameter of rust-coloured Tremolecia atrata were occasionally observed, however, Acarospora sinopica is rare. This zone is largely colonized by lichens which account for more than 80% of the cover.

3.2.3.e Zone 4

A characteristically ferruginous surface of c. 2x10m in extent, dipping 12-16° . The ferruginous Acarospora sinopica, Huilia cf. melinodes (stictic acid),Lecidea silacea and Tremolecia atrata are widespread, as are the non-rust-coloured Lecanora sub-

aurea and Lecidea umbonella. Lecidea vorticosa, Rhizocarpon hochstetteri and Sporastatia polyspora are frequent.

3.2.3.f Zone 5

This zone was found to be the most diverse in lichen species, with approximately 50% of all the lichens recorded from the entire site occurring in this predominantly grey zone (Plate 2A) of c. 3x10m, dipping 15-18° ESE. A particular feature of this zone is the development of extensive mosaics of a range of lichens, mainly belonging to the genera Aspicilia, Huilia and Lecidea. Species reaching maximum size and abundance in this zone include Aspicilia alpina, A. cinerea, Huilia panaeola, H. tuberculosa, Lecanora badia, Lecidea confluens, L. lactea, Lecidella stigmatea and Rhizocarpon badioatrum. This latter species here is particularly vigorous, forming patches frequently 30cm in diameter in moist hollows in the rock where it often assumes a characteristic blue-grey tinge.Lecidea lithophila also abundant, forms large colonies, particularly where it is affected by run-off from soil and then often shows a ferruginous coloration. Lecanora polytropa, Lecidea griseoatra, L. lapicida and L. swartzioidea are also frequent, the last mentioned species is confined to this zone. Caloplaca magni-filii and Lecidea paupercula are rare and also restricted to this zone. Caloplaca magni-filii was observed to parasitize Aspicilia cinerea. Another parasitic species, Lecidea umbonella was found to be parasitic upon both Lecidea lactea and Huilia tuberculosa. Well developed thalli of Huilia flavocaerulescens, including both sorediate and fertile material occur immediately beneath the contact with the upper ferruginous zone 6.

3.2.3.g Zone 6

The uppermost zone of the outcrop is characterized by an extensive ferruginous surface c. 5x10m in extent (Plate 1B). This is horizontal to inclined, with a dip of 12° ESE. Acarospora sinopica, Tremolecia atrata, Lecidea silacea and an unidentified, sterile species of Porocyphus are characteristic of the most intensely ferruginous surfaces, where the lichen cover may often be less than 50%. Extensive oxidation of pyrrhotite has led to pitting of the surface. In these hollows water may collect. These are typically surrounded by Huilia cf. melinodes (stictic acid). The most elevated areas of the rocks are more species rich and here the lichen cover can be 100%. There is little evidence of nutrient enrichment. Several ferruginous lichens are present including ochraceous states of Huilia cf. macrocarpa, Lecidea lapicida, L. lithophila and L. lactea. Additional species present include Rhizocarpon jemtlandicum, Aspicilia subsorediza, Huilia panaeola (occasionally rust-coloured), H. tuberculosa, Lecidea griseoatra, L. vorticosa and Rhizocarpon geographicum. Stereocaulon vesuvianum is locally abundant, though absent from the more intensely ferruginous surfaces, whereas Pseudephebe pubescens, Stereocaulon dactylophyllum, Umbilicaria cylindrica and U. hyperborea are less frequent in similar situations and usually poorly developed.

3.2.4 Analysis of lichen distributions

Some 60 lichen species were recorded from this single outcrop (Table 2). The lichens are not randomly distributed throughout the

zones, but 3 distinctive lichen communities are recognizable. These coincide with the three distinctive colour zones. Each community contains a number of similarly coloured species, of a predominantly either rusty, yellow-green or grey nature, which give rise, in part, to the general colours of these zones.

Perhaps the most striking of these zones are the ferruginous zones 0,2,4 and 6 which share similar lichens; these are either very rare or absent in the other zones. Here the characteristic lichens belong to the 'heavy metal association' Acarosporetum sinopicae Wirth ex James et al. 1977 i.e. the ferruginous Acarospora sinopica, Lecidea silacea, Tremolecia atrata and non-rusty Lecanora subaurea. Another ferruginous species, Lecidea atrofulva, which is considered by Creveld (1981)to be characteristic of the alliance Acarosporion sinopicae in Scandinavia, is occasionally present in zone 6. Ochraceous states of lichens are also frequent in the ferruginous zones e.g. Huilia cf. macrocarpa, H. panaeola, H.tuberculosa, Lecidea lactea, L. lapicida, L. lithophila and Rhizocarpon lavatum. However, not all ferruginous lichens are restricted to these four rusty zones. For instance, Huilia flavocaerulescens is frequent in the grey zone 5, an ochraceous state of H. macrocarpa (TLC: contains stictic acid restricted to grey, non-rusty areas of thallus) occurs in the yellow-green zone 3 and ochraceous Rhizocarpon lavatum is conspicuous in the central part of the grey zone 1, but immediately beneath the ferruginous zone 2 (Plate 1).

The second community, restricted to zone 3, is dominated by the yellow-green lichen species Rhizocarpon geographicum and R.

alpicola. Aspicilia sp. (norstictic acid), Lecidea griseoatra and Sporastatia polyspora are best developed in this community. Lecidea nigroleprosa and Umbilicaria polyphylla are only present in this zone. The third and final community recognized occurring on the outcrop corresponds to the grey zone 5. This community is typified by predominantly grey lichens, including Aspicilia cinerea, Huilia cf. contraponenda, H. cf. musiva, Lecanora badia, Lecidea confluens, L. lithophila, Lepraria neglecta, Rhizocarpon badioatrum and Stereocaulon evolutum.

Thus, on the basis of the similarity of the lichen communities, it appears that zones 0, 2, 4, and 6 are similar in some manner, but unlike zone 3, which in its turn differs from zones 1 and 5. Because of the proximity of the lichen communities and the absence of major environmental differences, the obvious inference is that the zones supporting similar lichen communities represent similarities in lithology not shared by those zones in which distinctly different communities grow. However, since the rock outcrop is not a flat surface but, in places steeply inclined, the environmental factors operating at the uppermost surface of the outcrop, will differ from those influencing the base of the outcrop. Obvious factors include a greater degree of shelter and moisture at the bottom of the outcrop as well as a longer duration of snow lie in this position. Such features could explain the fairly extensive development of Rhizocarpon lavatum, Ionaspis epulotica and I. cyanocarpa in the lowermost zones; these are species known to prefer moist situations and related species are often found in streams. Conversely, the upper surface of the boulder is more exposed and in places Umbilicaria spp. occur which elsewhere

only occur in similar situations in zone 3. Other factors which will influence the growth of the lichens on these surfaces include the variable surface relief and also run-off from small, soil-filled areas. Huilia cf. melinodes (stictic acid) shows a strong preference for growing at the margins of small, often water-filled cavities, in particular in ferruginous zone 6, though it occurs in similarly moist situations in zones 2 and 4. Lecidea lithophila is best developed in the grey zone 5 where it receives run-off from the soil. Small fissures on the rock surface in zone 1 are colonized by Stereocaulon vesuvianum, S. spathuliferum and S. evolutum. These species occur only infrequently elsewhere.

Only 3 lichen species are common to all 7 zones, notably Aspicilia subsorediza, Rhizocarpon geographicum and R. hochstetteri. However, Rhizocarpon geographicum was most conspicuous and best developed in zone 3. Likewise, Tremolecia atrata although widely distributed on the outcrop, is particularly abundant in the ferruginous zones. Several species of Huilia occur on the outcrop and have been identified, largely on the basis of their chemistry according to Hertel & Knoph (1984). It seems unlikely that the ochraceous states in the H. macrocarpa complex are variants of the 'normal' grey species occurring at this site. However, since there is a possibility that the lichen chemistry as revealed by TLC may be masked through possible complexing with metal cations, (Purvis et al. 1985, see appendix) this possibility cannot be ignored and a more thorough investigation of these taxa is desirable. In this respect, it is interesting to note that TLC failed to demonstrate stictic acid in the conspicuous ochraceous Huilia cf. macrocarpa, apparently restricted to zone 3, however small areas lacking this

coloration were shown to possess this acid.

In conclusion, the distribution of any one species occurring on the outcrop is unlikely to provide any information on the possible similarity of rock types. Clearly information regarding both the identity and frequency of occurrence of associated species is required before such comparisons can be made. Furthermore, since the total area of each zone is different, it is not possible to assess the similarity of the rocks on the basis of the total number of species recorded in each zone.

3.2.5. Chemical analyses of rocks and mineralogical compositions

The bulk composition of the rock in terms of the major oxides and copper was determined using plasma emission spectrophotometry (sections 2.5.1 and 2.5.2) on a single sample from each of the seven zones. The results obtained (Table 4) show considerable variation between zones. However, a petrological investigation of the constituent mineralogies of the rocks (Table 3) suggests the reason for this variation and allows reasonable conclusions to be drawn regarding the mineral sites in which the principal elements are located.

The original igneous mineralogy of these volcanic rocks has been reduced by deformation and metamorphism to an assemblage characteristic of the greenschist facies. Original ferromagnesian minerals, such as clinopyroxene (e.g. augite) form chlorite, and plagioclase feldspar breaks down to form albite, calcite and epidote. Albite is an ubiquitous mineral in all lithologies

Table 3. Petrography of rock samples from Litlfjellet site

Rock Number	Zone	Mineralogy
WPCS482	6	Albite, chlorite groundmass with occasional stilpnomelane, epidote, sphene and goethite seams. 2-3% by volume sulphides. Pyrrhotite dominant (grossly altered) with occasional pyrite and chalcopyrite.
WPCS382	5	Chlorite, albite groundmass with epidote and sphene. 10-15% by volume sulphides. Dominant sulphide pyrite remaining unaltered. Also some chalcopyrite, pyrrhotite rare.
WP3483N	4	Chlorite, albite groundmass with epidote and goethite. 2-3% by volume sulphides. Pyrrhotite dominant (grossly altered) with occasional pyrite and chalcopyrite.
WPCS282	3	Quartz, albite groundmass with epidote, chlorite rare, sulphides very rare.
WPCS182	2	Chlorite, albite groundmass with epidote, some sphene and goethite seams present. 1-2% by volume sulphides. Pyrrhotite dominant (grossly altered) with some pyrite. Chalcopyrite rare.
WP3383N	1	Chlorite, albite groundmass with abundant epidote. Pyrite occasional.
WP3283N	0	Quartz, albite groundmass with stilpnomelane and epidote. Chlorite and sulphides rare.

Table 4. Chemical composition of rock samples from Litlfjellet site

Rock No.	%wt loss at 950°C 24hrs	Zone	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cu	Totals
WPCS482	6.2	6	51.55	1.16	15.69	21.13	0.47	4.51	1.69	3.83	0	0.13	0.133	100.32
WPCS382	3.8	5	51.55	1.01	16.1	16.03	0.57	4.51	4.78	2.49	0	0.14	0.037	97.25
WP3483N	5.6	4	53.8	0.88	15.09	19.77	0.38	4.51	2.98	2.86	0	0.068	0.074	100.45
WPCS282	1.6	3	69.49	0.32	12.68	6.88	0.066	1.79	4.78	3.25	0	0.058	0.05	99.39
WPCS182	4.0	2	56.04	0.845	15.29	16.03	0.39	3.98	3.28	3.55	0	0.071	0.05	99.56
WP3383N	3.0	1	53.8	0.88	15.29	14.08	0.47	3.82	5.53	2.82	0	0.094	0.043	96.9
WP3283N	1.7	0	73.97	0.14	12.07	4.49	<0.11	0.195	1.42	6.19	0	0.037	0.053	98.61

examined at Litlfjellet and quartz occurs in the Acid range of rock composition. The formulae of these minerals and accessory minerals identified at the Litlfjellet site are given below:

Silicates

Quartz	SiO_2
Albite	$NaAlSi_3O_8$
Epidote	$Ca_2(Al,Fe)_3(SiO_4)_3(OH)$
Stilpnomelane	$(K,Ca)(Fe,Al)_{7-8}Si_8O_{23-24}(OH)_4{}^{2-4}H_2O$
Chlorite	$(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$

Sulphides

Pyrite	FeS_2
Pyrrhotite	$Fe_{1-X}S$
Chalcopyrite	$CuFeS_2$
Covelline	CuS

Oxides

Goethite	FeO.OH
Limonite	$Fe(OH_3)$

Variation in SiO_2 content is due largely to the original variability in composition of the igneous rocks, but also partly reflects hydrothermal and metamorphic remobilization of quartz. The main assemblage is one of basaltic to andesitic greenstones with SiO_2 contents averaging around 53%. Keratophyric rocks, probably metamorphosed rhyodacites with much higher SiO_2 contents of the

order of 70% are present in zones 0 and 3. This association of metamorphosed, basaltic rocks and Acid keratophyres is typical of the spilitized volcanic suites of the Palaeozoic greenstone terrains in the Scandinavian Caledonides. These compositional differences are fairly easily observable in the field. The Acidic rocks are much harder than the Basic rocks and have a brighter, more resonant sound when hammered. Zones 0 and 3 are substantially less ferromagnesian in composition than the other zones.

A decrease in the percentages of MgO and to a lesser extent Al_2O_3 in zones 0 and 3 is reflected in their lower chlorite contents. TiO_2 values are also lower in these zones on account of smaller amounts of sphene. The iron contents of the 7 rocks are variable, this is largely due to variation in the abundance of the iron sulphides present. The highest values, 16.03 - 21.13 wt.% Fe are restricted to the ferruginous zones 2, 4 and 6. In these zones, a capping of the hydrated iron oxide, goethite has formed on the surface of the rock, which is of basaltic composition and contains disseminated pyrrhotite. Pyrrhotite is readily oxidized by surface waters, leading to formation of sulphuric acid and goethite. The oxidation of sulphide is aided by microbial processes and is discussed in section 1.2.3.a. Lower values of c. 15% Fe_2O_3 were recorded in the grey zones 1 and 5 which lack a goethite capping, but do however, contain pyrite which in this environment is evidently more resistant to weathering than pyrrhotite (Table 3). The lowest Fe_2O_3 values of 6.88% (Zone 3) and 4.49% (Zone 0) reflect the almost complete absence of iron sulphide minerals. However, some slight iron staining of the rock surface was noted in the field in Zone 0. Significant quantities of copper, ranging from

370 $\mu g\ g^{-1}$ in the grey Zone 5 to 1530 $\mu g\ g^{-1}$ in the rusty Zone 6 were recorded. Copper is visible mainly as chalcopyrite, with some alteration to covelline seen by reflected polarized light in polished section (Table 3). It is to be expected that the abundance of pyrrhotite here will create a chemically favourable environment for the oxidation of other sulphides (section 1.2.3.a).

3.2.6. Comparison between lichenological and mineralogical data

Three distinct lichen communities have been observed on the outcrop. The first of these, the Acarosporetum sinopicae Wirth ex James et al. 1977 (section 1.1.4.c) occurs in Zones 0, 2, 4 and 6. The last three of these zones are capped by hydrated iron oxides, have high contents of iron (ranging from 16-21 wt%) and contain the iron sulphide pyrrhotite. These zones have additionally low SiO_2 contents and are Basic or Intermediate in terms of their rock chemistry. In contrast, the lowermost zone 0, whilst supporting a similar lichen flora, is Acidic with 73% SiO_2 and the lowest Fe_2O_3 content of 4.49% was found in this part of the outcrop. These observations demonstrate the need for extreme caution in interpreting chemical data in such studies and emphasize the importance of both a knowledge of the rock mineralogy and of careful observation in the field. Zone 0 was apparently subject to run-off from the pyrrhotite-rich bands as shown by the rusty coating on its surface. Evidently, the factors responsible for the development of the Acarosporetum sinopicae on this outcrop are availability of iron (pyrrhotite) and a low pH caused by oxidation of this pyrrhotite. These findings are essentially in agreement with those of Wirth (1972), though in this instance, iron pyrite

abundant in the grey zones 1 and 5, is apparently not significantly decomposed by weathering and consequently the Acarosporetum sinopicae does not occur here as it did in the example quoted by Wirth (1972) (section 1.1.4.c). The decomposition of pyrite during weathering is evidently affected by a number of compositional and environmental factors.

Although significant concentrations of copper were found in these oxide-rich zones, reaching a maximum of 1330$\mu g\ g^{-1}$ Cu in zone 6, there was no evidence to suggest that this element was producing an effect on the lichen community, similar to that described at other sites (Chapter 4). Moreover, the presence of the secondary mineral covelline, suggested that copper was being made available during weathering, but the mobility depends upon the pH of the leaching surface water. This aspect is considered further in section 4.5.

The second community, consisting of essentially grey lichens belonging to the genera Aspicilia, Huilia, Lecidea and Rhizocarpon is restricted to the Basic to Intermediate rocks in zones 1 and 5 which lack pyrrhotite, but contain pyrite. Otherwise, both mineralogically and chemically these zones are very similar to zones 2, 4 and 6. The lichen communities, however, are strikingly different, both in terms of species and coloration. The final community occurring in zone 3 is characterized by conspicuous yellow - green species of Rhizocarpon. Zone 3 is highly Acidic (69% SiO_2) and lacks obvious sulphide mineralization. The typical species Rhizocarpon geographicum and R.alpicola are known to prefer exposed, quartz-rich rocks (Wirth 1972). In zone 0, which is also

Acidic in character, the presence of iron and the sheltered, moist situation allowed the formation of the Acarosporetum sinopicae.

3.2.7. Summary

Three distinct lichen communities occur on the Litlfjellet outcrop, each of which has its own characteristic coloration. The colour of these zones is partly due to the intrinsic coloration of the associated lichen floras and partly due to the crust of the iron-rich rocks, to surface iron oxidation and incorporation of iron into the lichen thallus. Since similar colour zones possess a similar rock mineralogy, the lichen communities can serve as indicators of these mineralogical environments on the outcrop. It is suggested that the presence of weathering sulphides (pyrrhotite) and the silica content of the rock are important factors in the development of these lichen communities. Whilst significant quantities of copper occur in the outcrop, this element did not have any observable effect on the species morphology, colour or composition of the lichen communities.

3.3. Annlifjellet site

3.3.1. Site description

The site is located c. 4km WNW. of Gjersvika ($13^{o}25'$E., $64^{o}53'$N.), in Nord Trøndelag, Norway, Map NGO 1:50000, sheet number 1924 IV Røyrvik, UTM 216946, altitude 610m.

The site was first visited on 11 August 1982 and subsequently studied 17 August 1982 and 31 July 1983. It is a large boulder,

consisting of a laminated, quartz-magnetite rock c. 10m x 3m in extent, running east-west (Plate 3A). The north side of the boulder is level with the soil surface, so there is a local effect of run-off. In contrast, the southern side falls steeply to the ground, some 3m below. The Norwegian term for this particular rock type is 'blå kwarts' because of the presence of finely disseminated magnetite (Fe_3O_4) in a matrix of quartz, occurring occasionally as veins, which gives this rock a bluish appearance. On account of the high content of magnetite, a compass is strongly deflected near this rock. Traces of magnetite can be seen in the photograph shown in Plate 3B.

3.3.2. Local vegetation

Vegetation typical of base-poor, acidic soils in vidda terrain is present in the immediate vicinity of the boulder. Species present are Betula nana, Empetrum hermaphroditum, Vaccinium uliginosum, Loiseleuria procumbens, Arctous alpina and Rhacomitrium lanuginosum. The macrolichens Nephroma arcticum and Cetraria delisei are abundant.

3.3.3. Lichen vegetation of boulder

The lichen community occurring at this site consists of both crustose and foliose lichens. The crustose lichens Rhizocarpon geographicum and Schaereria tenebrosa are conspicuous, giving rise to yellow-green and grey-black patches respectively. A range of macrolichens belonging to the genera Parmelia, Hypogymnia and, in addition, Allantoparmelia alpicola are also frequent. On the

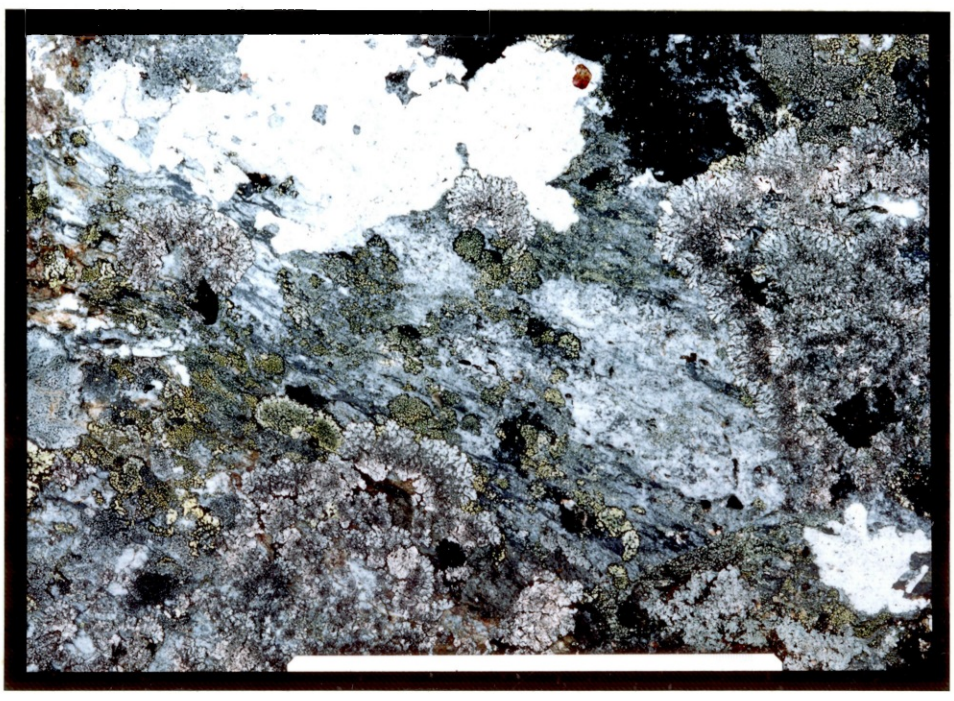
PLATE 3.

A. General view of outcrop studied on Annlifjellet. Note the lack of ferruginous lichens.

B. Close-up of lichens occurring on Annlifjellet outcrop. The most conspicuous species present on the photograph are the grey, foliose Hypogymnia intestiniformis and the chalk-white, crustose Aspicilia myrini which is seen here to react K+ red. Scale = 17cm.



A



B

Table 5. Lichens recorded from Annlifjellet site

Acarospora peliscypha
Allantoparmelia alpicola
Amygdalaria pelobotryon
Aspicilia myrini
Bryoria bicolor
Caloplaca holocarpa
Candelariella vitellina
Cetraria hepatizon
islandica
nivalis
Cladonia chlorophaea
Coeolocaulon aculeatum
Dermatocarpon luridum
Euopsis granatina
Haematomma ventosum
Huilia crustulata
macrocarpa
tuberculosa
Hypogymnia atrofusca
intestiniformis
oroarctica
Lecanora badia
intricata
polytropa
Massalongia carnosa
Microglaena corrosa
Ochrolechia androgyna
frigida
Parmelia centrifuga
incurva
omphalodes
saxatilis
stygia
sulcata
Phaeophyscia orbicularis
Physcia caesia
dubia
wainioi
Pseudephebe pubescens
Rhizocarpon copelandii
geographicum
grande
subgeminatum
Rinodina cacuminum
Schaereria tenebrosa
Sphaerophorus fragilis
globosus
Stereocaulon vesuvianum
Tremelocia atrata
Umbilicaria decussata
deusta
hyperborea
polyphylla
proboscidea
Xanthoria candelaria

boulder surface, Rinodina cacuminum and Xanthoria candelaria are common in areas under the influence of bird-droppings. Umbilicaria species are well-developed, particularly in areas subject to leaching from soil.

A list of the lichen species recorded from this site is given in Table 5. In addition, a general view of the site and close-up of a component of the lichen community is shown in Plate 3.

3.3.4. Discussion

The lichen community occurring on this boulder has a high proportion of macrolichens, including Hypogymnia intestiniformis which is abundant. This is in contrast with the lichen communities on the ferruginous zones at the Litlfjellet site (section 3.0) where iron sulphides are abundant and macrolichens are rare. It appears that the lichens of the Annlifjellet site share affinities with the community Ochrolechio-Hypogymnietum intestiniformis, typical of boulders in sheltered situations, described by Creveld (1981).

Although the rock contains high contents of iron, the lichens are not typically rusty in coloration, as in several species occurring on the Litlfjellet outcrop. Magnetite is resistant to weathering, unlike the iron sulphides, and thus iron is not readily available to the lichens for uptake. Moreover, it is unlikely that magnetite is having any significant effect on the composition of the lichen communities. At this site iron is not readily released by oxidation, since sulphur is absent and the pH

of the surface waters is not affected by oxidation of the sulphide to sulphate, as in sulphide-rich environments.

CHAPTER 4. THE INFLUENCE OF COPPER SULPHIDE MINERALIZATION ON LICHEN COMMUNITIES

4.1. Introduction

The sites at Gjersvik (section 4.2), Røros (section 4.6) and Ramundberget (section 4.4) in central Scandinavia contain significant concentrations of copper, in the form of chalcopyrite. These and sites in the vicinity of Coniston Copper Mines in Britain (section 4.3), provided an opportunity to study the effect of copper on the composition of lichen communities. The metal contents of selected species were also subsequently investigated, the results of which are given in chapter 6.

4.2. Gjersvik locality

4.2.1. Locality description

The sites are located at Gjersvika ($13^{o}25'$E., $64^{o}53'$N.), Nord Trøndelag, Norway, map NGO 1:50,000, sheet number 1924 IV Røyrvik, UTM:VM 254937, altitude c. 450m.

This is an area of old mine workings and outcrops situated on a south-facing slope. The mine was worked during the early years of this century, from 1909 on a small scale , but has been abandoned since the 1950's. The sites studied lie on an extensive area of glaciated outcrops and also include boulders, areas of contaminated soil and spoil heaps. The outcrops occurring in the vicinity of the

PLATE 4.

A. The 'kisplant' or ore-flower, Viscaria (=Lychnis) alpina at Gjersvik with outcrops studied in the distance, 24 July 1983.

B. Stratiform sulphide ore body outcropping near surface at Gjersvik, showing an extensive range of metalliferous habitats available for colonization by lichens, 15 August 1982.



A



B

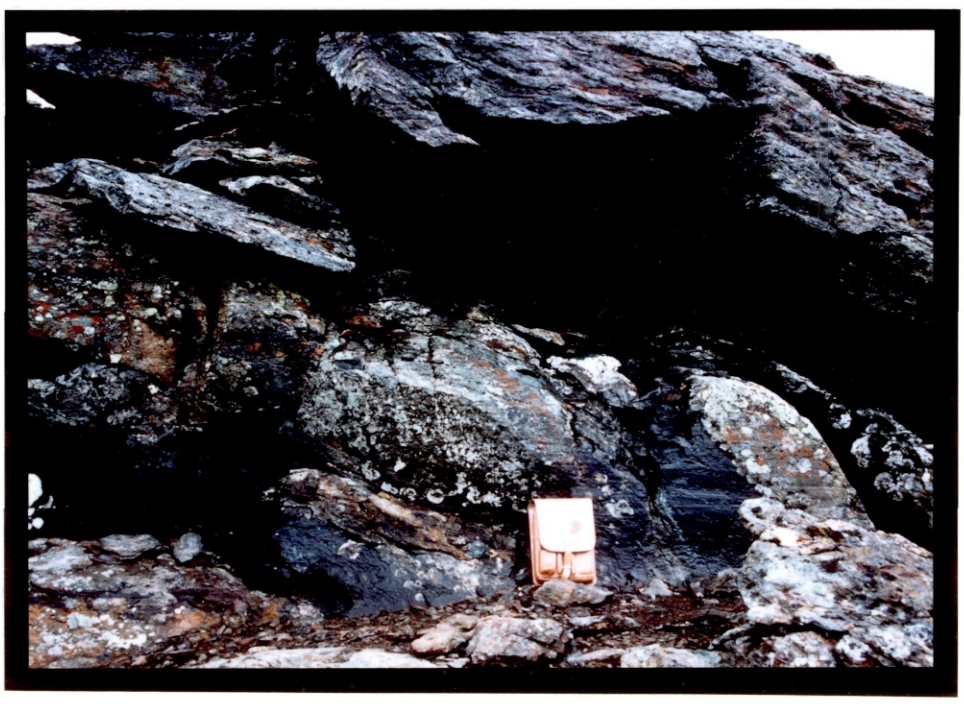
PLATE 5.

A. Gjersvik site 1, ± vertical, W.-facing, dry rock surface. A close-up of the community dominated by the Cu-rich ecotype of Aspicilia alpina, occurring to the left of the field note case (22 x 16 cm) is illustrated in Plate 7B.

B. Gjersvik site 6, S.-facing, moist rock surface. The dominant grey lichen, including the chalk-white specimen towards the bottom left of the photograph, is Aspicilia mashiginensis. Several blue-green stains of secondary copper compounds are evident. Scale : field note case, 22 x 16 cm.



A



B

Table 6. Lichens occurring at selected sites at Gjersvik

	A	B	C	D	E	F
Acarospora chlorophana	–	f	–	–	–	–
molybdina	o	–	–	–	–	–
rugulosa	–	–	o	–	r	–
sinopica	la	la	la	la	la	–
smaragdula	l	f	–	–	l	–
Aspicilia alpina	a	–	r	–	o	–
cinerea	–	–	–	–	o	–
cinereorufescens	–	–	r	–	o	–
complanata	–	–	–	r	–	–
diamarta	–	–	–	la	–	–
mashiginensis	o	la	la	–	o	–
simoensis	o	–	o	–	o	–
subsorediza	r	–	–	–	la	–
Baeomyces roseus	–	–	–	–	–	f
Caloplaca nivalis	o	–	–	–	–	–
Cetraria commixta	o	–	–	–	f	–
hepatizon	o	–	–	–	o	–
Cladonia arbuscula	–	–	–	–	–	a
bellidiflora	–	–	–	–	–	a
chlorophaea	–	–	–	–	–	a
deformis	–	–	–	–	–	f
furcata	–	–	–	–	–	a
luteoalba	–	–	–	–	–	o
macrophylla	–	–	–	–	–	r
pleurota	–	–	–	–	–	f
uncialis	–	–	–	–	–	a
Diploschistes scruposus	–	–	–	–	f	–
Huilia contraponenda	–	–	–	–	o	–
flavocaerulescens	r	–	–	–	f	–
macrocarpa	–	–	–	–	f	–
melinodes	–	r	–	–	o	–
musiva	–	–	–	–	o	
panaeola	–	–	–	–	f	–
tuberculosa	f	o	f	–	a	–
Ionaspis cyanocarpa	–	–	–	–	o	–
epulotica	f	–	–	–	f	–
Lecanora badia	o	f	–	–	f	–
frustulosa	r	–	–	–	–	–
intricata	–	–	–	–	f	–
leptacina	o	–	–	–	f	–
polytropa	f	f	o	f	f	–
subaurea	–	–	–	–	l	–
Lecidea aglaea	–	–	–	–	a	–
arctogena	–	o	r	–	a	–
armeniaca	o	–	–	–	–	–
atrofulva	a	f	l	l	l	–
caesioatra	o	o	–	–	–	–
commaculans	–	–	–	–	la	–
confluens	–	–	–	–	a	–
fuscocinerea	–	–	–	–	a	–
griseoatra	f	–	–	o	o	–
impavida	–	–	–	–	f	–
ivalensis	–	–	–	–	r	–
lactea	f	f	o	–	f	–
lapicida	f	–	–	–	f	–
leucothallina	–	la	–	–	–	–
limosa	–	–	–	–	–	a
lithophila	–	–	–	o	f	–
lulensis	f	f	–	–	–	–
nigroleprosa	–	–	–	–	f	–
paupercula	f	o	–	–	f	–
pycnocarpa	o	r	–	f	o	–
silacea	la	–	–	la	la	–
swartzioidea	r	–	–	–	–	–
umbonella	a	–	–	a	f	–
vorticosa	–	–	–	–	o	–

Table 6 continued:

	A	B	C	D	E	F
Lecidella bullata	a	a	-	-	o	-
stigmatea	-	-	-	-	f	-
Lepraria neglecta	f	-	-	-	-	-
Ochrolechia frigida	-	-	-	-	-	f
geminipara	-	-	-	-	-	f
Pertusaria oculata	-	-	-	-	-	f
Porocyphus coccodes	o	-	-	a	-	-
Pseudephebe pubescens	-	-	-	-	f	-
Psora demissa	-	-	-	-	-	a
Pyrenopsis granatina	o	-	-	-	-	-
pulvinata	o	-	-	-	-	-
Rhizocarpon alpicola	-	-	-	-	a	-
badioatrum	-	-	-	-	a	-
birgittae	la	-	-	-	-	-
eupetraeoides	-	-	-	r	-	-
ferax	r	-	-	-	-	-
geographicum	r	-	o	-	a	-
hochstetteri	-	-	-	-	a	-
inarense	r	-	-	-	-	-
intermediellum	r	-	-	-	-	-
jemtlandicum	-	-	-	-	a	-
lavatum	-	-	o	-	f	-
obscuratum	f	-	o	-	-	-
oederi	-	-	-	la	la	-
vainioense	-	-	-	f	a	-
viridiatrum	r	-	-	-	-	-
Sporastatia polyspora	a	-	-	-	-	-
testudinea	r	-	-	-	-	-
Stereocaulon condensatum	-	-	-	-	-	o
dactylophyllum	-	-	-	-	-	f
evolutum	-	-	-	-	-	f
leucophaeopsis	o	o	-	-	l	-
nanodes	-	-	-	o	-	-
paschale	-	-	-	-	-	o
rivulorum	-	-	-	-	-	a
saxatile	-	-	-	-	-	f
tornensis	-	-	-	a	-	-
vesuvianum	-	-	-	-	-	a
Tremolecia atrata	la	f	r	-	la	-
Umbilicaria cylindrica	-	-	-	-	f	-
decussata	o	-	-	-	o	-
hyperborea	o	-	-	-	f	-
polyphylla	-	-	-	-	f	-
torrefacta	f	f	-	-	f	-

Legend

A - Steeply inclined, dry rock surfaces.
B - Underhangs.
C - Steeply inclined, moist rock surfaces.
D - Small stones.
E - Flat to slightly inclined surfaces.
F - Terricolous communities.

a - abundant

la - locally abundant

f - frequent

o - occasional

r - rare

vr - very rare

mine entrance and exposures of the stratabound ore body itself (Plate 4B) are open and well-illuminated.

The site was first visited on 15 August 1982 and subsequently some 18 days were spent carrying out a detailed survey during the period 29 July 1983 to 22 August 1983. The climate of this region is typified by a high rainfall, ranging from 1500-2000mm per annum. Because of the difficulties caused by bad weather, the study could by no means be considered exhaustive. In particular, it is possible that some small lichens may have been overlooked. The generally wet surface conditions, however, enabled the pH of the water on the rock surface to be readily measured.

4.2.2. Local vegetation

There are few trees present at the mine site; however, stunted Betula pubescens, Juniperus communis and Sorbus aucuparia are present. Several vascular plants occur in the vicinity of the rock outcrops, the flora being dominated by members of the ericaceae indicating the rather base-poor nature of the soil, including Arctous alpina, Calluna vulgaris, Deschampsia caespitosa, D. flexuosa, Empetrum hermaphroditum, Festuca ovina, Hieracium scandicum, Juncus trifidus, Melampyrum pratense, Molinea caerulea, Solidago virgaurea, Vaccinium myrtillus, V.uliginosum, V. vitis-idaea, Viola palustris and Viscaria (=Lychnis) alpina. A large number of terricolous lichens occur on the less metal-contaminated surfaces, frequently associated with the moss Rhacomitrium lanuginosum. These species include Baeomyces roseus, Cladonia amaurocraea, C. bellidiflora, C. carneola, C. chlorophaea, C. coccifera,

C. cornuta, C. crispata, C. deformis, C. luteoalba, C. macrophylla, C. squamosa, C. uncialis, Lecanora leptacina, Lepraria neglecta, Ochrolechia androgyna, Omphalina luteovitellina, Stereocaulon condensatum, S. dactylophyllum, S. evolutum, S. nanodes, S. paschale, S. rivulorum, S. saxatile and S. vesuvianum.

4.2.3. Lichen flora of selected sites

4.2.3.a Steep, well-illuminated rock surfaces

Site 1

At this site, a good example of a lichen community occurs which is occasional at Gjersvik. A general view of this site and detailed close-up of the lichen community occurring at this site are shown in Plates 5A and 7B. A part of the rock face, 1m in height and 3m long was studied in detail. Its surface is relatively smooth, dipping 64° WNW. At the top of this rock face, a projecting ledge dipping 120° to 130° overhangs this site. A high percentage of cover by lichens is a feature of the site. Cover ranges from 75% beneath the projecting, overhanging rock at the top of the outcrop, to 100% in the central area. Here green, copper-rich Aspicilia alpina is dominant and conspicuous, up to 50cm across, but consisting of a mosaic of smaller thalli, ranging from 1cm to 10cm in diameter. There are relatively few lichens directly associated with A. alpina. These include Rhizocarpon birgittae, Lecidea paupercula and the copper-rich states of Lecidea lactea and Lecidea umbonella var alumnula; the last mentioned species is parasitic upon L. lactea. The copper-rich state of Aspicilia subsorediza and

of Lecidea swartzioidea (= L. lactea?) are rare. Other species occurring in this community include Huilia tuberculosa, Lecanora polytropa (occasionally with green, copper-rich apothecia) and Umbilicaria torrefacta. A number of rusty lichens were observed on the rock surface, mainly restricted to a region with an obvious goethite capping. Here Acarospora sinopica and Tremolecia atrata are abundant and Lecidea atrofulva and L.silacea occasional. In addition, one specimen of Lecidea lactea was observed to be of a partly green and rusty coloration. Sporastatia polyspora is frequent immediately beneath the overhanging portion, at the top of the outcrop. Close to the base of the outcrop, a green example of Aspicilia cf. simoënsis was noted. A fresh rock sample (No. WP1983N) was collected from this site. Additionally, pH measurements were made on several occasions and ranged from 4.5 to 5.5.

Site 2

Approximately 3-4m above site 1 and in direct continuity with it, a similar, though slightly more shaded habitat with a WNW. aspect and dipping 100-120^{o} was found. Aspicilia alpina and Lecidea lactea are not so well developed here as in the first site, but they have a typically green colour. Of particular note, however, is an extensive developement of Lecidella bullata, frequently bearing unusually green, pruinose discs. Another species present here with occasional greenish discocarps is Lecanora polytropa. Lichens frequent at this site include Lecidea atrofulva, L. caesioatra, L. griseoatra, Lepraria neglecta, Porocyphus coccodes, Pyrenopsis granatina, Rhizocarpon obscuratum and Sporastatia polyspora. Cetra-

ria hepatizon is poorly developed and Lecanora frustulosa, Lecidea armeniaca, Umbilicaria hyperborea and U. torrefacta occur occasionally. Caloplaca nivalis is also rarely present.

Site 3

A few metres below the first site, a similar rock face dipping 70°W. and approximately 4m x 4m in extent was studied. This site was, at that time, partially shaded by a single, small specimen of Betula pubescens some 1.5m distant. The surface of the outcrop is relatively smooth, though in places an extensive siliceous framework is evident on the surface and additional, occasional encrustations of secondary copper compounds were noted. Lecidea lactea is dominant on the rock surface, particularly on the central and upper portions of the rock face and is typically of a bright green-yellow coloration, though some normal grey L.lactea is also present. Associated species present include Acarospora smaragdula, Huilia melinodes, Ionaspis epulotica, Lecanora leptacina, Lecidea atrofulva, L. caesioatra, L. lulensis, L. pauperc-ula, L. pycnocarpa, Lecidella bullata, Tremolecia atrata, Umbilicaria hyperborea and U. torrefacta. Lecidella bullata with green, pruinose discs is frequent. In addition, the green, copper-rich state of Lecidea lulensis is common. At the base of the rock surface, Aspicilia mashiginensis is particularly abundant, some examples of this species are parasitized by Rhizocarpon viridiatrum. Several rock samples were collected from this site, including two specimens WP2383N and WP2483N in the vicinity of the green examples of Lecidea lactea. WP2583N was collected from close to where the white examples of Lecidea lactea occur and WP2683N was

collected from the lowermost regions, where Aspicilia mashiginensis is abundant.

Site 4

A further two east-facing boulders adjacent to one another, situated just below the outcropping ore body, were carefully examined. The boulders have strikingly contrasting lichen communities. The first is characteristically oxide-encrusted, dipping 40-50^{o} and supports a large number of ferruginous species, though approximately 15% of the rock is uncolonized by lichens. Here Tremolecia atrata and Lecidea atrofulva form continuous crusts up to 30cm in diameter. Other lichens found here include Acarospora sinopica, Huilia melinodes, Lecanora polytropa, Lecidea lapicida, L.silacea, Umbilicaria decussata and U.torrefacta. On the surface of this boulder, Lecidea arctogena, L.paupercula and Rhizocarpon geographicum are additionally present. In contrast, the neighbouring boulder does not support a large number of conspicuously ferruginous lichen species, nor is it goethite-capped. Acarospora sinopica and Lecidea silacea are absent. The lichen flora here is dominated by a mosaic of small thalli, (c. 2-3cm in diameter) of the green copper-rich states of Aspicilia subsorediza, Lecidea lactea and the non-green Rhizocarpon birgittae. Lesser amounts of Lecidea atrofulva, L. lactea, L. vorticosa, Rhizocarpon geographicum and Tremolecia atrata are present. Umbilicaria torrefacta is rare and poorly formed on this boulder (less than 0.5cm in diameter), in contrast to material occurring on the adjacent goethite-capped boulder.

4.2.3.b Underhangs

Site 5

Several underhangs occur at the mine site; a restricted species diversity and additionally a low lichen cover is a general feature of these. Perhaps the most striking of the underhangs occurs directly above site 2, just outside the field illustrated in Plate 5B, on the left hand side. The underhang itself has an average lichen cover of less than 50%. Here the striking, bright yellow Acarospora chlorophana is most conspicuous. Frequent associates include Lecidella bullata, Lecidea lulensis (occasionally the green, copper-rich state), Tremolecia atrata and a form of Lecanora badia reduced to scattered areoles. In a more or less horizontal position beneath the underhang, a number of additional lichens were recorded, including predominantly the green, copper-rich state of Lecidea lactea accounting for 30% of the lichen cover, Acarospora rugulosa, A. sinopica, Lecanora polytropa and Lecidea silacea. Other characteristic lichens present here include Umbilicaria torrefacta, Huilia tuberculosa and, more rarely, Toninia (=Stereocaulon) leucophaeopsis (see section 5.18).

At a second underhang dipping 130-140° SE., a similar flora was observed, though here Lecidea leucothallina is particularly abundant.

4.2.3.c Steeply inclined moist rock surfaces

Site 6

An illustration of one example of this habitat which was carefully studied is given (Plate 5B). The site is south-facing and appears to receive substantial run-off from above. Towards the bottom left-hand side of this site, a large, chalk-white, crustose lichen (c. 20 cm diam.) is shown. In view of its apparent unhealthy appearance and since secondary copper minerals were noted in its immediate vicinity, it was initially thought that this lichen was dead. However, a subsequent anatomical investigation of this material showed that this was not the case, and furthermore that the lichen is an unusually large example of Aspicilia mashiginensis. This specimen is dominant at this site, where it even occurs directly on secondary copper minerals as illustrated (Plate 10B). Measurement of the pH of the rock surface in the immediate environment of this species was made on several occasions and found to range from pH 4 - pH 5. Aspicilia mashiginensis occurs on both vertical surfaces and on moist, horizontal ledges, as can be seen (Plate 5B). Associated, less abundant species, include Acarospora rugulosa occasionally growing on atacamite [$Cu_2Cl(OH)_3$], Huilia tuberculosa, Lecidea lactea (occasionally copper-rich green ecotype) Rhizocarpon geographicum, R. obscuratum and Tremolecia atrata.

In the vicinity of this site there was some local influence of iron derived from seepage from pyrrhotite-rich bands. In one instance, extensive sheets of Acarospora sinopica were found with

no associates, where pH values of 2 were recorded.

4.2.3.d Small stones

Site 7

A critical survey of the lichen communities of pebbles, with relation to rock type and other ecological considerations, was not undertaken at this site. However, immediately above site 1, a number of lichens were recorded which are typical for this environment at the Gjersvik locality. These include the dominant Bilimbia (= Stereocaulon) tornensis apparently restricted to this habitat, Porocyphus coccodes and Lecidea umbonella. Other lichens noted include Rhizocarpon hochstetteri, R. vainioense, Lecidea griseoatra, L. lithophila and Lecidella bullata. The last-named was occasionally observed with green, pruinose, copper-rich apothecia.

Site 8

A number of ore samples rich in pyrite, with lesser quantities of pyrrhotite and chalcopyrite, were studied. Common species present include Acarospora sinopica, Aspicilia (= Bellemerea) diamarta, Huilia tuberculosa, Lecidea atrofulva, Lecidea silacea and Rhizocarpon oederi.

4.2.3.e Horizontal to slightly inclined surfaces

The greater part of the surface of the major rock outcrop studied is colonized by members of the genera Lecidea, Huilia,

Aspicilia, Lecanora, Rhizocarpon and Umbilicaria. Of particular importance are Lecidea aglaea, L. arctogena, L. confluens, L. fuscocinerea, L. impavida, L. nigroleprosa Rhizocarpon alpicola and R. vainioense which are most abundant on the uppermost rock surface and rare elsewhere. In one instance, a specimen of Lecidea arctogena was discovered which was unusually grey and yellow in patches. This specimen occurred on the top of the boulder above site 6. A single rock sample (WP 2983N) was collected from a situation where Lecidea paupercula and several species of Umbilicaria are abundant. Here neither rusty lichens nor those which had evidently been subjected to copper-containing run-off are present.

A number of similar sites, but with contrasting lichen floras, were chosen for more specific study of both the lichen communities and their substrata.

Site 9

A large, low-lying, south-facing boulder dipping c. 25-30° was examined. The boulder receives run-off from metal-contaminated soil and small spoil heaps of sulphide ore, situated directly above it. The surface of the boulder has a variable relief. A series of ridges and hollows are marked by the almost total lack of lichens in the hollows and 100% cover on the summits of the ridges. Tremolecia atrata is the dominant lichen on the goethite-capped areas, accounting for approximately 60% of the cover. The next most abundant lichen is Lecidea silacea with 30% cover. Other species

present here include Acarospora sinopica, Aspicilia cinereorufescens, Lecidea atrofulva, L. commaculans, L. fuscocinerea, L. paupercula, Lecanora polytropa, Rhizocarpon geographicum, R. oederi and Umbilicaria decussata. Locally, grey areas lacking a goethite-capping are present on usually elevated areas, but which have a characteristic "fringe" of ferruginous lichens, including typically Lecidea silacea, Acarospora sinopica and Tremolecia atrata, close to the hollows where lichens are absent. These grey areas are characterized by an undescribed species of Lecidea s.lat. Associated species present include Cetraria hepatizon, Huilia contraponenda, Lecidea lithophila, L. paupercula, L. pycnocarpa, Lecanora polytropa, Pseudephebe pubescens, Rhizocarpon geographicum and R. hochstetteri.

Measurements of pH were made in the hollows and also on the surrounding ridges. Extremely low values of pH 2 were recorded in the hollows receiving moisture from sulphide-rich, waste ore material above, whereas, in contrast, the much higher values of pH 5 were recorded on the ridges. A rock sample was collected from both the goethite-capped areas (WP2083N) and the grey zone (WP2183N).

Site 10

On the principal outcrop investigated, there is a small area of around $2m^2$ in extent in which Lecanora subaurea is abundant. The rock surface here is strongly pitted. Only a few lichens are directly associated with L. subaurea, notably Acarospora sinopica, Huilia tuberculosa, Lecidea atrofulva, L. silacea and Rhizocarpon

oederi. Other lichens present, though in poor condition, include species more widespread on the upper surface viz, Aspicilia cinerea, A. cinereorufescens, Huilia flavocaerulescens, H. panaeola, Lecidea fuscocinerea, L. ivalensis, L. lapicida, L. paupercula, L. pycnocarpa, L. umbonella, Rhizocarpon geographicum, R. lavatum, R. viridiatrum and Sporastatia polyspora. A rock sample was collected (WP3083N) and a pH measurement of 3 was obtained from water in contact with Acarospora sinopica.

Site 11

Immediately beneath site 6, at the foot of the large specimen of Aspicilila mashiginensis, a flat boulder occurs situated at the soil surface. The surface has a characteristically rough texture with prominent quartz veins up to 2cm thick. Here the rock has a lichen cover of approximately 60% and evidently receives copper-rich run-off from above. The dominant lichen is the green copper-rich ecotype of Aspicilia subsorediza. The moss Grimmia doniana is also abundant. Other lichens occurring here include Acarospora smaragdula (green, copper-rich ecotype), A.rugulosa, Aspicilia mashiginensis, Ionaspis cyanocarpa, Lecidea lactea (green, copper-rich ecotype) and Rhizocarpon lavatum. These lichens were also found in seepage tracks. In elevated situations, presumably not exposed to copper-rich solutions, a more urbane lichen flora occurs, including Lecanora polytropa, Lecidea lithophila, L.paupercula, Rhizocarpon geographicum and R.hochstetteri. A rock sample was collected (WP3183N) from where the green, copper-rich ecotype of Aspicilia subsorediza is particularly abundant.

4.2.4. Ecology of lichen communities

Several distinctive lichen communities occur at Gjersvik. The Acarosporetum sinopicae (section 1.1.4.c) is well represented here, occurring in a variety of habitats including flat surfaces, fragments of ore-material and steep, well-illuminated, dry surfaces. The most frequent species belonging to this association include Acarospora sinopica, Lecidea silacea, Tremolecia atrata and Lecidea atrofulva, whereas Aspicilia diamarta and Rhizocarpon oederi are less frequent. The underhangs are characterized by Acarospora chlorophana, a species restricted to this habitat and a characteristic taxon of the association Lecanora cavicolae-Acarosporetum chlorophane (Creveld 1981). Other species also frequent in this habitat include Lecidea lulensis and, locally Lecidea leucothallina. The lichen community of the uppermost surface of the major outcrop studied shares an affinity with the Rhizocarpetum alpicolae. Creveld (1981) describes the Scandinavian lichens of this community.

Of particular interest, however, are those communities which are dominated by green, copper-rich lichens. At Gjersvik, Aspicilia alpina and Lecidea lactea are the most abundant lichens which may accumulate copper under certain conditions. Other lichens which may also be copper-rich include Acarospora smaragdula, Aspicilia cf. simoensis, A. subsorediza, Lecidea arctogena, L. lulensis, L. swartzioidea (= L.lactea?), L. umbonella and the discocarps of Lecanora polytropa and Lecidella bullata. All these copper-rich lichens occur primarily on well-illuminated, moderately dry,

inclined surfaces, though they are also found on flat surfaces. Rarely, examples are found in moist situations and on small stones. Relatively few other lichens occur with the copper-rich lichens which are not also found elsewhere. However, Acarospora rugulosa, Aspicilia mashiginensis, Rhizocarpon birgittae and Stereocaulon leucophaeopsis are exceptions. Rhizocarpon birgittae is a common associate of the copper-rich states of Aspicilia alpina and Lecidea lactea in open situations. In contrast, Acarospora rugulosa is at Gjersvik more frequent in crevices, where it even occurs on atacamite and has been found to concentrate copper oxalate (Purvis 1984). Aspicilia mashiginensis is more or less restricted to moist, vertical and horizontal, sheltered situations at Gjersvik, where there is usually abundant evidence of copper mineralization, in the form of secondary deposits of copper. Occasionally the species was observed to occur directly on secondary copper minerals. Stereocaulon leucophaeopsis is occasional in crevices, underhangs and horizontal situations where it is associated with green, copper-rich examples of Acarospora smaragdula and Lecidea lactea.

4.2.5. Chemical analyses of rocks and mineralogical composition

The bulk composition of the rock, in terms of the major oxides and copper was determined using plasma emission spectrophotometry (sections 2.5.1, 2.5.2) on ten rock samples, collected from sites at Gjersvik. The results obtained are shown in Table 7. The silica content of the rock samples is high due to the presence of quartz stringers and veins, though the rocks were not originally Acidic in composition. These analyses are not representative of original rock composition, they are evidently due

Table 7. Chemical composition of rock samples collected at Gjersvik

Site	1	2	2	2	2	11	9	10	9	[Sect. 4.2.3.e]
Sample No.	WP1983N	WP2383N	WP2483N	WP2583N	WP2683N	WP3183N	WP2083N	WP3083N	WP2183N	WP2983N
SiO_2	71.73	78.45	73.97	73.97	69.49	73.97	65	58.28	73.96	76.22
TiO_2	0.026	<0.025	0.035	<0.025	0.072	<0.025	0.12	<0.025	0.12	0.05
Al_2O_3	8.25	6.44	8.05	7.02	8.05	7.04	8.46	7.44	6.64	6.64
Fe_2O_3	15.73	12.29	12.88	14.84	17.23	14.38	20.23	28.62	14.68	12.58
MnO	0.09	0.13	0.074	0.17	0.088	0.115	0.019	0.046	<0.11	0.054
MgO	2.99	2.05	2.37	2.27	2.46	2.19	2.99	2.48	2.56	2.05
CaO	0.39	0.58	0.066	0.25	<0.017	0.088	0.026	0.262	<0.17	<0.017
Na_2O	<0.017	0.15	0.472	0.38	0.059	0.018	<0.017	0.18	<0.17	0.029
K_2O	0	0	0	0	0	0	0	0	<0.034	0
P_2O_5	0.034	<0.023	<0.023	<0.023	<0.023	0.023	<0.023	0.43	<0.023	0.023
Cu	0.071	8.5	0.27	0.187	0.22	7.8	0.29	7.7	0.29	0.18
Total	99.36	108.67	98.24	99.17	97.7	105.68	97.2	105.49	98.35	97.87
% loss on ignition	2.83	2.54	2.45	3.18	3.9	3.46	5.03	9.2	3.53	2.69

to the effects of silicification of basic lithologies (basalt-andesite), now chlorite-schist, during the hydrothermal process. The actual rock matrix itself, as revealed by petrological examination, consists dominantly of chlorite, with lesser amounts of epidote and albite. The total Fe and Cu contents are very variable. This arises because of the variation in the amounts of the iron and copper sulphides present. The highest contents of chalcopyrite occur in samples WP2383N, WP3183N and WP3083N. These rocks have copper values in excess of c. 7wt%. High contents of pyrrhotite are present in samples WP2083N and WP3083N. These rocks have correspondingly high (greater than 20wt%) of iron.

4.2.6. Discussion of the influence of mineralogy and rock chemistry on the composition of lichen communities at Gjersvik

The silicate mineralogy is fairly uniform and appears not to play an important role in determining the major distribution patterns of lichens at this site. In contrast, there are two specific mineral assemblages which can be readily observed to have a dramatic effect on the composition of the lichen communities. These are, notably, the primary iron and copper minerals present at the site and their supergene oxidation products.

It is now well established that the weathering of sulphides present in a rock may favour the growth of the Acarosporetum sinopicae (section 1.1.4.c). This community is widespread at Gjersvik and is here represented at sites 9 and 10, from which rock samples have been collected. Both samples contain high contents of pyrrhotite and have correspondingly higher iron values than in the

other analysed samples from Gjersvik. These other samples virtually lack pyrrhotite and high contents of other iron-rich minerals.

The rock samples collected from the sites which have lichen communities evidently affected by copper mineralization, mostly contain some chalcopyrite, as revealed by petrographic examination. In addition, they contain pyrite which is relatively unweathered. As a consequence of the abundance of chalcopyrite, these samples often have high copper contents of several percent. However, these results are exceedingly variable. Thus, whilst 3 rock samples were collected close to where abundant green, copper-rich crusts of Lecidea lactea occur, their copper contents vary by a factor of approximately 40. This large variation in copper content, even over a small distance, is not surprising, since chalcopyrite is an accessory mineral. Of geat interest, however, is the observation that sample WP3083N from site 10 contains high copper contents similar to those occurring at sites 3 and 11, and yet site 10 is dominated by lichens belonging to the Acarosporetum sinopicae. In this instance, there is additionally a substantial proportion of pyrrhotite present, which is responsible for the development of this alternative lichen community (see also section 4.2.6). It is notable that the field measurement of pH of moisture on rock surfaces colonized by the Acarosporetum sinopicae gave characteristically low values, down to pH 3 at site 10. These results are in agreement with those reported by Wirth (1972) from similar substrata (section 1.1.4.c). In contrast, the field measurement of pH of moisture on rock surfaces colonized by lichens evidently affected by copper mineralization, gave consistently higher values of around pH 5. The pH of rain water is normally pH

5.6. Further details of the factors responsible for the development of the two contrasting lichen communities, dominated by either iron-rich or copper-rich species are given in section 4.2.6.

4.3. Coniston

4.3.1. Introduction

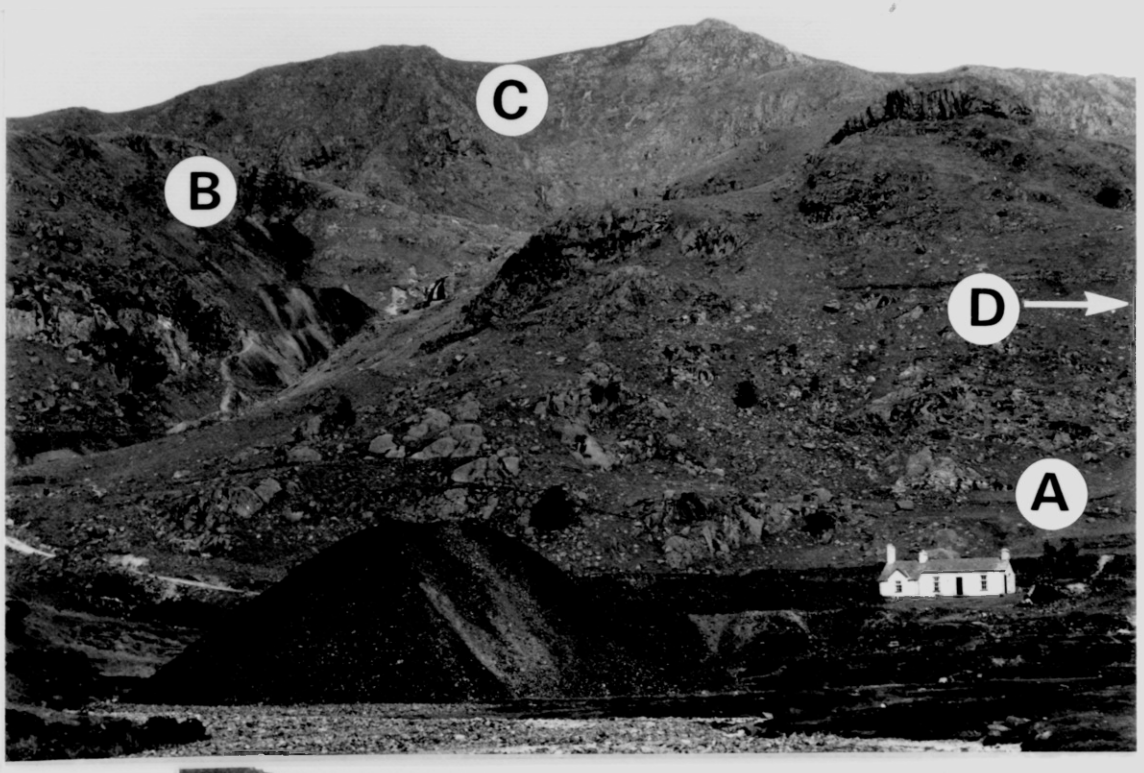
The lichen communities associated with copper sulphide mineralization and associated secondary oxidation products are described from an old mining area at Coniston in the English Lake District. Five lichen species new to Britain were discovered, viz, Lecidea atrofulva, L. inops, Lecanora handelii, Rhizocarpon furfurosum and Stereocaulon symphycheilum. The taxonomy, ecology and distribution of these species is discussed in chapter 5.

Four particular areas were studied (Plate 6A), notably: A the sheltered Bonsor ore-dressing floor walls (section 4.3.2.a), B a moist, vertical exposure with sulphide mineralization at Simon's Nick (section 4.3.2.b), C small fragments of rock detritus forming a scree of quartz-bearing malachite and azurite on a steep south-facing slope (section 4.3.2.c) and, D sunny, exposed minespoil heaps situated above the Youth Hostel with large sulphide-rich boulders and rock fragments (section 4.3.2.d). Species lists for sites A and D are given (Table 8); lists of lichens from sites B and C have not been cited since these localities are limited in extent and all species which were recorded are mentioned in the text.

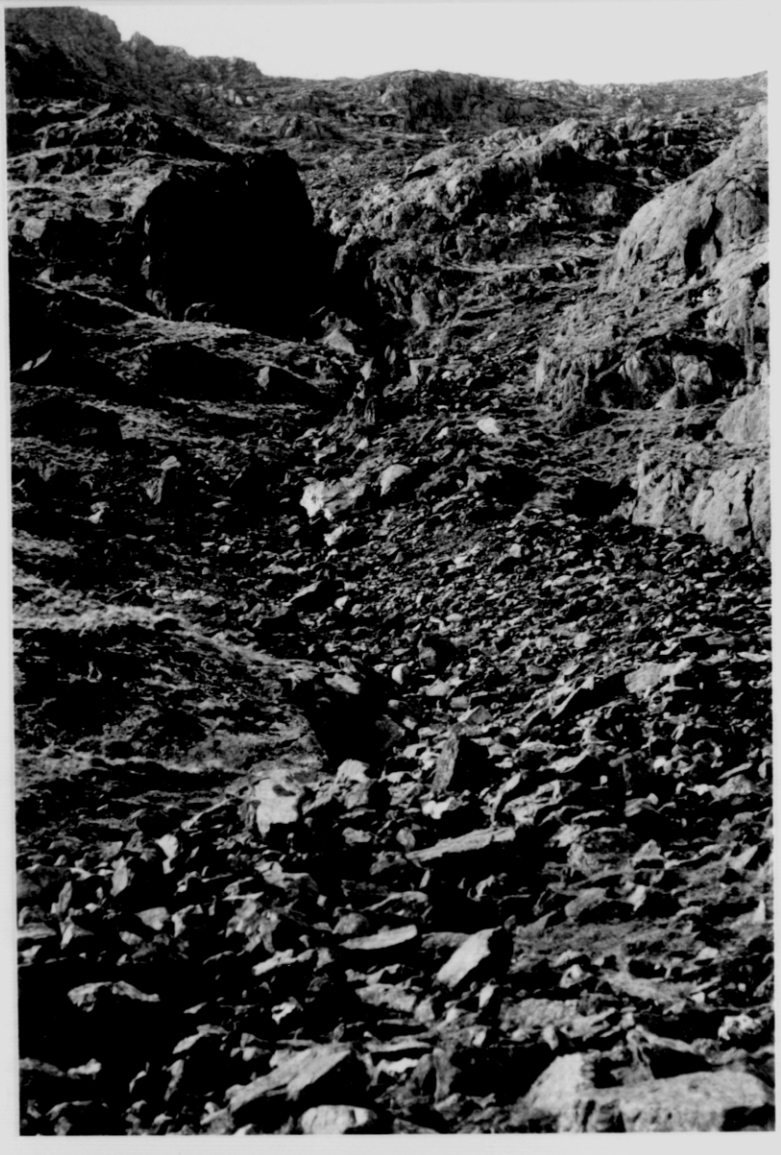
PLATE 6.

A. View to north-west in the Copper Mines Valley, Coniston. Sites investigated : A, Bonsor ore-dressing floor walls; B, Simon's Nick; C, Black Scar Workings; Little How Crags; D, Mine spoil heaps above Youth Hostel.

B. Habitat of Lecidea inops at Black Scar Workings, Coniston.



A



B

Table 8. Lichens occurring on metalliferous and associated substrata at Coniston. Site A, Bonsor ore-dressing floor walls and site D, spoil heaps above Youth Hostel.

	SITE	
	A	D
Acarospora fuscata	.	+
A. sinopica	+	+
A. smaragdula	+	+
Amygdalaria pelobotryon	+	+
Arthrorhaphis citrinella	+	+
Aspicilia caesiocinerea	.	+
A. sp. K- (sterile)	+	+
A. sp. K+ red (sterile)	+	+
Bacidia delicata	+	+
B. inundata	.	+
Baeomyces rufus	.	+
Buellia aethalea	+	+
B. stellulata	.	+
B. verruculosa	.	+
Caloplaca festiva	.	+
Candelariella vitellina	.	+
Catillaria chalybeia	.	+
Cladina ciliata	.	+
C. portentosa	.	+
Cladonia coccifera	.	+
C. furcata	.	+
C. macilenta	.	+
C. polydactyla	.	+
C. squamosa	.	+
C. subcervicornis	.	+
C. uncialis	.	+
Coelocualon aculeatum	.	+
Diploschistes scruposus	.	+
Fuscidea cyathoides	.	+
F. tenebrica	.	+
Huilia cinereoatra	.	+
H. crustulata	+	+
H. macrocarpa	+	.
H. tuberculosa	+	+
Hymenelia lacustris	.	+
Hypogymnia physodes	.	+
Lecanora atra	.	+
L. badia	.	+
L. dispersa	.	+
L. epanora	+	.
L. gangaleoides	.	+
L. handelii	+	.
L. intricata	.	+
L. muralis	.	+
L. polytropa	.	+
L. soralifera	+	+
L. subaurea	.	+
Lecidea atrofulva	+	.
L. fuscoatra	.	+
Lecidea lactea	+	+
L. lapicida	.	+
L. leucophaea	+	+
L. lithophila	+	+
L. plana	.	+
L. pycnocarpa	.	+
L. silacea	.	+
L. sulphurea	.	+
L. vorticosa	+	+
Lecidella scabra	.	+
Lepraria incana	+	+
Micarea intrusa	.	+
M. lignaria	+	+
M. lutulata	+	+
Opegrapha gyrocarpa	.	+
O. zonata	.	+
Parmelia conspersa	.	+
P. glabratula	.	+
P. omphalodes	.	+
P. saxatilis	.	+
P. sulcata	.	+
Pertusaria dealbescens	.	+
P. lactea	+	+
P. pseudocorallina	.	+
Placopsis gelida	+	+
Placynthiella icmalea	.	+
Polyblastia theleodes	+	.
Porina chlorotica	.	+
Rhizocarpon concentricum	+	.
R. furfurosum	+	.
R. geographicum	.	+
R. hochstetteri	+	+
R. lavatum	+	+
R. obscuratum	+	+
R. oederi	+	+
R. polycarpum	+	+
Schaereria tenebrosa	.	+
Scoliciosporum umbrinum	+	+
Stereocaulon dactylophyllum	+	+
S. evolutum	.	+
S. nanodes	+	.
S. pileatum	+	.
S. vesuvianum	+	+
Thelidium pyrenophorum	.	+
Trapelia coarctata	+	+
T. involuta	+	+
Trapeliopsis granulosa	.	+
Tremolecia atrata	+	+

4.3.2. Sites and floras investigated

4.3.2.a Site A. Old ore-dressing floor walls behind Youth Hostel, Coniston, (34/289986; alt. 200m; 27.4.1984)

The derelict walls of the old Bonsor ore-dressing floors (Plate 6A) support a relatively limited, but highly distinctive, assemblage of predominantly crustose lichens. Some large boulders of sulphide-bearing ore material containing chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and sphalerite (ZnS) were used in the wall construction. These are characterized by a weathered, rusty goethite capping and are easily visible from a distance, particularly on account of their luxuriant covering of bright yellow-green patches of Lecanora epanora. A frequent associate of this community here is Lecanora handelii, occasionally forming colonies up to 18cm diam. and commonlly accompanied by Scoliciosporum umbrinum, Stereocaulon pileatum and Rhizocarpon furfurosum. R. furfurosum is often found intermixed with, and overgrown by, the more vigorous Lecanora handelii. Buellia aethalea, B. stellulata, Rhizocarpon obscuratum, Lecidea leucophaea and Placopsis gelida are invariably present in the community but usually in smaller quantities. Unusual features of Placopsis gelida in the area are the absence of cephalodia and its small size, particularly where this species occurs on metalliferous substrata. It is possible that this form corresponds to material assigned to the undescribed species Placopsis lambii cited in Wirth (1972), Hertel (1977) and Santesson (1984). Stereocaulon nanodes is also a common representative and is particularly well developed and occasionally fertile. Other Stereocaulon species present include

S. dactylophyllum, S. evolutum and S. vesuvianum.

In contrast, rocks lacking a rusty, weathered surface are dominated by Huilia macrocarpa, Lecidea lactea, L. lithophila, Rhizocarpon obscuratum, Aspicilia sp. (cf. simoënsis aggr.), Pertusaria lactea, Trapelia coarctata and T. involuta. Lecanora epanora, L. handelii and Rhizocarpon furfurosum, characteristic of the mineralized rocks, are scarce on these less mineralized substrata. There is some local calcareous enrichment from mortar in crevices and here Polyblastia theleodes occurs on mortar and Lecania erysibe and Rhizocarpon concentricum on associated siliceous rocks.

A striking feature of this site is the relative scarcity of ferruginous lichens such as Acarospora sinopica, Rhizocarpon oederi and, particularly, Tremolecia atrata; Lecidea silacea is absent. Of great interest, however, was the discovery of the rusty Lecidea atrofulva in a shaded, moist recess with ferruginized thalli of Micarea lutulata and Scoliciosporum umbrinum. Lecidea atrofulva had been previously incorrectly recorded in Britain (Hawksworth et al. 1980). The list of the species recorded for this site is given in Table 8.

4.3.2.b Site B. Simon's Nick (34/282988; alt. 430m ; 27.4.1984)

A shaded, moist, east-facing, vertical exposure was investigated at the lowest part of Simon's Nick mine working (Plate 6A). Local concentrations of sulphide (chalcopyrite and pyrite) have here given rise to a rusty goethite surface c. $2m^2$ in extent which is dominated by conspicuous ferruginous lichens. Here

Rhizocarpon oederi, Acarospora sinopica and Lecidea atrofulva form a continuous mosaic and are particularly well developed. Scoliciosporum umbrinum and Huilia tuberculosa are also an important part of the community and are noteworthy in lacking a rusty coloration. A species not necessarily dependent on the mineralization though common on these moist, shaded cliffs is Fuscidea intercincta. Hymenelia lacustris with ferruginized thalli was frequently observed in seepage runnels, strongly suggesting that their rusty nature is derived from mineral-rich solutions flowing over the thallus surface. Site B was particularly noteworthy for the best developed examples of Lecidea atrofulva discovered during this survey.

4.3.2.c Site C. Black Scar Workings. Little How Crags above Levers Water (34/273997; alt. c. 650m; 29.4.84)

The Paddy End Vein passes below Levers Water and outcrops on the steep fellside between Great and Little How Crags where it appears from a distance as a white streak of vein quartz. Here, at an altitude of about 670m, the early miners mined copper at the so-called Black Scar Workings (Holland 1982). At this site the mineralization is an oxidation assemblage, dominated by malachite [$Cu_2CO_3(OH_2)$], azurite [$Cu_3(CO_3)_2(OH)_2$] and with smaller amounts of chrysocolla [$Cu_2H_2Si_2O_5(OH)_4$], covelline (CuS) and bornite (Cu_5FeS_4) cementing fractured quartz (Stanley 1979).

The waste material from the Black Scar Workings occurs on a steep south-facing slope forming a scree-rake in places. Most of the copper-bearing rocks are less than 15cm in width and numerous

freshly broken, unweathered rock fragments are present, a sign of recent disturbance by geologists. A very restricted species diversity is a feature of this site and those present as the dominant lichens were not seen at the other sites. Here Lecidea inops is the dominant lichen occurring on almost every rock fragment with secondary copper minerals but was not observed on other copper-free rocks in close proximity. Stereocaulon leucophaeopsis is also abundant. A study of these and other collections of these two species has led to a re-assessment of their taxonomic status which is discussed in section 5.18. Also noteworthy is the occurrence of Stereocaulon symphycheilum, which was occasionally observed on more stabilized rocks bearing copper. Other species infrequently recorded on these substrata include Huilia tuberculosa, Lecanora soralifera, Trapelia involuta, T. coarctata, Rhizocarpon furfurosum and a Lecidea sp. possibly corresponding to L. lithophila but with an unusually thick, extremely areolate-rugose thallus which is dull smoky-grey in colour. Similar material was also noted from site D where it occurs with Acarospora sinopica and Lecidea silacea. It seems likely therefore that this modification in thallus morphology of L. lithophila arises from its growth on metalliferous substrata.

4.3.2.d Site D. Spoil heaps above Youth Hostel. (34/289990; alt. 300m; 29.4.1984)

A number of extensive, relatively undisturbed spoil heaps, including several large boulders of predominantly pyrite and chalcopyrite ore-containing material, were examined on the exposed and sunny, west-facing hillside above the Youth Hostel.

Particularly conspicuous on rusty surfaces are very well-developed Acarospora sinopica, together with sheets of Lecidea silacea. The latter species was only noted at this site in this survey. Associated taxa, also abundant, include Acarospora smaragdula, Buellia aethalea, B. stellulata, Huilia tuberculosa, Lecanora soralifera, Placopsis gelida and Rhizocarpon obscuratum (sometimes with rusty-pruinose discs). Other common ferruginous lichens present are Rhizocarpon oederi, Tremolecia atrata and examples of Micarea lutulata frequently intergrown with Scoliciosporum umbrinum. The last two species are particularly frequent in the sheltered openings to mine shafts and underhangs on rusty, goethite-capped surfaces. Other species characteristic of shaded mine entrances include Bacidia delicata, Opegrapha gyrocarpa, O. zonata, Porina chlorotica, Rhizocarpon lavatum and R. obscuratum. However, these species are absent from the more heavily mineralized surfaces. Lecidea plana, Lecanora polytropa and Trapelia coarctata are well represented on exposed, sunny rocks, but are not characteristic of the more heavily oxidized, rusty surfaces. Lecanora subaurea is well developed in one small area on small overlying pebbles and boulders and is not found here on weathered ferruginous surfaces which are its usual habitat.

A considerable species diversity was observed at this site which was no doubt in part due to the wide range of habitats and also to the variation in the degree of mineralization. The most intensely ferruginized surfaces support a limited, specialized flora but adjacent zones are more species rich. A list of the species recorded for this site is given in Table 8.

4.3.3. Discussion

The varied lichen floras present at each site illustrate both their specialized mineralogical affinities and particular ecological requirements. The Bonsor ore-dressing floor walls (site A), The outcrop of Simon's Nick (site B) and the spoil heaps above the Youth Hostel (site D) all share several species in common, including, most importantly, Acarospora sinopica. However, the lichen flora at the Black Scar Workings (site C) is strikingly different, dominated by Lecidea inops and lacking Acarospora sinopica. The lichen flora at site A belongs to the association Lecanoretum epanorae V. Wirth ex James et al. (1977), whilst that of sites B and D belong to the association Acarosporetum sinopicae V. Wirth ex James et al. (1977). These two associations belong to the alliance Acarosporion sinopicae and are discussed in section 1.1.4.c.

At site C, the basic copper carbonates, malachite and azurite predominate. Here, the Lecidea inops dominated community is particularly associated with the high concentration of copper in the substratum and a more neutral to slightly basic pH regime. In this latter respect, it is interesting to note that L. inops was entirely lacking at sites A, B and D where significant quantites of copper are present together with iron in a more acidic, sulphide-rich environment. Unfortunately, because of limited time, no field measurements of pH of these substrata were undertaken during the present survey but relevant comparative data has been obtained from similar sites at Gjersvik (section 4.2) and Rǿros (section 4.6.).

A further lichen new to Britain, Lecanora gisleri, characteristic of the Acarosporetum sinopicae (Wirth 1972) has recently been identified: V.C. 6, North Somerset, Mendip Forest, Charterhouse, Velvet Bottom, 31/505557, parasitic on Lecanora subaurea, growing on slag, 23 March 1967, P.W. James (BM!). L. gisleri is characterized by its orange-red apothecia, c. 1mm diam., surrounded by an irregular, pale brown margin. The apothecia may occur alone or in small groups and the thallus is usually indistinct, reduced to small orange-grey areoles. It is known to additionally parasitize Lecanora epanora and L. hercynica (= L. subaurea) (Poelt & Ullrich 1964).

Certainly old mine spoil heaps and other sites rich in toxic metals are lichenologically much underworked but potentially interesting habitats in Britain.

4.4. Ramundberget

4.4.1. Introduction

A visit was made on the 17 and 18 August 1983 to the abandoned copper mines at Ramundberget, Härjedalen, Sweden ($12^{o}25'$E., $62^{o}42'$N.). The aim of this account is to provide a geological basis for a discussion of the chemical factors responsible for the development of the lichen community characterized by Lecidea inops and green, copper-rich ecotypes. The community dominated by lichens modified by copper mineralization was first noted at Gjersvik where, however, it is relatively rare

(section 4.2). In addition, L. inops has a restricted distribution at Coniston (section 4.3).In contrast, a community including both copper-rich ecotypes, L. inops and other specialized lichens is well-developed at Ramundberget, providing an opportunity to study the rocks on which this lichen community grows. However, a detailed account of the lichen flora occurring at Ramundberget is in preparation by Professor Santesson and therefore only a brief account of the more important ecological and geological factors are presented.

4.4.2. Locality description

Sites at three separate mines were studied at Ramundberget. These were at Norrgruvorna, Glimsjön and Gammalgruvan, which are located c. 1.3km ENE., c. 2km NE. and c. 2km ENE. of Ramundbergets Fjällgård respectively. The mines occur at about the limit of the tree line which is at c. 940m. In this region Betula pubescens, Sorbus aucuparia, Salix queternea and Alnus incana are the main trees present. The phanerogamic flora in the area is varied and locally includes a number of calcicolous species, including Daphne mezereum, restricted to the calcareous meta-arkose, situated at lower altitudes. However, in the vicinity of the mines within the greenschist, the flora is less varied. Betula nana and dwarf species of Salix are abundant. There are extensive spoil heaps at Ramundberget and, in addition, large outcrops of naturally mineralized rock and areas of copper-contaminated soil. As a consequence, there is a great diversity of metalliferous habitats available for colonization by lichens. A special feature of the rocks is the variety of secondary copper minerals, basic carbonates

and sulphates, including brochantite ($Cu_4(SO_4)(OH)_6$) which form conspicuous crusts in the weathered, mineralized outcrops. The geology of the Ramundberget deposit is discussed in section 2.8.3.

Five rock samples from Glimsjön, Norrgruvorna and Gammalgruvan have been chemically analysed and studied petrographically. The results of the petrographic examination and chemical analysis are given in tables 9 and 10 respectively, and discussed in sections 4.4.4 and 4.4.5.

4.4.3. Description of lichens associated with specific rocks analysed

4.4.3.a WP2783N 18.8.1983 Norrgruvorna

This sample was taken from an epidote-magnetite-chalcopyrite rock c. 30cm in diameter, lying on the spoil heap. It has a surface iron oxide coating and is colonized abundantly by Aspicilia alpina, A. subsorediza and Stereocaulon leucophaeopsis. Aspicilia alpina and A. subsorediza are green in colour because of the accumulation of copper (Chapter 6).

4.4.3.b WP2883N 18.8.1983 SW. of Glimsjön

A number of schistose, calcite-epidote rocks ranging from 5 to 30cm diam., bearing magnetite and chalcopyrite, both disseminated and occurring as schlieren, with a conspicuous surface deposit of brochantite were discovered. One of these was selected for analysis. The dominant lichen occurring here is Acarospora

rugulosa, material of which was subsequently shown to contain copper oxalate (Purvis 1984). Associated species growing on the bronchantite itself include Aspicilia mashiginensis, Lecidea inops and the copper-rich ecotype of L. lactea.

4.4.3.c WP3583N 17.8.1983 Glimsjön

The south western shore of Glimsjön is overhung by cliffs and pierced by mine adits which have now flooded. Here, the rock is typically bright green because of the abundance of epidote. A sample was collected for analysis. The lichens colonizing these surfaces are few. Lecidea inops is dominant, especially on the vertical surfaces and was subsequently shown to contain copper oxalate (Purvis 1984). Associated species include the green, copper-rich ecotypes of Acarospora smaragdula which is abundant and of Aspicilia subsorediza which is less common here. Lecidea auriculata was observed growing together with L. inops, but in the field could be distinguished from this species by its plane discocarps. In contrast, the shaded underhangs of the mine entrances are dominated by a hitherto undescribed species of Psilolechia which is described in section 5.14.

4.4.3.d WP3783N 17.8.83 Glimsjön

This site occurs close to site WP3583N. A sample was collected from another cliff located on the shores of Lake Glimsjön, though with a south-east aspect. The rock is of a typical pale green colour, similar to that of WP3583N. Locally some enrichment in nitrogen had occurred due to bird-droppings, since

Table 9. Petrography of rocks from Ramundberget

WP2783N	Mesocrystalline groundmass consisting of epidote (c. 40% by vol.) and quartz (c. 20% by vol.) with lesser amounts of actinolite (c. 5% by vol.), containing abundant seams and disseminations of magnetite (c. 30% by vol.) with chalcopyrite (c. 5% by vol.). Pyrite rare.
WP2883N	Epidote (c. 50% by vol.), calcite (c. 15% by vol., individual grains to 700μm), actinolite (c. 5% by vol.), magnetite (c. 5% by vol.) schist with disseminated chalcopyrite and as schlieren (c. 15% by vol.) with extensive alteration to goethite at margins. Some quartz veins present.
WP3583N	Blebs of mesocrystalline epidote (c. 50% by vol.) present in a microcrystalline, quartz (c. 40% by vol.), actinolite (c. 10% by vol.) -rich matrix. Sulphides absent.
WP3683N	Epidote (c. 40% by vol.), quartz (c. 5% by vol.) -rich groundmass with segregations of actinolite (25% by vol.), magnetite (5% by vol.), chalcopyrite (15% by vol.) and calcite (10% by vol.).
WP3783N	As for WP3583N.

Table 10. Chemical composition of rock samples collected at Ramundberget.

	WP2783N	WP2883N	WP3583N	WP3683N	WP3783N
% loss on ignition 950°C 24hrs	10.73	4.66	1.03	2.05	1.28
SiO_2	27.6	38.32	67.25	34.3	60.522
Al_2O_3	8.4	8.25	9.86	14.29	11.27
Fe_2O_3	43.1	23.53	6.88	27.86	8.39
MgO	0.5	2.98	1.95	2.66	2.24
CaO	9.5	19.29	11.21	17.19	16.0
Na_2O	0.0	0.0	0.0	0.0	0.0
K_2O	0.0	0.0	0.0	0.0	0.0
P_2O_5	0.2	0.108	0.13	0.27	0.15
MnO	0.1	1.07	0.32	0.33	0.54
TiO_2	0.2	0.19	0.24	0.32	0.27
Cu	10.2	7.6	0.048	8.3	0.18
Total	99.8	101.33	97.88	105.52	99.56

Xanthoria elegans and Physcia dubia are abundant. Acarospora intricata, Lecidea circumnigrata are also frequent, together with Rhizocarpon geminatum. Copper-rich material of Lecanora ludwigii and Acarospora rugulosa (both containing copper oxalate) were observed, but otherwise there was little evidence from the lichen communities that this particular rock face was rich in copper.

4.4.3.e WP3683N 18.8.1983 Gammalgruvan

Abundant green, copper-rich Aspicilia alpina was observed together with Lecidea inops growing on a boulder on a spoil heap.

4.4.4. Chemical analyses of rocks and mineralogical composition

The major oxide and copper contents of 5 representative rock samples from Ramundberget were analysed by plasma emission spectrophotometry (sections 2.5.1 and 2.5.2). The results of this analysis are shown in Table 10. In addition, these rocks were examined petrographically, the results of which are shown in Table 9.

Samples WP3583N and WP3783N, collected from Glimsjön are most similar, both in terms of their bulk chemical composition and mineralogy. They have a typically pale green colour because of a high content of epidote. These rocks may consequently be termed epidotites. The occurrence of these rocks at Ramundberget is discussed by Hill (1980). Lesser contents of actinolite and quartz are present. Albite is absent. Petrologically, these rocks are Intermediate in terms of their silica content. Chalcopyrite is rare

in sample WP3783N and absent in WP3783N.

WP2783N is heterogeneous in composition, consisting of an epidote-rich matrix and subordinate amounts of actinolite and quartz, similar to that in WP3583N and WP3783N. However, a major difference is the high content of copper (10.2 wt%) due to abundant chalcopyrite in WP2783N, occurring as lenticular segregations up to 1cm in diameter. Additionally, the iron content is high (43.1 wt%) which is largely due to magnetite, present as conformable layers reaching 1cm in diameter.

WP2883N and WP3683N are the only samples which effervesce with dil. HCl, showing the presence of appreciable quantities of carbonate, occurring here as calcite. Both samples have, in addition, high contents of copper (c. 7wt%) predominantly in the form of chalcopyrite, though sample WP2883N has some superficial brochantite as a result of surface oxidation. Furthermore, these samples also have high contents of iron (c.25 wt%), due primarily to the presence of magnetite. WP3683N has obvious actinolite, visible in hand specimens.

Because the analyses of rock samples WP2783N, WP2883N and WP3683N are not representative of original rock composition, it follows that the silica contents in these cases cannot be used in their classification. However, a petrological examination of the matrix in samples WP2783N, WP2883N and WP3683N confirms that these are Basic to Intermediate in composition.

4.4.5. Discussion

Five rock samples, previously colonized by lichens typical of copper-rich environments, have been chemically analysed and examined petrologically. The most obvious result of these investigations, is that copper, in the form of chalcopyrite, is usually present in large quantities to 10.2 wt% Cu at these sites. However, samples WP3583N and WP3783N contain significantly less copper, but none the less lichens at these sites are obviously receiving copper, because some contain copper oxalate and others have green copper-rich thalli. In these instances, copper was evidently derived in solution from other copper-rich areas, in the vicinity of the lichens. A second important aspect of these investigations, is that the content of iron sulphides in these samples is very low, a factor which partly explains the special composition and abundance of the lichen community affected by copper mineralization at Ramundberget. However, the iron contents of these rocks are mostly very high, reaching 43.1 wt%, which largely reflects the abundance of iron as the oxide, magnetite, in these samples. Magnetite is relatively resistant to weathering, by both chemical and biochemical processes, compared with the sulphide minerals pyrite and pyrrhotite. Thus iron is not released in abundance to affect the lichen communities, cf. Annlifjellet (section 3.3). A further important feature of these rocks is their high calcium content, ranging from 9.5 wt% to 19.29 wt%. These values reflect, in part, the high contents of epidote, and samples WP2883N and WP3183N contain additionally high contents of calcite and therefore effervesce strongly in dil. HCl. The presence of calcite in these rocks is important in increasing the pH and in

fixing copper on the environment surface, as has been shown at Gjersvik (section 4.2). Further discussion of the influence of chemical factors on the lichen communities is given in section 4.5.

There are two further aspects which must be considered: firstly, the sample WP2783N was unusual since it had a superficial iron oxide surface, which usually supports ferruginous lichens. However, copper-rich Aspicilia alpina was abundant on this boulder. This anomaly might be explained by the boulder receiving additional copper-rich solutions from other sources, this phenomenon was only observed on this one occasion during the entire project. A second feature, obvious at site WP3783N, relates to the modifying effect of bird-droppings on the composition of the lichen communities on copper-rich rocks. At this site, Xanthoria elegans and Physcia dubia are abundant and occur together with Acarospora rugulosa and Lecanora ludwigii, both of which contain copper oxalate. In this respect it is interesting to note that in Shetland e.g. on the lower slopes of Muckle Heog c. 5km NE. of Baltasound, Unst, dunite boulders have been obseved to support relatively luxuriant lichen growths, where subjected to the influence of bird-droppings, whereas these boulders are typically almost devoid of lichens (Purvis, unpubl.). It would appear that nitrogen enrichment in the environment can in some way ameliorate the toxic effects of a range of elements on lichens. This has, of course been long recognized in agriculture where the use of fetilizers can dramatically improve crop growth on soils enriched with a range of toxic elements.

4.5. A chemical explanation for the development of the lichen communities dominated by iron-rich and copper-rich species

An explanation to account for the development of the contrasting lichen communities observed at Gjersvik, Ramundberget and Coniston must be considered in terms of the concentration, availability and mobility of iron and copper in the environment. The factors that ultimately cause the breakdown of minerals are mechanical, chemical and biological. It is well recognized that the availability of elements is affected by the stability of the minerals that have to be decomposed and by the pH of the substratum.

Essentially two methods have been used in this study to assess the pH of the environment in which a saxicolous lichen grows. The first method involves the direct measurement of the pH of water (section 2.2). The second method involves a consideration of the nature and abundance of certain minerals present in the vicinty of the lichen, which might affect the pH of the water in contact with the lichen. This latter method does not give an absolute pH value, though will give a useful indication of the limits of pH which might be experienced over a period of time by the lichen. Important minerals to consider in this respect include the sulphides and rock-forming carbonates, most commonly calcite. In the case of the sulphides, which produce sulphuric acid during the process of weathering (section 1.2.3.a), it has been necessary to study their state of decomposition. The presence or absence of secondary oxidation products will also give important information regarding the relative mobility of the associated elements,

including Fe and Cu. The occurrence of carbonates in the immediate environment will naturally have a strong influence on the rate at which the acid products of oxidation are neutralized and thus on the mobility of the elements released during this process.

Another important factor affecting the mobility of elements in the environment is the electrode (or oxidation-reduction) potential (Eh) which is a measure of the degree of oxidation or reduction in a reversible oxidation-reduction system. It is defined as the potential of a half-cell, referred to the standard hydrogen half-cell being taken as zero at all temperatures. The higher the Eh, the greater the degree of oxidation in the redox system and the lower the Eh, the greater the degree of reduction. The electrode potential may depend on the ambient pH and therefore can affect the oxidation states of the elements. Because of the interrelationships between Eh and pH, it is possible to show mineral stability relations by use of Eh-pH diagrams, as shown in Fig. 2 taken from Garrels & Christ (1965). The system $Cu-H_2O-O_2-S-CO_2$ has been chosen which illustrates the stabilities of malachite and Cu^{2+} under varying pH and Eh regimes (Fig. 2A). The stability relations of iron oxides and sulphides in water are shown in Fig. 2B. In addition, the field of stability of chalcopyrite is also indicated on this latter diagram. However, for simplicity other oxidation products of chalcopyrite have been ommited. From Fig. 2 it is apparent that both pyrite and chalcopyrite are stable under reducing conitions over a wide pH regime. The presence of sulphides favours the growth of populations of sulphur- and iron-oxidizing bacteria under ambient oxidizing conditions (section 1.2.3). These bacteria are aerobic autotrophs and their metabolic activities help

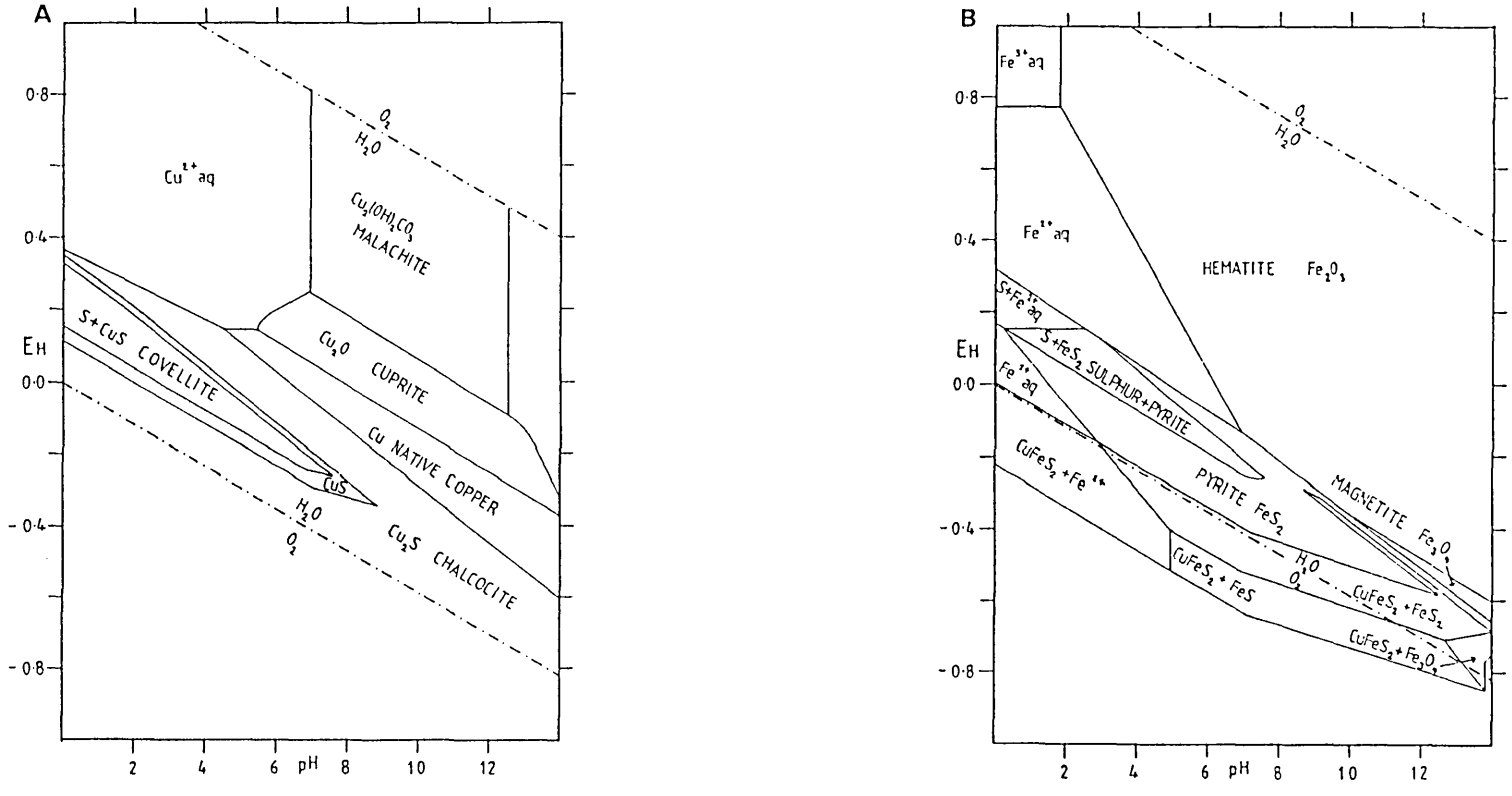


Fig. 2. Stability relations of A. some copper compounds in the system $Cu-H_2O-O_2-S-CO_2$, $P_{CO_2} = 10^{-3.5}$ and B. iron oxides and sulphides in water incorporating the stability of $CuFeS_2$ from the system Cu-Fe-S-O-H. Both diagrams at 25°C, 1 atmosphere total pressure and at an activity of dissolved sulphur of 10^{-1}. (Adapted from Garrels & Christ 1965).

to drive the oxidation process and promote acidic conditions, in which both iron and copper is liberated into the environment.

As can be seen in Fig. 2B, Fe^{2+}, the geochemically mobile form of iron occurs predominantly under oxidizing conditions at low pH and also under reducing conditions at higher pH's near neutrality. Consequently, under conditions of high pH, Fe^{2+} is oxidized to Fe^{3+} which is unstable and precipitates as one of a variety of oxides and hydrated iron oxides. Cu^{2+} is also stable in solution at low pH's under oxidizing conditions, but is unstable under reducing conditions. However, under oxidizing conditions, Cu^{2+} is stable in solution over a greater pH range than in the case of Fe^{2+}. Consequently, in an oxidizing environment Fe^{2+} will become oxidized to Fe^{3+} at lower pH values than will Cu^{2+}, which remains stable until near neutrality, at which stage it will usually precipitate as an oxide, basic sulphate or carbonate, according to the mineralogical environment.

It appears obvious that lichens may assume a rusty coloration, due to iron accumulation in iron sulphide-rich environments, where Fe^{2+} is liberated during weathering and fixed in the surface environment as an oxide or hydrated oxide. Equally, it is not surprising that lichens might accumulate copper in an environment rich in copper minerals. A complication arises, however, when one considers situations where both copper and iron minerals are present in appreciable amounts, as in site 10 at Gjersvik, where both pyrrhotite and chalcopyrite are abundant. A copper concentration of 7.7 wt% was recorded at this site and yet there was no visible sign that lichens were accumulating this

metal. This paradox is partly explained by the greater concentration of iron and also by the different mobilities of Fe^{2+} and Cu^{2+} in the environment. At the rock surface of this site, Fe^{2+} liberated during weathering of pyrrhotite, oxidizes to Fe^{3+} and precipitates in the form of hydrated iron oxides. The Cu^{2+} derived from weathering of corroding chalcopyrite remains in solution because of the existing acid conditions of the surface environment. It is not surprising therefore, that copper is not fixed either on the surfaces of the lichens, or in the immediate environment of the lichens, because it remains in solution. Thus a purely inorganic precipitation of copper compounds would not occur under these circumstances, though copper could, of course, be concentrated by some physiological process within lichen thalli.

High contents of copper also occur at the Coniston site dominated by Lecidea inops (section 4.3.2.e). However, in this instance copper is present in the form of malachite and azurite, minerals stable under oxidizing conditions at high pH (Fig. 2A). In this instance copper is available to interact with the lichens. This may occur by virtue of an interaction of the lichen biochemistry with the substratum, as in the case of oxalic acid produced by the mycobiont which leads to the formation of copper oxalate (Purvis 1984). Alternatively, a slight local decrease in the pH of the environment, caused for example by the presence of low concentrations of sulphides or humic acids, would lead to the liberation of Cu^{2+} which could interact with the lichens. A similar explanation can be applied to the lichens occurring on the basic copper chloride, atacamite at Gjersvik and basic copper sulphate, brochantite at Ramundberget. In all these cases the environment has

a characteristically basic pH.

In other instances, at both Gjersvik and Ramundberget, a similar lichen community has been observed on copper sulphide-rich rocks, with lesser quantities of iron sulphides. At the particular sites which were investigated during the course of the survey, the chalcopyrite mineralization was usually associated with calcite, which could often be demonstrated by effervescence using dil. HCl. It is anticipated, therefore, that the calcite might help to maintain copper in the environment by decreasing its mobility. It is notable that the sites at which pyrrhotite is abundant and upon which the community Acarosporetum sinopicae fluorishes, do not contain significant calcite.

In conclusion, it is evident that the community Acarosporetum sinopicae, dominated by ferruginous, iron-rich lichens is typical of low pH, iron-rich environments. In contrast, the community dominated by copper-rich ecotypes is typical of a more basic, copper-rich environment.

4.6. The Lecideion inopis, a new lichen community specific to copper mineralization

4.6.1. Introduction

A new lichen community, the Lecideion inopis, specific for certain types of copper mineralization (see section 4.5), is described here on the basis of relévе data from several sites in the vicinity of Røros, Sør Trøndelag, Norway and one at Coniston

Copper Mines, England. The geology of these sites is discussed in sections 2.8.2 and 2.8.4. The new community is very distinctive and characterized by the faithful species Lecidea inops, not found in other metal-rich communities. Other species which are characteristic of the Lecideion inopis in central Scandinavia include Acarospora rugulosa, Aspicilia mashiginensis, Psilolechia leprosa, Rhizocarpon birgittae and Stereocaulon leucophaeopsis. In addition, several abnormally yellow-green, Cu-rich lichens, which are regarded as ecotypes of widely distributed lichens, are also an important component of the new community: Acarospora smaragdula, Aspicilia alpina, A. subsorediza and Lecidea lactea are the most frequent of these Cu-rich ecotypes; whilst the ecotype of Lecanora polytropa is less common. The new community is also present at Gjersvik (section 4.2) where however Lecidea inops is absent, and was also cursorily observed at Ramundberget (section 4.4). At Gjersvik, some additional Cu-rich ecotypes occur in the Lecideion inopis including, importantly, Lecidea lulensis and Lecidella bullata. Other associated Cu-rich taxa, only very infrequently noted, include Aspicilia myrini (observed once at Ramundberget), A. cf. simoensis, Lecidea arctogena, L. swartzioidea (= L. lactea?) and L. umbonella. The taxonomy of the lichens characteristic of the Lecideion inopis is discussed in chapter 5.

The results of the relevés are presented in Table 11, a description of the sites and the details of the relévés are given below.

Table 11. Relevé data

Lichen species	Relevé No. 1	2	3	4	5	6	7	8	9	10	11
Acarospora rugulosa	–	–	–	–	–	–	–	–	–	+	–
smaragdula	–	–	–	–	–	–	+	–	–	–	–
Aspicilia alpina	7	5	4	3	8	–	3	3	5	6	–
cinereorufescens	5	4	3	3	5	–	–	–	–	–	–
mashiginensis	–	–	–	–	–	–	–	–	–	(+)	–
subsorediza	5	4	5	7	4	–	3	–	–	–	–
Baeomyces placophyllus	–	–	–	–	–	–	–	(+)	–	–	–
Catolechia wahlenbergii	–	–	–	–	–	–	(+)	–	–	–	–
Huilia contraponenda	–	–	–	4	–	–	1	–	–	–	–
nigrocruenta	–	–	–	–	–	–	(+)	(+)	–	–	–
tuberculosa	3	4	3	–	–	–	–	–	4	–	–
Ionaspis epulotica	–	–	3	–	–	–	–	–	–	–	–
Lecanora badia	–	–	–	–	–	–	–	–	3	–	–
dispersa	–	2	–	3	2	–	–	–	–	–	–
polytropa	3	2	–	4	3	–	2	–	4	–	–
Lecidea atrofulva	–	–	–	2	–	–	2	3	–	–	–
auriculata	–	–	–	–	–	–	–	(+)	–	–	–
fuscoatra	–	–	–	–	–	–	–	–	3	–	–
inops	3	8	5	5	–	5	6	7	7	7	7
lactea	–	–	–	–	–	–	(+)	(+)	–	–	–
lithophila	–	–	–	–	–	–	–	–	4	–	3
paupercula	–	–	–	–	–	–	–	2	–	–	–
plana	3	–	–	–	–	–	–	–	–	–	–
vorticosa	–	–	–	–	–	–	–	(+)	–	–	–
Psilolechia leprosa	–	–	–	–	–	–	–	–	–	(+)	–
Rhizocarpon birgittae	1	–	–	–	–	–	–	(+)	3	–	–
geographicum	–	3	–	+	1	–	–	–	3	–	–
polycarpum	–	1	–	–	4	–	–	–	–	–	–
norvegicum	–	–	–	–	–	+	–	–	–	–	–
riparium	2	–	–	–	–	–	–	–	–	–	–
furfurosum	–	–	–	–	–	–	–	–	–	–	2
Stereocaulon alpinum	+	–	–	–	–	–	–	–	–	–	–
denudatum	+	–	–	–	–	–	–	–	–	–	–
leucophaeopsis	5	–	–	–	–	7	4	3	–	–	3
nanodes	–	2	–	–	3	–	(+)	–	–	–	–
tornensis	–	–	–	+	–	–	2	+	–	–	–
vesuvianum	+	–	–	–	–	–	–	–	–	–	–
Tremolecia atrata	–	–	–	–	–	–	2	–	–	–	–
Umbilicaria cylindrica	+	–	–	–	–	–	–	–	–	–	–

Legend

The numbers refer to the percentage cover of a particular species within a relevé, corresponding to the Domin scale where (+) = present outside the relevé, + = a single individual, 1 = 1–2 individuals, 2 = less than 1%, 3 = 1–4%, 4 = 4–10%, 5 = 11–25%, 6 = 26–33%, 7 = 34–50%, 8 = 51–75%, 9 = 76–90%, 10 = 91–100%.

Habitat details and descriptions of the relevés are given in the text.

4.6.2. Descriptions of sites and relevés

4.6.2.a Muggruva Copper Mine (Disused), Rugldalen c. 16km NNW. of Røros alt. c. 850m [map reference UTM 176566 (map 1720 III)]

General site description

An extensive area of copper-poisoned soil situated immediately below the spoil heaps occurs. A characteristic feature of the contaminated areas is the boulder-strewn landscape where the individual boulders reach a maximum diameter of 2m and a height of 60cm, though they are usually less than 45cm and 15cm in height. Vegetation is local and restricted to hummocks situated above contaminated areas. Here Betula nana, Vaccinium myrtillus and Empetrum hermaphroditum are dominant, with lesser amounts of Vaccinium vitis-idaea V. uliginosum, Loiseleuria procumbens and Salix herbacea. Betula verrucosa occurs infrequently, 3-4m in height. Macrolichens in these vegetated areas are well represented, including Cladonia alpestris, C. arbuscula, C. bellidiflora, C. carneola, C. coccifera, C. furcata, C. rangiferina, Cetraria islandica, C. nivalis and Nephroma arcticum.

Description of relevés studied at Muggruva

Relevé 1. Studied 2.7.1984. Area c. $1m^2$. Group of stones, c. 5-15cm in diameter. On horizontal surface situated on Cu-contaminated soil beneath spoil heaps in an open situation. Lichens mostly crustose, dominantly green and containing copper, forming close mosaics where individual lichens are a maximum of 5cm in diameter. Lichen cover

on stones is 100%.

Relevé 2. Studied 2.7.1984. Area c. 30cm^2. Boulder dipping 32^o NW. on a horizontal surface, surrounded by copper-contaminated soil beneath spoil heaps in an open situation. Lichens mostly crustose, dominantly bright yellow-green, copper-rich, forming close mosaics. Lecidea inops lacked an obvious thallus in this relevé, however, abundant pycnidia were visible, produced especially along the foliation of the phyllite along the edge of the boulder.

Relevé 3. Studied 2.7.1984. Area c. 60cmx45cm. North-facing, low lying boulder subject to run-off from copper-contaminated soil from above. The base of the boulder was moist, being situated next to a small rivulet. The pH of the water flowing at the base of the boulder was 4.5 wheras a pH measurement of 5-6 was recorded for moisture in contact with the green, copper-rich form of Aspicilia alpina. At this relevé, 50% of the rock was bare.

Relevé 4. Studied 3.7.1984. Area c. 30cmx45cm. Boulder in a horizontal position receiving run-off from copper-contaminated soil above. Lichen cover c. 80%.

Relevé 5. Studied 6.7.1984. Area c. 30cmx20cm. Low-lying boulder receiving irrigation from copper-contaminated soil. lichen cover c. 95%.

Relevé 6. Studied 6.7.1984. Area c. 1m^2. Shingle, comprising small stones up to 15cm in diameter, surrounded by copper-contaminated soil. Lichen cover c. 60%.

4.6.2.b Storvartsgruva Copper Mine (Disused), spoil heaps c. 9km NE. of Røros, alt. c. 840m. [map reference UTM 298470 (map 1720 III)]

General site description

Extensive spoil heaps present in the vicinity of Klettjern lake. Lichen flora very diverse. Many rocks present rich in iron sulphides supporting characteristically ferruginous lichen species, including Acarospora sinopica, Lecidea silacea and Tremolecia atrata. Phanerogamic vegetation is also varied. Viscaria(= Lychnis) alpina, Melandrium rubrum, Betula nana and Salix lanata are abundant. However, locally, calcicolous plants including Silene acaulis, Saxifraga aizoides and Salix reticulata are present. Associated with the latter phanerogams include the terricolous lichen Catolechia wahlenbergii, together with Stereocaulon nanodes, Stereocaulon leucophaeopsis and Lecidea inops. The last 3 species occur on pebbles and Stereocaulon leucophaeopsis was also noted growing on wood.

Relevé 7. Studied 7.7.1984. Area c. $1m^2$. Group of small stones to 15cm in diameter. On ground in horizontal situation, subjected to copper-containing run-off. Lichen cover c. 50%. Great diversity of lichens on individual pebbles, with up to 6 species occurring on a single pebble, of only 2.5cm in diameter (Plate 7A).

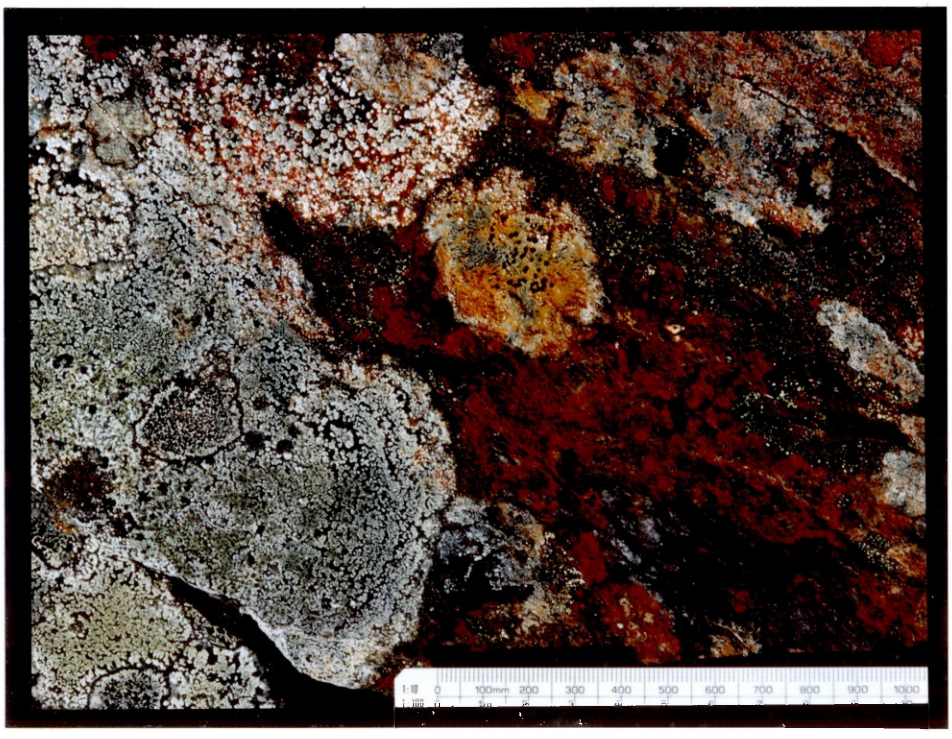
PLATE 7.

A. Close-up of pebble from relevé 7, Storvartsgruva Copper Mine. Colonised by the green Cu-rich ecotypes of Aspicilia alpina and A. subsorediza, Lecidea inops (black fruits), Stereocaulon leucophaeopsis (grey-white crust on side of pebble) with traces of the ferruginous Lecidea atrofulva and Tremolecia atrata. (hb. BM L. inops) Scale in mm.

B. Close-up of part of lichen community occurring at site 1, Gjersvik.The conspicuous green lichen is the Cu-rich ecotype of Aspicilia alpina. A small, ± circular specimen of the Cu-rich ecotype of Lecidea lactea above the centre of the photograph, is here unusually partly ferruginous in colour. The dominant rust-coloured species present is Acarospora sinopica with lesser amounts of Lecidea atrofulva and L. silacea.



A



B

4.6.2.c Kvintushögda Copper Mine (Disused). Spoil heaps c. 10km NE. of Røros, alt. c. 860m [map reference UTM 307472 (map 1720 III)]

General site description

Extensive spoil heaps present with a varied lichen flora. A rich and diverse calcicolous phanerogam flora occurs in the surrounding areas with abundant Bartsia alpina, Gymnadenia conopsea, Pinguicula alpina, Primula scandinavica, Salix reticulata, Saxifraga aizoides and Tofieldia palustris. In areas adjacent to the spoil heaps, a sparse, stunted vegetation has developed, on account of toxic concentrations of metals derived from run-off from the spoil heaps. White encrustations were frequently noted on both soil and vegetation, including lichens and phanerogams. This has been examined by EPMA which suggests that this material is gypsum ($CaSO_4.2H_2O$). It would appear that the precipitation of gypsum has formed as a result of the interaction of sulphuric acid, produced by the weathering of sulphides, with calcium carbonate (calcite) present in the rocks. Certainly abundant calcium carbonate is present in the environment; certain rocks effervesce with dil. HCl and the phanerogamic flora is also a strong indicator of the presence of $CaCO_3$. In addition to the encrustation of gypsum, a blue botryoidal precipitate was also noted, mainly restricted to a boggy patch of ground close to a spoil heap. Material of this precipitate was also examined by EPMA and found to consist of significant quantities of aluminium, sulphur and copper with lesser concentrations of silicon, iron and calcium. The local abundance of this copper-rich colloid is a clear indication of the abundance and

the availability of copper in the environment. On a quartz boulder, situated just above the water level in the copper-poisoned flush, abundant Lecidea inops occurs which was the only lichen recorded in this inhospitable environment. Some of the discocarps of this species are covered in a crystalline pruina of calcium sulphate, as indicated by EPMA.

Relevé 8. Examined 8.7.1984. Area $1m^2$. Group of small stones less than 15cm in diameter, at soil surface. Some pebbles present rich in iron-sulphides and characterized by a goethite capping. These support Lecidea atrofulva. Lichen cover of stones 100%, 50% bare soil present.

4.6.2.d Olav's gruva copper mine (disused), spoil heaps c. 11km NE. of Røros, alt. c. 850m [map reference UTM 314 473 (map 1720 III)]

General description

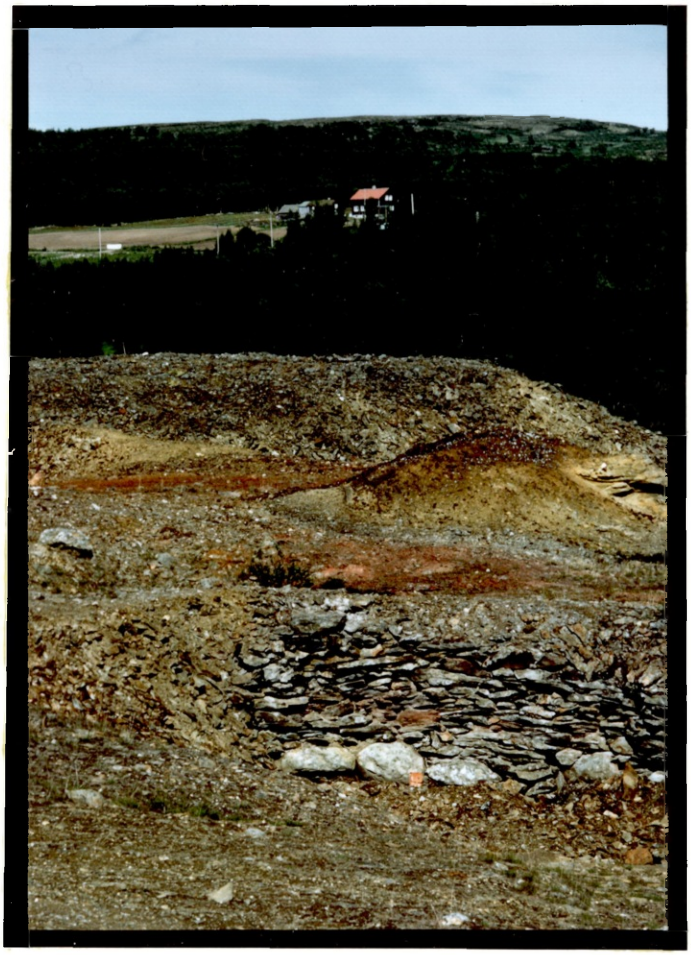
Extensive spoil heaps are present with large boulders predominantly rich in iron sulphides. However, the local influence of copper mineralization on the lichen communities is noticeable. In one instance, the green, copper-rich ecotype of Lecidea lactea was noted growing next to a ferruginous example of L. lapicida. Both specimens were of the order of 15cm in diameter and along one margin were in direct contact.

Relevé 9. Examined 9.7.1984. Area 45cmx20cm. Horizontal boulder receiving run-off from copper-contaminated soil. Lichen cover 100%. Lecanora polytropa was observed to have green, copper-rich discocarps at this site.

PLATE 8.

A. General view of relevé 10, St. Olav's gruva looking NE., 9 July 1984. Quartz boulders subject to irrigation by copper-rich seepage are dominated by Cu-rich Aspicilia alpina and are visible behind and on either side of field note case.

B. General view of relevé 1, Muggruva. In the foreground the stones subject to irrigation by copper-rich seepage are dominated by Cu-rich Aspicilia alpina.



A



B

Relevé 10. Examined 9.7.1984. Area 30cm^2. Quartz boulder at the bottom of a wall facing south-west. This site is illustrated in Plate 8A. The striking feature of this relevé is the bright green, copper-rich Aspicilia alpina with a prominent black hypothallus. Close to this relevé, Aspicilia mashiginensis was recorded in a vertical, north-west situation. On a sheltered, dry, horizontal ledge immediately above the Aspicilia , a single specimen of Psilolechia leprosa was collected. This specimen is new to science and described in section 5.14.

4.6.2.e Black Scar Workings. Little How Crags above Levers Water, Coniston, Westmoreland, England, alt. c. 650m (map reference 34/273997).

General description

This site is discussed in section 4.3.2.c.

Relevé 11. Examined 29.4.1984. Area 30cm^2. Group of stones less than 15cm in diameter bearing obvious malachite, on steep, south-facing scree-rake. Lichen cover 80%.

4.6.3. Discussion

Data has been provided for 11 relevés, 10 of these were studied in the vicinity of Røros, Norway and one at Coniston Copper Mines, England. There is a marked similarity between the lichen communities studied here and those affected by copper mineralization at Gjersvik (section 4.2). This demonstrates the extreme importance of the chemical environment of the lichens

involved. At virtually all sites, with the notable exception of Coniston, green, copper-rich lichens are associates. Similar Cu-rich ecotypes are present at both the Gjersvik and Røros sites including, importantly, Aspicilia alpina and A. subsorediza. Furthermore, Acarospora rugulosa, Aspicilia mashiginensis, Rhizocarpon birgittae and Stereocaulon leucophaeopsis, which at Gjersvik were only found on copper-rich substrata, also occurred in similar environments at Røros. S. leucophaeopsis was also an important part of the community at Coniston. Acarospora rugulosa, Aspicilia mashiginensis and Rhizocarpon birgittae have not, so far, been recorded for the British Isles. However, whilst there are similarities in the types of lichens occurring at these different localities, it would appear that the abundance of particular species at the various sites is due to other environmental factors, in addition to the chemical environment. For instance, Aspicilia mashiginensis is locally frequent at Gjersvik, where it occurs predominantly on steep, ± vertical, moist rock surfaces with copper mineralization, a habitat which was rarely observed at Røros. Likewise, Acarospora rugulosa was found predominantly in crevices on secondary copper minerals at Gjersvik, another rare habitat at Røros. The most important discovery at both Coniston and Røros was the abundance of Lecidea inops. The taxonomy of this species is discussed further (section 5.10). Its absence at Gjersvik can possibly be explained by the lack of suitable habitats, as indicated by the relative scarcity of common associates, including the Cu-rich ecotypes at this site.

Lecidea inops shows a high degree of tolerance for certain types of copper mineralization, which may be paralleled with that

shown by Acarospora sinopica for iron sulphide mineralization. Thus Lecidea inops is very abundant on malachite cementing fractured quartz at Coniston and also was the only species recorded from an extremely inhospitable copper-poisoned flush at Røros. In contrast, Acarospora sinopica was the only species recorded on certain surfaces receiving abundant seepage from pyrrhotite-rich bands at Gjersvik (section 4.2.3.e). Both species are therefore excellent indicators of the different chemical environments; Acarospora sinopica being typical of iron-rich environments at low pH and Lecidea inops favouring more basic, copper-rich situations. The lichens belonging to the Lecidea inops-dominated community are different from those characteristic of the Acarosporion sinopicae (section 1.1.4.c). In addition to Acarospora sinopica, the other characteristic species of the Acarosporion sinopicae, including Aspicilia diamarta, Lecanora epanora, L. gisleri, L. handelii, L. subaurea, Lecidea atrofulva, L. silacea, Rhizocarpon oederi, R. furfurosum and Tremolecia atrata are either very rare or absent in the Lecidea inops-dominated community. Since both of these communities are so distinctive in terms of their species composition and their chemical environment, the new community dominated by Lecidea inops must be considered at an equal level in the phytosociological hierarchical classification system as the Acarosporion sinopicae, notably as an alliance. Relevé 10 at St. Olav's gruva is chosen as the type record for the new alliance, the Lecideion inopis. This site is illustrated in Plate 8A. A new community at the rank of association, the Lecideetum inopis can also be recognized. This association is typical of open, well-illuminated situations where characteristic species in Scandinavia include Aspicilia alpina, A. subsorediza, Lecidea lac-

tea and Rhizocarpon birgittae. Two further facies may be recognized. The first of these is dominated by Aspicilia mashiginensis which may be regarded in central Scandinavia as a moist facies of the Lecideetum inopis. It occurs typically on steep, shaded rock surfaces in humid environments with Acarospora rugulosa, A. smaragdula and Stereocaulon leucophaeopsis as frequent associates. A second facies, that of dry underhangs, is typified by Psilolechia leprosa in Norway, Sweden and Iceland (see section 5.14). It is probable that these two communities deserve the rank of association, but an investigation of further sites is needed for confirmation.

CHAPTER 5. TAXONOMY

5.1. Introduction

The problems involved in the identification of crustose lichens from metal-rich habitats are considerable (section 2.1). A taxonomic investigation of the species belonging to the community associated with certain copper-rich rocks, the Lecideion inopis, defined in section 4.6, is therefore of fundamental importance to this study. Various apects of these lichens are considered, including their morphology, anatomy, ecology, distribution, chemistry and nomenclature. It has been important to study Lecidea inops in some detail (section 5.10, Purvis & James 1985, in press) and to compare it with the closely related Lecidea auriculata and L. diducens, since L. inops is here considered to be a faithful species of the Lecideion inopis and hence restricted to this community (section 4.6). A new species, Psilolechia leprosa is described (section 5.14) which is typical of shaded, cupriferous substrata, though it is not possible at this stage to state whether or not the new species is restricted to these substrata. The other species characteristic of the Lecideion inopis in central Scandinavia, though not restricted to it, notably, Aspicilia mashiginensis (section 5.5), Acarospora rugulosa (section 5.2), Rhizocarpon birgittae (section 5.15), and Toninia leucophaeopsis (section 5.18, Purvis & James 1985, in press), are also considered. The latter species, together with the closely related Bilimbia tornensis have recently been referred to the genus Stereocaulon by P.W. James and myself (section 5.18, Purvis & James 1985, in

press). Stereocaulon tornensis does not, however, belong to the Lecideion inopis. In addition, the widely distributed lichens which were frequently observed to be either wholly or partly yellow-green in colour when growing on certain cupriferous substrata are also described, notably, Acarospora smaragdula (section 5.3), Aspicilia alpina (section 5.4), A. subsorediza (section 5.6), Lecanora polytropa (section 5.8), Lecidea lactea (section 5.11), L. lulensis (section 5.12) and Lecidella bullata (section 5.13).

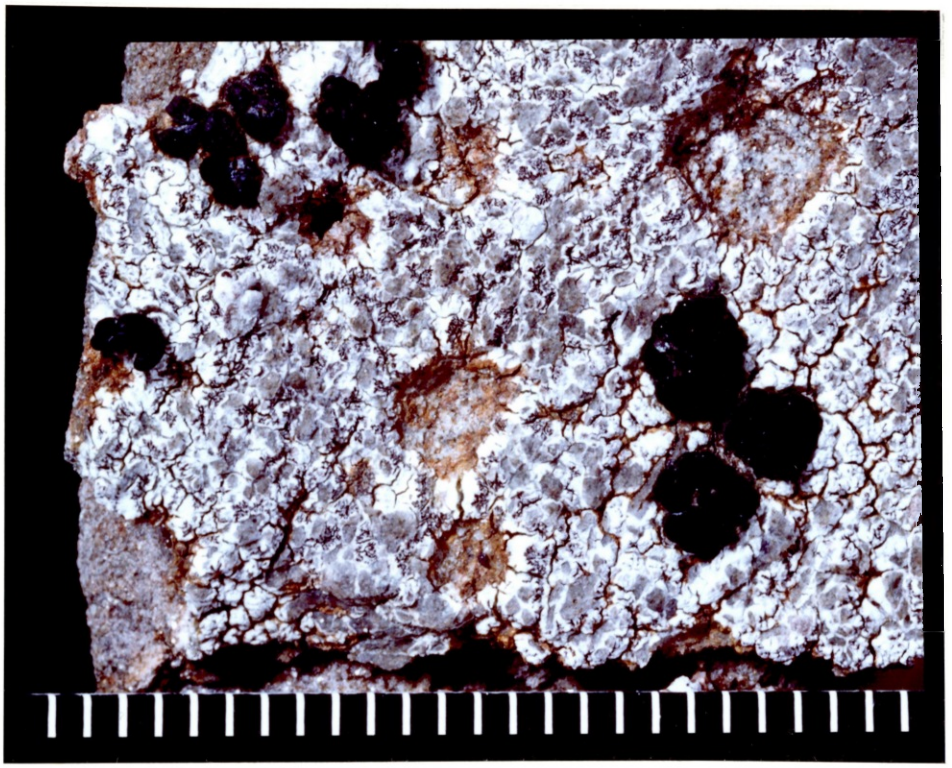
The taxonomy of new British records of lichens recently discovered from metal-rich rocks at the Coniston Copper Mines (section 4.3) is additionally discussed, including Lecanora handelii (section 5.7), Lecidea atrofulva (section 5.9), Rhizocarpon furfurosum (section 5.16) and Stereocaulon symphycheilum (section 5.17, Purvis & James 1985, in press).

The species are treated in alphabetical order. A brief description of each species is given from material as it appears on mineralized substrata, with a discussion of its nomenclature, ecology, distribution and chemistry. Comparisons are made with material from other types of mineralized substrata and with closely related species where relevant.

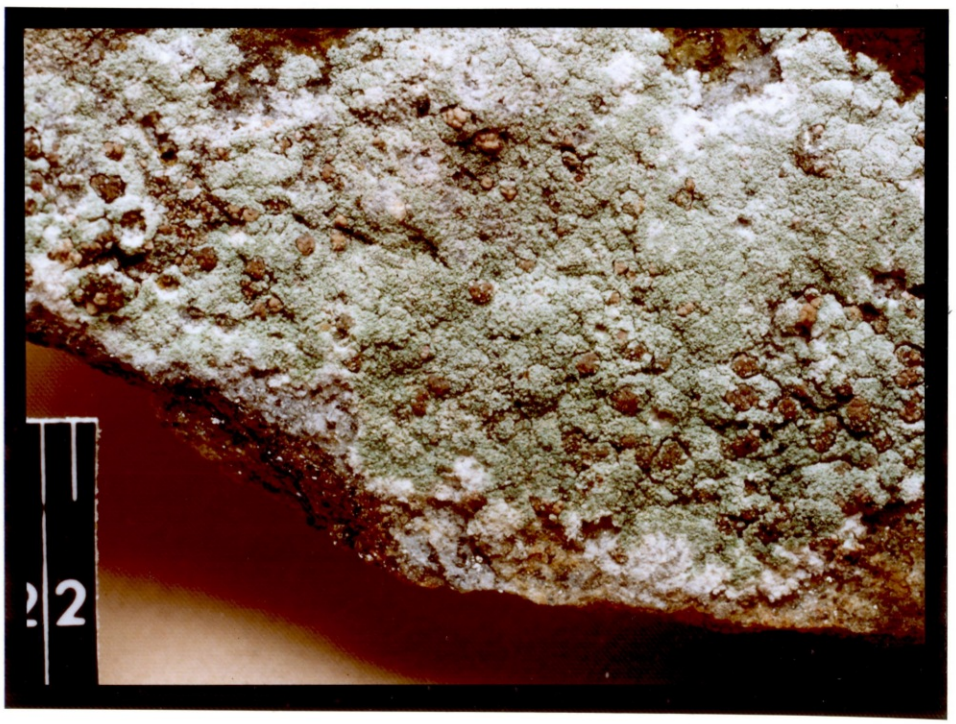
PLATE 9.

A. Lecidea inops, Norway, Sør Trøndelag, c. 16km NNW. Røros, Rugldalen, Muggruva Copper Mine, alt. c. 850m, on pebble irrigated by copper seepage, relevé 6, 6 July 1984, Purvis (BM). Scale in mm. Note the abundant pycnidia on thallus surface.

B. Psilolechia leprosa sp. nov., Norway, Sør Trøndelag, c. 11km NE. Røros, Olav's gruva Copper Mine. On a sheltered, dry horizontal ledge near relevé 10, c. 850m, 9 July 1984 Purvis (BM-holotype). Scale in mm.



A



B

PLATE 10.

A. Acarospora rugulosa Sweden, Härjedalen, Tännäs parish, Mt. Gruvvålen, SW. of Glimsjön (c. 2km NE. of Ramundbergets Fjällgård), 920m, growing on brochantite, 18 August 1983 Purvis (BM) Scale = 3mm. This specimen contains abundant blue inclusions of copper oxalate; SEM micrographs are shown in Plate 22.

B. Aspicilia mashiginensis Norway, Nord Trøndelag, Gjersvik, an abandoned copper mine, c. 450m,overgrowing a secondary copper mineral, 8 August 1983, Purvis (BM). Scale in mm.



A

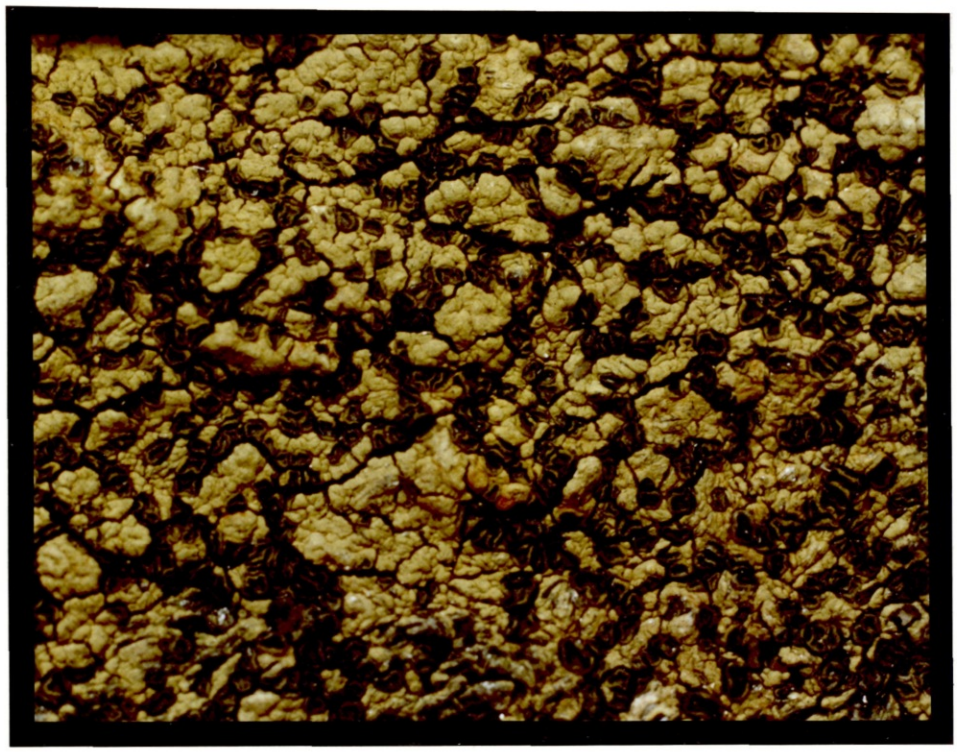


B

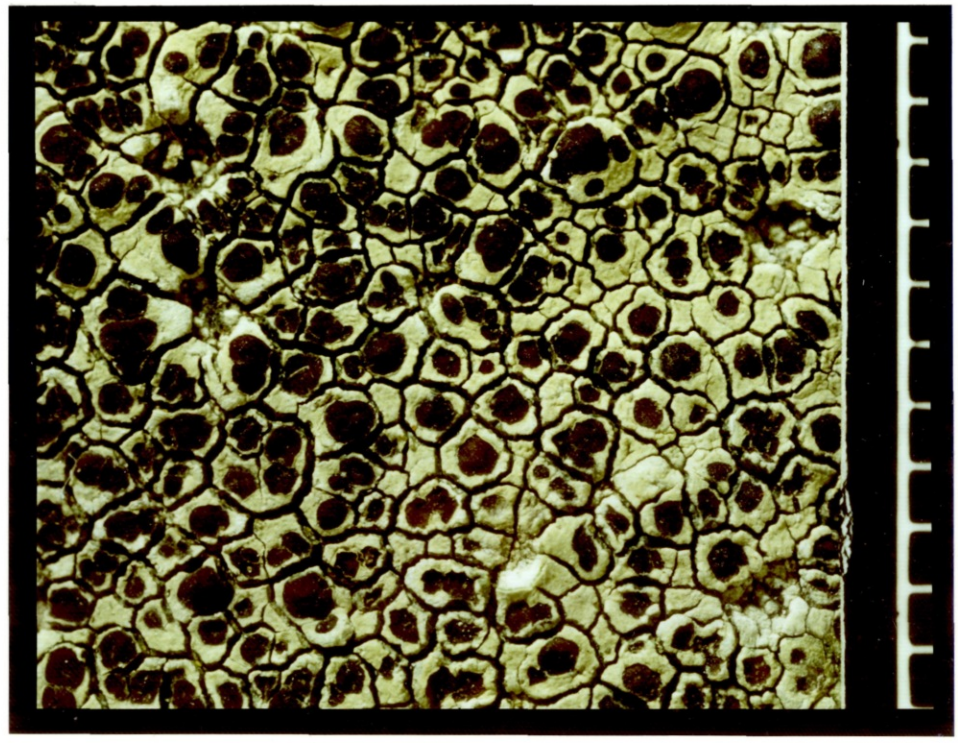
PLATE 11.

A. Lecidea lactea (Cu-rich ecotype) Norway, Sør Trøndelag, c. 10 km NE. Røros, Kvintushögda Copper Mine spoil heaps, alt. c. 860m, 8 July 1984. Scale = 7mm. Note that the thallus is unusually verrucose and that the black apothecia frequently have a green margin, concolorous with the thallus. See Plate 17F.

B. Aspicilia alpina (Cu-rich ecotype) Norway, Nord Trøndelag, Gjersvik, an abandoned copper mine, site 1, c. 450m, 3 August 1983, Purvis (BM). Scale in mm.



A

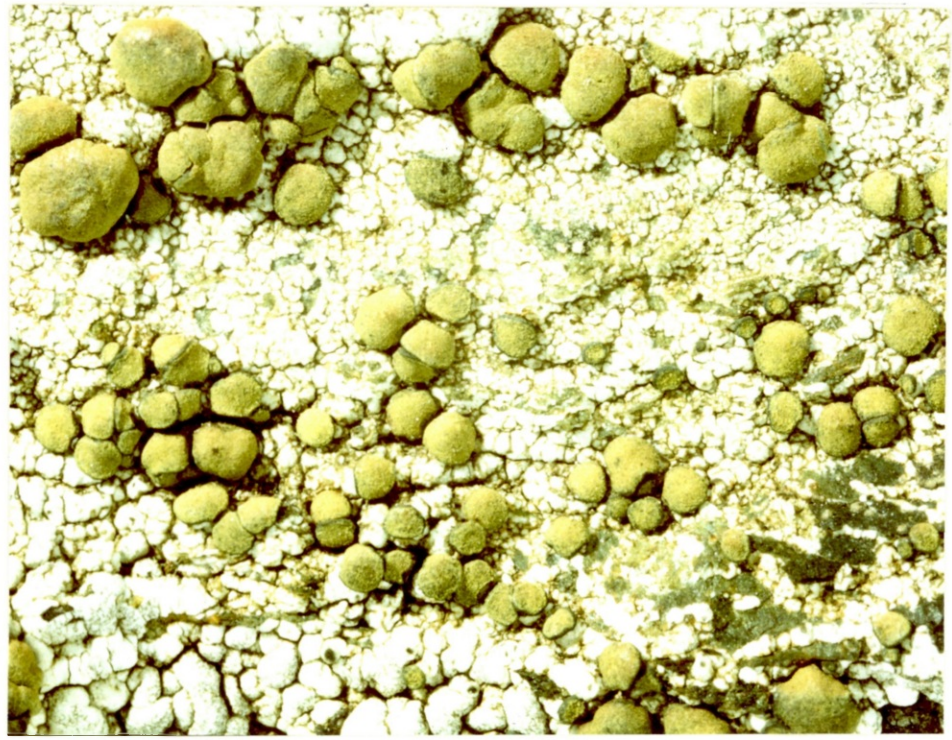


B

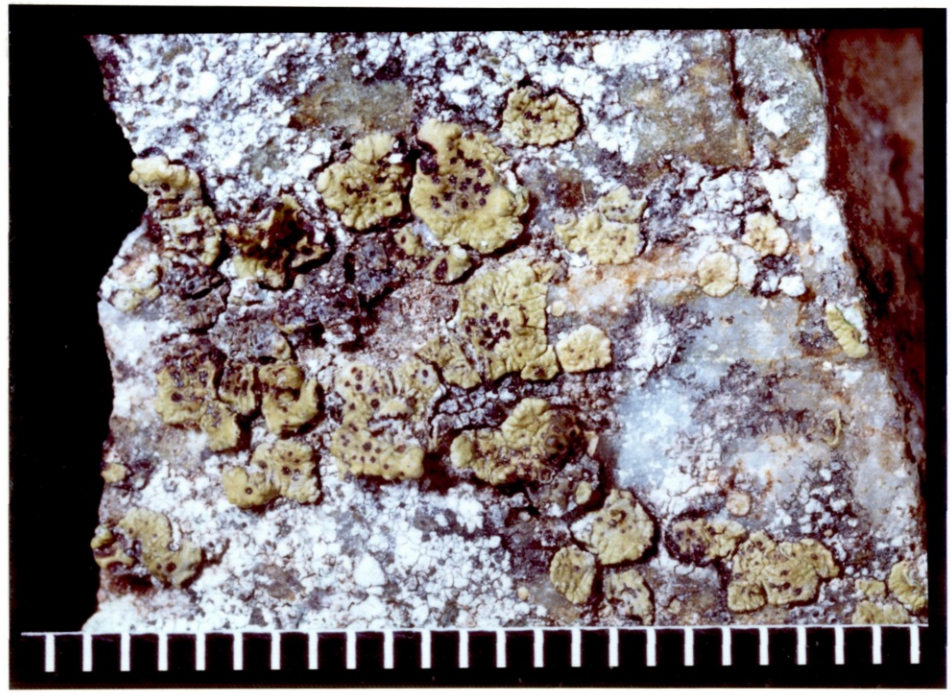
PLATE 12.

A. Lecidella bullata (Cu-rich ecotype) Norway, Nord Trøndelag, Gjersvik, an abandoned copper mine, site 2, c. 450m, 21 August 1983, Purvis (BM). Scale = 5mm. Note striking colour of pruina contrasting with the white thallus. The pruina is less green here than in the original material.

B. Acarospora smaragdula (Cu-rich ecotype) Sweden, Härjedälen, Tännäs parish, Gruvvålen, Glimsjön, c. 2km NE. Ramundbergets fjällgård, 920m, 17 August 1983, Purvis (BM). Scale in mm. Note the plicate nature of the thallus.



A



B

PLATE 13.

A. Lecanora polytropa (Cu-rich ecotype) Norway, Nord Trøndelag, Stormyrfjellet, c. 15 km ENE. Røyrvik, UTM: VM 465977 (map 1924 I), c. 960m, 25 July 1982, Purvis (BM). Scale in mm. Note the rather uneven apothecial coloration, a feature common to this Cu-rich ecotype.

B. Lecanora polytropa (Cu-rich ecotype) (above) with Rhizocarpon birgittae (below) Norway, Sør Trøndelag, c. 11 km NE. Røros, Olav's gruva Copper Mine, relevé 10, c. 850m, 9 July 1984, Purvis (BM). Scale in mm.



A



B

5.2. Acarospora rugulosa Körber

Parerga Lich. 59 (1859); type: Austria, Tyrol near Mittersill, on mica schist, Metzler (not seen).

?Acarospora montana Magnusson K. svenska VetenskAkad. Handl. 7: 287-289 (1929) (type as in A. rugulosa).

Thallus crustose, pale to dark chestnut brown, shiny, consisting of uneven, convex squamules, forming at first small groups of discrete, ± orbicular colonies, c. 5mm diam., slightly lobate at margins, later becoming less regular in shape with often poorly defined marginal lobes, occasionally a pale blue coloration (copper oxalate) may be visible within the cracks and abrasions in the thallus surface. Apothecia initially immersed and punctiform, 1-6 per squamule, later becoming prominent and elevated, with an expanded, flat to concave, rugose-convolute disc of a typically darker coloration, 0.5-1.5mm diam. with a pronounced, raised, usually simple margin.

Thecium (70-) 90-100 (-120)µm high, colourless. Epithecium pale brown pigment disappearing in K. Asci clavate, occasionally saccate, (66-) 80-100 (-100) x 15-25 (-27)µm. Spores simple, colourless, oblong-ellipsoid, >100 per ascus, 3-4 (-5) x 1.8-2µm. Paraphyses sparingly branched, septate, c. 1.5-2µm thick, conglutinate, but separating in K, not or with slightly swollen apices (<3µm). Hypothecium pale straw, hyphae unorientated. Exciple well developed with a brown outer edge, concolorous with epithecium.

Pycnidia not observed.

Chemistry: Thallus K-, C+ red, KC+ red, I-. Gyrophoric acid.

Distribution: Material corresponding to the description given above has been found on cupriferous substrata at Gjersvik, Ramundberget and Alta (Finnmark).

Comment: The aspect of Acarospora rugulosa growing on copper-rich rocks in Scandinavia is very distinctive. In its typical state it is distinguished by the large, conspicuous apothecia with a rugose disc and the small thallus, composed of convex areoles with a usually distinct, shortly lobed margin. An illustration of material collected from Ramundberget is given in Plate 10A. This species has a high tolerance for copper mineralization, growing frequently on secondary copper minerals, including, brochantite and atacamite. Under these conditions it often contains abundant copper oxalate crystals within the medulla.

Acarospora montana was described by Magnusson (1929), based on part of the type collection of A. rugulosa in Körbers herbarium. Thus he states that one specimen of A. rugulosa from Mittersill, collected by Metzler is referable to A. montana and another from Biebersteinen, collected by Körber A. peliocypha (= A. peliscypha). Since there was no necessity to describe A. montana as a distinct species, it seems likely that A. montana is a synonym of A. rugulosa. Unfortunately, the type material of A. rugulosa appears to have gone missing since Magnusson studied this species. Consequently, for the purpose of discussion, it is useful to

maintain the name A. montana. There have been frequent collections of material named as A. montana from several countries, including Norway, Sweden, Germany, Czechoslovakia and USSR (hb. BM! & UPS!). At many of its sites, A. montana typically occurs on rocks rich in iron sulphides, where common associates, at least on herbarium samples are Acarospora sinopica, Buellia aethalea, Lecidea silacea and Lecanora subaurea; it is particularly frequent on slags and mine dumps in the Harz and Erzgebirge and has been considered an acidophyte characteristic of the community Acarosporetum sinopicae (Wirth 1972). A. montana has also been considered typical for the Scandinavian vicariant association the Rhizocarpo norvegicae-Acarosporetum sinopicae (Creveld 1981). This material has not been examined. However, the collections of A. montana from central Europe are morphologically different from those studied by me on copper-rich rocks in Scandinavia. In particular, the specimens of central European material have small, frequently punctiform apothecia with a prominent central umbo of sterile tissue; they are not rugulose. The thallus margin is also rarely lobulate.

A third species, A. peliscypha also contains gyrophoric acid and occurs predominantly on bird perches in central Europe and Scandinavia (Wirth 1972, Creveld 1981). It has been considered to be characteristic of the association the Ramalinetum capitatae (Klement 1955). A. peliscypha has lobed margins, flattened areoles with a blackish undersurface and apothecia with expanded, rugose discs, similar to material of A. rugulosa collected from cupriferous substrata in Scandinavia. The areoles often become imbricate, which together with its darker undersurface appears to be the most significant character separating this species from

material of A. rugulosa collected during this survey.

Acarospora montana (= A. rugulosa) is considered to be a synonym of A. peliscypha (Clauzade & Roux 1981). However, A. rugulosa on the grounds of priority would be the correct name for this species if these taxa were united, an assumption, however, which was not based on a thorough examination of type material. Santesson (1984) also tentatively suggests that A. peliscypha might be conspecific with A. rugulosa. Unfortunately, the taxonomy of Acarospora subgenus Phaeothallia is unclear, a conclusion which is also reached by Clauzade & Roux (1981) in their review article on this subgenus. The fundamental problem relates to the difficulty in defining characters of taxonomic importance in this group. Material named as A. montana, A. peliscypha and the material of A. rugulosa collected in this survey all share similar internal anatomical features, though all have different ecologies. The question arises therefore, whether all three taxa are really modifications induced by environmental conditions. For instance, imbrication, a feature of A. peliscypha is known to occur in several lichens including Lecanora poliophaea and Acarospora fuscata in response to eutrophication (James pers. comm.). It is clear that this matter can only be resolved by a careful study of all these species in the field. If this proves to be the case, A. rugulosa would assume priority.

Specimens of Acarospora rugulosa examined from cupriferous substrata

Norway: Nord Trøndelag, Gjersvik, UTM: VM 254937 (map 1924

IV), an abandoned copper mine, often overgrowing copper minerals e.g. atacamite, c. 450m, 21 August 1983. Purvis (BM, several collections), Sør Trøndelag, Olav's gruva, 11km NE. Røros, UTM: 314473 (map 1720 III) in crevice on SW.-facing wall at an old copper mine, c. 850m, 9 July 1984. Purvis (BM). Finnmark, Alta, Mt.Sakkubadni, near Kvenvika. UTM: EC 8060 (map 1834 I), W.-facing slope, c. 100m, 14 June 1984 Timdal 4303 (O). Sweden: Härjedalen, Tännäs parish, Mt Gruvvålen, SW. of Glimsjön (c. 2km NE. of Ramundbergets Fjällgård) 920m, old copper mine, 18 VIII 1983. Santesson 30996a (UPS), Purvis (BM), Härjedalen, Tännäs parish, Gammalgruvan, an old copper mine between Ramundberget and Dalsvallen (S. of St. Mittåkläppen), c. 940m, 7.VIII.1976 Santesson 27166 (UPS)

5.3. Acarospora smaragdula (Wahlenb.) Massal. (Copper-rich ecotype)

Ricerch. Auton. Lich., (1852): 29.

Acarospora alberti G. Samp. Liquenes inéditos (1920): 5-6 Type: exs. Sampaio Lich. de Portugal, 115 Ponte do Lima: Sá (Paredes) November 1920 G. Sampaio (lectotype BM !)

Acarospora isortoqensis Alstrup Nord. J. Bot. 1: 120-124. Type : Greenland, søndre Isortoq, Ivnarssuaq, 65°26'N., 52°11'W., north-facing rock wall, 31 July 1977, Alstrup 77899 (C-holotype!)

Acarospora undata Clauz, Roux & V. Wirth Bull. Mus. Hist. nat. Marseille 41: 35-39. Type: West Germany: Baden Südscharzwald, Präg (Kr. Lörrach), auf abgesprengten Felsen an der Straße Kurz oberhalb des Ortes, 4 September 1971, Wirth (hb. Wirth-holotype !).

Thallus crustose, yellow-green, of usually rounded, dispersed

areoles c. 0.5-3mm diam., often concentrically folded and becoming minutely lobulate at margins, occasionally forming a ± continuous areolate crust. Apothecia innate, remaining punctiform, c. 0.1-0.5mm diam., 1-8 per squamule, disc pale brown.

Thecium 85-135µm high, colourless. Epithecium pale brown. Asci clavate 100-120x10-25µm. Spores oblong-ellipsoid 2.3-5.2 x 0.9-1.8µm, >100 per ascus. Paraphyses usually simple, septate, occasionally branched towards apices, c. 1.5µm thick with slightly swollen apices (c. 2.5µm), conglutinate, not separating in K. Hypothecium pale to colourless.

Chemistry: Thallus surface K+red, C-, KC-, Pd+yellow, I-. Norstictic acid (K+ red crystals) usually scarcely detectable by TLC.

Distribution: Acarospora smaragdula is widely distributed throughout Europe from the Arctic to the Mediterranean. Specimens corresponding to the ecotype from cupriferous substata are known from Britain, Norway, Sweden, Germany, France, Portugal and Iceland. Material examined is cited in Purvis et al. (1985) (see appendix), with the exception of the type of A. alberti cited in synonymy and one further Portuguese specimen collected by C.N. Tavares, Lich. Lusitaniae sel exs.: 14, Minho-Peso, prope Melgaco, ad rupes granticas apricas, circa 150m.s.m. 11.VI.1947 (BM!). A further specimen, from France, cited in Clauzade et al. (1981) as A. undata has not been examined. It was collected at Gard, Cevennes, Mont-Aigual, near the arboretum of L'hort de Dieu and indicates the copper-rich nature of the site.

Comment: Acarospora smaragdula is characterized by its small, rounded areoles with numerous punctiform, pale-coloured discs. It grows particularly in crevices in shaded situations, but has a wide ecological amplitude. The bright yellow-green colour of the ecotype of A. smaragdula from copper-mineralized sites is usually striking and uniform (Plate 12B). Occasionally, normal fawn-grey squamules can sometimes occur in close proximity, though the colours of individual squamules remain uniform. The thallus surface of the ecotype is often uneven, tending to develop a series of concentric ridges, a feature not observed in normal A. smaragdula. The reason for the development of the irregular surface is unknown, but this feature has also been observed in other copper-rich lichens, e.g. Lecidea lactea and Aspicilia alpina. In view of these characteristics, it is not surprising that the ecotype of Acarospora smaragdula has been described as a distinct species. The two recently described as such are A. isortoqensis and A. undata which have subsequently been recognized to be modifications of A. smaragdula from cupriferous substrata (Purvis et al. 1985, see appendix). Subsequent to this publication, a further species, A. alberti G. Samp. has been found by EPMA to also correspond to copper-rich material of A. smaragdula and is therefore also a synonym. It is interesting that Magnusson (1929) also recognized the similarity of A. alberti to A. smaragdula and as a result reduced the former to the taxonomic status of a form.

Since the green, copper-rich ecotype of Acarospora smaragdula is frequent in certain copper-rich environments, it is important to compare A. smaragdula with the morphologically similar Fe-rich species of Acarospora which occur in iron-rich environments. An

iron-rich form of A. smaragdula which is K- has been described by Magnusson (1926) as the pale ferruginous-yellow A. smaragdula var. lesdainii f. subochracea. Magnusson's material of this species has not been examined, but it is possible that it corresponds to an unusually pale form of the ferruginous Acarospora sinopica. A. sinopica which favours iron-rich, low pH (c. 2-3) environments (section 1.1.4.c), is, according to Magnusson (1929), one of the crustose lichens that has most often been treated in the literature. Because of the morphological and anatomical similarity of A. sinopica with A. smaragdula, considerable doubt exists as to the exact relationship between these two species. Thus A. sinopica has been considered by many authors, including Flagey, Th. Fries, Leighton, Lindsay, Massalongo, Olivier, Stitzenberger and Vainio to be a form of the non-rust-coloured A. smaragdula, whilst others including Arnold and Norrlin have classified this species under A. fuscata. Since A. sinopica and A. fuscata differ in morphology, anatomy and chemistry from one another, these taxa must be regarded as different species, a view also held by Magnusson (1929). It appears that the most important factors distinguishing A. sinopica from A. smaragdula are their habitat, ecology and chemistry. A. sinopica which is K- may form widespreading patches on often horizontal surfaces of rocks, though seems largely indifferent to aspect. In contrast, A. smaragdula is essentially a crevice species, though the species may also occur in horizontal situations where the thallus is usually represented by scattered areoles. A. smaragdula is K+ red (norstictic acid). Whilst it has been suggested (Purvis et al. 1985, see appendix) that the complexing of copper by norstictic acid in the copper-rich ecotype could be responsible for the difficulty in detecting the acid by TLC, the

acid could still be demonstrated by KOH. It is unlikely therefore, that a similar mechanism of complexing the acid by Fe^{3+} can be invoked in the case of A. sinopica. At Gjersvik (section 4.2) Cu-rich A. smaragdula was observed together with both the normal fawnish grey areolae of A. smaragdula and rust-coloured areoles of A. sinopica in close proximity to each other (c. 5cm). Whilst the ferruginous coloration of A. sinopica varied from pale yellow to red-brown in different areoles, norstictic acid could not be demonstrated in them. No examples of partially fawn and rust-coloured areoles were seen. With the evidence available, A. sinopica must be considered a distinct species, although closely related to A. smaragdula.

5.4. Aspicilia alpina (Sommerf.) Arnold (copper-rich ecotype)

Lecanora alpina Sommerf., Suppl. Fl. Lappon.: 91 (1826); Th. Fries Lichen scand. (1871): 283–284.
Aspicilia alpina (Sommerf.) Arnold, Verhandl. zool.-bot. Ges. Wien 21: 1107 (1871).
Bellemerea alpina (Sommerf.) Clauz. et Roux c.n. Bull. Soc. Bot. Centre-Ouest, Nouv. Ser., 15: 129–133 (1984).

Thallus crustose, pale yellow-green, thin to moderately thick, continuous, rimose-areolate crust, of angular, convex or ± flattened, verrucose areolae, c. 0.3–1.5mm diam., usually limited by a conspicuous black prothallus, occasionally occurring as dispersed areoles. Apothecia 0.4–1 (–1.5)mm, innate, dark brown-black (reddish brown when moist), ± pruinose, usually circular, 1–2(–3) per areole, surrounded by a thin thalline margin.

Thecium (55-)60-75µm high, colourless to pale brown. Epithecium pale brown pigment disappearing in K. Asci clavate, 34-60x15-20µm. Spores oblong-ellipsoid, 9-20x5-12µm, I+ blue. Paraphyses mostly simple, occasionally branched at apices, septate (LKB) with capitate paraphyses, conglutinate, not separating in K.Hypothecium colourless to pale straw, hyphae unorientated.

Chemistry: Thallus surface K+red, C-, KC-, Pd+ yellow, medulla I+blue. TLC: norstictic acid.

Distribution: Cu-rich examples of Aspicilia alpina have been found in Austria, Norway and Sweden. A. alpina is widely distributed throughout the arctic, sub-arctic and the Alps including Britain, Greenland, Scandinavia, North America, Czechoslovakia, Germany and Austria. It has a bipolar distribution. In the Southern Hemisphere it occurs at high altitudes in Australia and New Zealand (Galloway 1985).

Comment: Aspicilia alpina is a distinctive species (Plate 11B), usually abundantly fertile and often forming large patches, consisting of several, fused, ± circular thalli. It is similar to A. cinereorufescens but this species is K- and has dark brown discs. Wirth (1980) considers A. alpina to favour moist, low-lying rocks with a prolonged snow cover and to be characteristic of the association, the Rhizocarpetum alpicolae in central Europe. It also may form a characteristic community with Tremolecia atrata in Scandinavia (Creveld 1981), though this has not been observed in this study. In the Cairngorms, Britain, it is

considered typical of snow-beds (Gilbert & Fox 1985). Aspicilia alpina has recently been transferred to a new genus, Bellemerea Haffelner & Roux (Clauzade & Roux 1984), together with Aspicilia cinereorufescens, A. cupreoatra and A. diamarta, on account of its I+ blue medulla, I+blue, halonate spores and ascus structure. Although this seems a correct delineation, the old name A. alpina is retained here in accordance with Hawksworth et al. (1980).

The ecotype of A. alpina from cupriferous substrata was described by Th. Fries (1871 loc. cit.) as A. alpina β sulphurata, though its Cu-rich nature remained unsuspected. Poelt (1955) discovered similar material in the Großarl, Salzburg, Austria which he considered to be a genetic modification of A. alpina (section 1.1.7.b). However, Santesson recognized this 'form' to be a modification caused by its growth on cupriferous substrata (section 1.1.7.b). The copper-rich nature of the thallus surface of material of A. alpina β sulphurata from Norway, Dovre, Knutshö, 1864, Th. M. Fries (BM !) has been confirmed in the present study by EPMA.

5.5. Aspicilia mashiginensis (Zahlbr.) Oxner

Nov. Sist. Nizsh. Rast. 9: 289 (1972).- Lecanora mashiginensis Zahlbr. Rep. Norw. Novaya Zemlya Exp. 1921 44 :20-21 (1928). Type: Novaya Zemlya, Mashigin Fjord: Fram Bay, 10.8.1921 B. Lynge (UPS-syntype !, O-syntype!) [TLC: unknown substance related to constictic acid (Elix, in litt.), HEF rf 0, brown, TDA rf 2, brown].

Lecanora bennettii Lynge Skr. om Svalbard og Ishavet 81: 90-91 (1940) Type: East Greenland, Hudson Land, Kapp Bennett, Dicksonfjorden, on a basaltic rock, containing no calcareous substance, B.Lynge "(O-holotypus!) [TLC: unknown substance related to constictic acid (Elix in litt.), HEF rf 0, brown, TDA rf 2, brown]

Thallus crustose, scurfy, thin (<0.1mm) to moderately thick (to 1.5mm), pale to dark grey to pale brown, rarely ochraceous, occasionally chalky white (calcium oxalate), forming ± circular colonies usually <3cm diam., but up to 15cm diam., radiately and tangentially fissured, areolate, individual areoles c. 0.2-1mm diam., slightly convex and smooth at thallus margin, often becoming roughened and bearing coarsely granular, efflorescent soralia, c. 0.5mm diam., especially towards thallus centre, occasionally developing into coarse isidia with eroding apices, soralia usually of a darker colour (olive-brown to grey-black) than the rest of the thallus, though paler when abraded. Margin of thallus preceded by a pale, usually fawn-brown (ochraceous), shiny prothallus, usually continuous, occasionally ± fimbriate.

Apothecia and pycnidia not observed.

Chemistry: I-, C-, K+ yellow, KC-, Pd dull orange-red. Unknown compound present (TDA brown rf 1, HEF brown rf 0) by TLC (related to constictic acid, Elix in litt.). Rarely norstictic acid detected.

Distribution: Aspicilia mashiginensis is an essentially

arctic and subarctic species. It has been recorded from East Greenland, Iceland, Spitsbergen, Novaya Zemlya, Sweden and Norway.

Comment: Aspicilia mashiginensis at the sites investigated at Gjersvik and Ramundberget is typically scurfy, sterile and dirty white in colour due to the accumulation and surface deposition of calcium oxalate crystals (both weddellite and whewellite). It has not been observed to accumulate copper oxalate, even when in direct contact with Cu. On cupriferous substrata it may form large, thick thalli (Plates 10B and 24A), though on volcanic glass in the arctic it is frequently present as thin traces. Magnusson (1939) classifies this species in his section Orbiculares, sub-section Reagentes and series Flavescentes together with Lecanora uplandica Magnusson, L. perradiata Nyl., L. subradiascens Nyl., L. rosulata (Kbr.) Stitz. and L. parasitica (B. De Lesd.) Zahlbr. In addition, Magnusson suggests that Lecanora eburnea, L. sorediza and L. bennettii, described subsequently from Greenland by Lynge (1940) may be confused with Aspicilia mashiginensis, though according to Magnusson these species are K negative. However, an examination of the type material of Lecanora bennettii shows that this species is merely a better developed form of the type material of Aspicilia mashiginensis. Its morphology and chemistry are identical. In contrast, Lecanora sorediza [type : East Greenland, Kierulffjorden, 13.8.1929, B. Lynge (holotypus-O!)] containing norstictic acid and L. eburnea [type : East Greenland, Ymerøya, Blomsterbukta, 15.8.1929 B. Lynge (holotypus-O!) with zeorin, differ both chemically and morphologically from Aspicilia mashiginensis. Lecanora eburnea has smooth, convex areoles and lacks soredia. L. sorediza has coarse isidia with concave apices bearing dark

soredia.

My discovery of Aspicilia mashiginensis at Gjersvik represents the first Norwegian record for this species (Santesson 1984). In fact A. mashiginensis had not previously been reported in Scandinavia, since Magnusson's collections from Torne Lappmark in the 1920's. However, subsequent to observing this species at Gjersvik, further material has been seen at Røros and also at Ramundberget. More recently, collections have been made by Timdal (O!) from several localities in Scandinavia. Representative examples of material examined is listed below. It is certain that this species has been overlooked.

Aspicilia mashiginensis has a high tolerance for copper and favours moist, often steep and shaded surfaces. During this survey it has been frequently observed overgrowing secondary copper minerals at Gjersvik (see Plate 10B) and other copper minerals at Ramundberget (see Plate 24A). Aspicilia mashiginensis is also associated with copper mineralization at Røros. In Finnmark (Timdal 4301) it occurs on a calcareous schist bearing secondary copper minerals together with Acarospora cf. rugulosa (Timdal 4303) which contains copper oxalate and also with Lecidea? (Timdal 4302) [= Cu-rich Lecidea lulensis]. However, other Scandinavian collections have been made by Timdal from moderately calcareous sites which were not apparently associated with 'heavy metals' (Timdal, in litt.). Furthermore, in the arctic, where many collections (more than 30 have been examined) have been made, A. mashiginensis may even occur on volcanic glass; these are probably not subjected to copper mineralization.

In summary, Aspicilia mashiginenis in Scandinavia is a characteristic component of the Lecideion inopis (section 4.6). It exhibits a high degree of tolerance for copper, though does not concentrate this element significantly (section 6.2.3). However, it appears not to be restricted to copper-rich sites. Since this species is so widespread in the arctic, Scandinavia could represent the southern limit of its distribution. If this assumption is correct, it is possible that its affinity for cupriferous substrata in Scandinavia might be explained by its ability to tolerate the mineralization, where it is also relatively free from competition by lichens which have less tolerance. A similar explanation has been invoked to explain the occurrence of Stereocaulon symphycheilum on malachite at Coniston (Purvis & James 1985, in press).

Selected specimens examined

Iceland, Sudhur Pingeyjar Sýsla: Laugarskoli 17.7.1937 Lynge (O) [as L. bennettii], Akureyri-Sýsla: nord for byen 10.7.1937 Lynge (O) [as L. bennettii], Spitsbergen, Litledalsfjellet ved varden 17.8.1926 Lynge (O) [as L. bennettii]. Novaya Zemlya, Solbugten, Mashigin 25.8.1921 Lynge (O), Fram Bay, Mashigin, 10.8.1921 Lynge (O). Sweden, Torne Lappmark, par. Jukkasjärvi, Abisko, Marmorbrottet, regio subalpina, 400m, 29.7.1921 Magnusson 6009a (UPS), Torne Lappmark, par. Jukkasjärvi, Björkliden, by kåppasjokk, regio subalpina, 400m, 1.7.1921 Magnusson 5452 (UPS), Härjedalen, Tännäs parish, Mt. Gruvvålen (SW. of Stora Mittåkläppen, southern slope, alt. 900m, an old copper mine (the northern mine), 5.VIII.1973. Santesson 24577 (UPS), Härjedalen, Tännäs parish, Mt.

Gruvvålen, N. of Glimsjön (c. 2km NE. of Ramundbergets Fjällgård, alt. 920m, an old copper mine, 18.VIII.1983 Santesson 30992c (UPS), Purvis (BM), several collections. Norway, Hordaland, Odda, SW.-slope of Mt Store Nup, UTM: LM 94-95, 37-38 (map 1414 IV), alt. 1170-1250m. Calcareous schist, SW.-facing scree in the low-alpine region. 1.VII.1982 Timdal 3459 (O), Finnmark, Alta, Mt Sakkubadni, near Kvenvika. UTM: EC 80 60 (map 1834 I), calcareous schist, near copper precipitate, in east-facing slope, alt. 60-150m, 14.VII.1984 Timdal 4301 (O), Troms, Bardu, Mt Rubbsnytten, above the farm Myre, UTM: DB 0127 (map 1432 II), west-facing scree, alt. 350-400m, 14.IV.1984, Timdal 4001 (O). Troms, Målselv, Iselvdalen Valley, canyon W. of Solheimsaetra. UTM: DB 14 42 (map 1532 IV), boulder by the riverside, alt. 400-460m, 31 March 1984 Timdal 3962., Troms, Målselv, Dividalen Valley, at the river Devdiselva. UTM: DB 43 38 (map 1532 I). Boulder by the riverside, alt. 280-320m, 22.VI.1983, Timdal 4199 (O). Nord Trøndelag, Gjersvik, UTM: VM 254937 (map 1924 IV), an abandoned copper mine, often overgrowing copper minerals, c. 450m, August 1983, Purvis (BM, several collections), Sør Trøndelag, Olav's gruva, 11km NE. Røros, UTM: 314 473 (map 1720 III), on SW.-facing wall at an old copper mine, c. 850m, 9 July 1984, Purvis (BM).

5.6. Aspicilia subsorediza (Lynge) R. Sant. (copper-rich ecotype)

in Vězda, Lich. Sel. Exs. No 1434 (1976) (BM!)

Lecidea subsorediza Lynge in Dahl et al., Skr. Svalbard Ishavet 70: 22 (1937)

Thallus crustose, thin, pale yellow-green-grey, areolate, forming

small, typically circular patches, c. 1-4cm diam., usually limited by a conspicuous black prothallus, occasionally reduced to scattered areoles, areoles c. 0.4-1.2mm diam., convex or plane, frequently with a roughened surface and bearing a central and orbicular, crateriform soredium. Soralia concolorous, c. 0.2mm diam., surrounded by a raised thalline margin. Apothecia not seen.

Chemistry: Thallus surface K+red (crystals), Pd+yellow, C-, KC-, I+ blue. TLC: Norstictic acid.

Distribution: Aspicilia subsorediza occurs in North East Greenland (Dahl et al. 1937, loc. cit.), Norway and Sweden (Santesson 1984) and New Zealand (Galloway 1985). The Cu-rich ecotype of this species is only known from Norway and Sweden.

Comment: Aspicilia subsorediza is distinguished by its small, ± circular, sorediate, areolate thalli, reacting K+red (norstictic acid). In common with many sterile lichens it is certainly an underrecorded species. In Scandinavia it is considered to occur mainly on siliceous rocks, especially in open alpine lichen communities. It is a pioneer species occurring near glaciers (Santesson 1984, Mathews 1973). In New Zealand, it is known from the summit rocks of Mt Cook where it is one of the lichens recorded from the highest altitude in New Zealand (Galloway 1985). It is interesting to note that the copper-rich ecotype of A subsorediza is also particularly abundant in pioneering situations and in open communities, where it often occurs with Lecidea inops. It is not so typical of the more closed communities dominated by Cu-rich Aspicilia alpina. The copper-rich ecotype of A. subsorediza has

neither been previously reported in the literature, nor has it apparently been described as another species.

Aspicilia subsorediza and A. alpina are similar in morphology and chemistry. It seems that A. subsorediza could be the sorediate counterpart of A. alpina.

5.7. Lecanora handelii Steiner

Annln naturh. Mus. Wien 23: 119-120 (1909); type: Turkey, Sandshak Trapezunt, an Andesitfelsen bei der Mine Oluklu südlich von Bakadjak, hart neben dem Bleierz, 1000m, Steiner (not seen).

Thallus crustaceous, grey-green, distinctly areolate, areoles sometimes becoming subsquamulose, flattened or ± convex, usually contiguous forming a ± continuous crust or more rarely widely dispersed. Soralia concolorous with or paler than the thallus, derived from edges of areoles, rarely spreading to upper surface. Apothecia unknown in British material but described as sessile, discs concolorous with thallus with pale brown-black pruina (Poelt & Ullrich 1964).

Chemistry: K-, C-, KC+yellow, Pd-, I-. Usnic acid and zeorin by TLC.

Distribution: Lecanora handelii is recorded from central Europe, Alps and Scandinavia from metalliferous rocks. It has recently been found at a second British locality: V.C.2, East Cornwall: Liskeard, Carradon Hill Copper Mine, 20/269698, 23 March

1984, Gilbert (BM!).

L. handelii has been designated a chalkophile and characteristic species of the Lecanoretum epanorae (Wirth 1972). Superficially, especially in the disposition of the soralia and habit, L. handelii resembles L. subaurea. However the latter is a brighter yellow-green and is clearly closely related to L. epanora. L. epanora contains rhizocarpic acid, epanorin and zeorin, and L. subaurea rhizocarpic acid, zeorin and pannarin (Earland-Bennett 1975). In contrast, my studies of L. handelii reveal the presence of zeorin and usnic acid, in common with several other species of the L. polytropa complex, including L. soralifera. In L. handelii the soralia are consistently marginal, often involving the entire margin of each areole; in L. soralifera they are laminal, mostly rounded and clearly delimited. The latter species, although sometimes also found on mineral-rich rocks, has a much wider ecological amplitude than L. handelii. The marginal distribution of the soralia in L. handelii is somewhat reminiscent of their development in L. orosthea but these two species are not related. L. handelii belongs to the L. polytropa complex and is closely related to L. soralifera.

5.8. Lecanora polytropa (Hoffm.) Rabenh. (copper-rich ecotype)

Deutschl. Kryptog.-Flora II (1845): 37

Thallus crustose, pale yellow-white, consisting of scattered squamules c. 0.2-0.6mm diam., flattened to convex, usually with lobed margins, occasionally absent.

Apothecia sessile, flattened, rarely convex, ± concolorous with thallus, with a thin margin, 0.25-0.8mm (-1.2mm) diam., disc surface becoming irregularly dark emerald green. Thecium (35-) 45-55µm high, colourless. Epithecium brown-green, K+green colour intensifying, but evanescent, Asci clavate, 20-30x11-15µm. Spores ellipsoid (7-)9-11x4.5-5(-6)µm. Paraphyses mostly simple, c. 2 µm, occasionally branched at tips, with slightly swollen apices (c. 2.5-3 µm), conglutinate, ± separating in K. Hypothecium colourless. Exciple pale green-brown, concolorous with epithecium.

Chemistry: Thallus surface K-, Pd-, C-, KC-, I-. Usnic acid, rangiformic acid and zeorin.

Distribution Material corresponding to the Cu-rich ecotype of Lecanora polytropa has previously been found in Greenland by Alstrup & Hansen (section 1.1.7.b) and also has been collected in Sweden, Härjedalen, Tännäs parish, Mt. Gruvvålen, Gammalgruvan (c. 2km ENE. of Ramundbergets Fjällgård), alt. 930m, 17.VIII.1983 Rolf Santesson 30959d (UPS!) [Koppargrün Lec. polytropa] Lecanora polytropa is a widely distributed species, occurring throughout the world.

Comment The copper-rich ecotype of Lecanora polytropa bears a strong resemblance to Lecanora intricata, particularly with regard to the typically flat apothecia and in the dark green colour of the apothecial disc, features common to both species (Plates 13A and B). However, the apothecia are usually more sunken and innate in L. intricata and also the thallus is usually better developed and continuous in that species. A further difference lies in the

nature of the green colour of the apothecial discs. This is due to an unknown copper compound in the ecotype of L. polytropa which is strongly birefringent under crossed polars, a characteristic not shown by the pigment responsible for the dark green-black coloration in the apothecial discs of L. intricata.

5.9. Lecidea atrofulva Sommerf.

Suppl. Fl. Lappon: 143 (1826); type: Norway, Nordland, Saltdalen. C. Sommerfelt. (O, not seen)

Thallus crustose, forming rounded, individual thalli, bordered by a grey or black prothallus, or ± continuous to form extensive patches, rusty yellow-brown, becoming paler or straw-coloured in shade, composed of small, c. 1mm, often scattered, ± convex areoles. Soralia dark blue-grey, at first well delimited, crateriform, 0.1-0.2mm diam., 1-4 per verruca, often becoming ± confluent and then obscuring the surface of the thallus. Apothecia rare and not recorded in British material (see Hertel 1975).

Chemistry: C-, I-, K+yellow, Pd+orange. Stictic acid, cryptostictic acid, norstictic acid (trace) by TLC; constictic acid absent.

Distribution: Widespread throughout Scandinavia, Iceland, Greenland and in the Alps. It has subsequently been found at 3 other sites in Scotland, Britain: V. C. 92, South Aberdeen: Braemar, Balmoral, Ballochbuie Forest above Bridge of Dee,

37/18-90-, 22 May 1984, P. James (BM!) and Coppins (E!); Invercauld Estate, E.-facing crags of Craig Leek, 37/18-92-, on ± sheltered, iron-rich overhangs, alt. c. 300m 25 May 1984, P. James(BM!) and Coppins (E!); Mar Forest, Luibeg Burn, 37/02-93-, on iron-rich rocks by stream-side in relict pine forest between Derry Lodge and Luibeg Bridge, 24 May 1984, P. James (BM!), and Coppins (E!).

The type gathering of Lecidea atrofulva is aberrantly corticolous, on poplar overhung by a low-lying rock (Sommerfelt 1826). Because of this, this widespread species may have been overlooked or misinterpreted. Furthermore, the species has been confused with Rhizocarpon oederi with which it often grows. The most distinctive features of Lecidea atrofulva are the rust-red, ± convex areoles contrasting with the small bluish-grey soralia and the prominent black prothallus. Rhizocarpon oederi, which is also areolate and rust-red in colour, lacks soralia and is usually fertile with black, often irregular, sub-gyrose fruits. Lecidea atrofulva has been recognized as a chalkophile (Hertel 1975) and is considered a characteristic taxon of the Acarosporion sinopicae in Scandinavia (Creveld 1981).

5.10. Lecidea inops Th. Fr.

Lich. Scand. 2: 501-502 (1874); type: Sweden, Varmland, Torskebackens Koppargruva, 1867, J.G. Lagergren (UPS-holotype!) [TLC: perlatolic acid and unknown, TDA rf 3 grey, HEF rf 5-6 fawn].

Lecidea diducens sensu Hertel, Herzogia. 2: 43-44 (1970).

Thallus crustose, white to sordid or dull drab grey, forming a thin, almost evanescent to moderately thick, uneven, rimose-cracked, continuous crust, occasionally occurring as dispersed, roughened, convex granules. A pale aeruginose-blue coloration (copper oxalate) is frequently visible in cracks and abraded areas.

Apothecia 1-3mm diam., adnate, matt black, occasionally pruinose, usually at first flattened with a thin, even margin, becoming irregularly convex or sublobate and emarginate, occasionally remaining flattened with a thin, persistent, markedly flexuose margin. Thecium 45-55µm high, colourless. Epithecium well defined, drab brown-olive, K+ dull greenish. Asci clavate, 22-45 x 6-9µm. Spores oblong-ellipsoid, 8-11 (-13) x (2.5) -3 (-4.0)µm. Paraphyses simple, c. 2µm thick (in water) with slightly swollen apices (2.5-3µm), conglutinate, not separating in K. Hypothecium upper part (15µm) pale brown, hyphae vertically orientated, lower part becoming dark brown-black, (110-230µm) hyphae unorientated. Exciple often poorly developed, edge concolorous with epithecium, gradually becoming colourless within and towards hypothecium.

Pycnidia conspicuous, 0.5mm diam., usually numerous, crateriform with a elevated, conspicuous thalline margin. Conidia bacillar, straight, 10-15x0.8µm.

Chemistry: Thallus surface K-, C-, KC-, Pd-, I+blue-purple; Apothecial sections C-.Perlatolic acid and unknown (TDA grey rf 3, HEF fawn rf 5-6) by TLC, both apparently restricted to the exciple and subhymenial hyphae.

Distribution: Lecidea inops has only been recorded from substrata rich in copper minerals and other substrata irrigated by copper-rich solutions in both Czechoslovakia [Vězda: Lich. Sel. Exs. Nos. 1432 (BM!), 1731 (BM!) (Vězda 1978)] and Scandinavia [e.g. Santesson 24576 (UPS!) (Santesson 1984)]

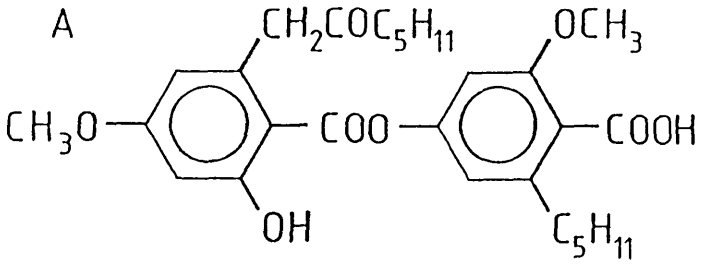
Hertel (1970) considered Lecidea inops as synonymous with L. diducens on account of its supposed C+ maroon reaction of the excipulum. However, he later inferred (Hertel 1977) that L. inops might be a distinct species distinguished by its dark hypothecium and by the narrow width of the excipulum. Material named as L. inops was distributed in Hertel's Lecideaceae exsiccatae as no. 86; this collection (BM!) which contains confluentic acid, appears to be close to L. auriculata with an unusually well developed thallus and an atypical dark hypothecium. It is clear from this confusion that more collections of L. inops were needed for a more detailed investigation of this complex. Vězda (1978) noted that the exciple of L. inops was negative with C and, like Hertel, correctly placed the species in the L. auriculata complex. According to Hertel (1970) L. diducens and L. auriculata are morphologically identical appearing only to differ in their ecology and chemistry. Confluentic acid (C-) occurs in L. auriculata and the structurally related depside 2'-O methylanziac acid, which is responsible for the C+ red excipular reaction, in L. diducens (Culberson & Hertel

1972). My studies of the type and other material of L. inops reveals the presence of perlatolic acid, an isomer of 2'-O methylanziac acid. Thus, interestingly, the chemistry supports the close relationship between the three species (Fig. 3).

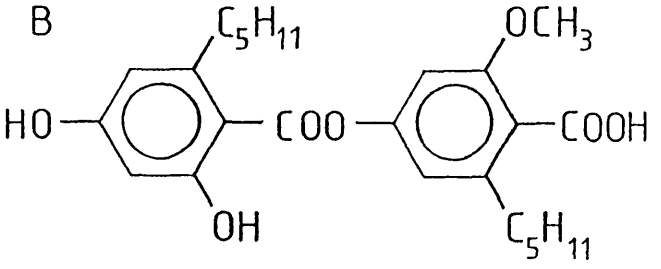
Lecidea inops, in contrast to L. diducens and L. auriculata, commonly possesses a well defined thallus. This is often well developed, as observed in most specimens found at Coniston. However, occasionally a thallus may be sparse, when numerous crateriform pycnidia with an elevated thalline margin usually become very conspicuous. The pycnidia tend to follow cracks and crevices in the rock surface and, being rather rare and inconspicuous in L. diducens and L. auriculata (Coppins pers. comm.), are a highly characteristic feature of L. inops. Furthermore, these characters, together with the more convex and matt-black discocarps of L. inops, usually facilitate identification of L. inops in the field.

The apparent restriction of this species to cupriferous substrata has already been noted (Hertel 1977, Vězda 1978, Santesson 1984). The examination and X-ray diffraction analysis of material from the blue areas within the thalli of L. inops from Coniston and elsewhere reveals the aggregation of plate-like crystals of copper oxalate (Purvis 1984).

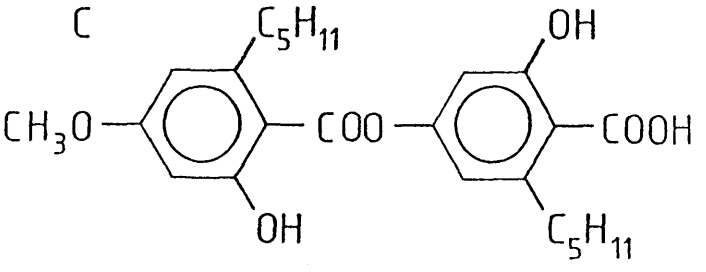
Although L. inops is confined to copper-rich rocks it may sometimes occur with L. auriculata, although the latter has a much wider ecological amplitude.At least, in Britain, L. diducens is almost exclusively a coastal species of hard Acidic rocks and is



Confluentic acid



2'-*O*-methylanziaic acid



Perlatolic acid

Fig. 3. Structurally related depsides occurring in a. Lecidea auriculata , b. L. diducens and c. L. inops.

Table 12. Comparison between Lecidea auriculata, L. diducens and L. inops.

	L. auriculata	L. diducens	L. inops
Thallus	Usually poorly developed, or as thin, dirty white to grey traces, often confined to minute declivities in the rock surface; blue coloration within the thallus absent	As for L. auriculata	Dirty white to dull frequently ± continuous, uneven, rimose-cracked, moderately thick, occasionally evanescent or as dispersed granules; blue coloration frequently observed within the thallus and on abraded surfaces
Pycnidia	Crateriform, immersed, without thalline margin, inconspicuous. Conidia 10-15x0.8µm	As for L. auriculata	Crateriform with a raised thalline margin, usually numerous. Conidia bacillariform, 10-15x0.8µm
Apothecia	Shining black, <3mm diam., usually plane when mature, often with an undulate-wrinkled, persistent margin	As for L. auriculata	Matt black, <3mm diam., often grey pruinose, soon typically convex and becoming emarginate
Thecium	30-35µm high, colourless to pale green	As for L. auriculata	40-55µm, colourless
Epithecium	Emerald-green to green-black	As for L. auriculata	Olive-green
Spores	6.3-10.2x2.2-3.3µm	As for L. auriculata	8-13x2.5-4µm
Paraphyses	Simple, 2µm wide, strongly conglutinated	As for L. auriculata	As for L. auriculata
Hypothecium	Dilute brown or brown	As for L. auriculata	Dark brown to black, opaque
Excipulum	Well developed, green black often mixed with a purple-brown pigment at outer margin, colourless within, C-	As for L. auriculata but C+ maroon-red	Poorly developed, brown-green, pale within, C-
Chemistry	Medulla I ± blue; T.L.C. confluentic acid and UV+ blue accessory visible after charring	Medulla I+ blue; T.L.C. 2'-O-methyl-anziaic acid	Medulla usually markedly I+ blue; T.L.C. perlatolic acid and an unidentified compound
Habitat	On siliceous rocks; mainly in upland Britain, rarely on ± metal-rich rocks	On siliceous rocks; mainly coastal in Britain, rarely on metal-rich rocks	Copper-rich substrata or those subjected to copper run-off in upland sites
Distribution	Widespread, often common, particularly in the Arctic, sub-Arctic and Fennoscandia, also Britain, N. Canada	Locally common in NW Europe, including Britain and Norway, rare in a few alpine localities	Very local (but there often abundant), Norway, Sweden, England and Czechoslovakia

the commonest species of the genus in such sites in Orkney and Shetland. A comparative table presenting details of the 3 species is given (Table 12). It is clear that L. inops is a well defined species with a distinct internal anatomy, external morphology, chemistry and ecology.

5.11. Lecidea lactea Flörke ex Schaerer (copper-rich ecotype)

Lich. Helvet. Spicileg. 127-128 (1828). Vainio, Acta Soc. F. Fl. Fenn. 57 (2): 119-125 (1934). Hertel, Khumbu Himal. 6: 253-256 (1977).

Lecidea theiodes Sommerf. Suppl. Fl. Lapp. (1826): 145. Type: Norway, Nordland, Saltdalen, in saxa in Ooslien, October 1921. (O-holotype!) [TLC: norstictic acid]; Vainio, Acta Soc. F. Fl. Fenn. 57 (2) 133-134 (1934).

Thallus crustose, yellow-green to grey-yellow-green, forming a moderately thick to thick, uneven, areolate crust, areoles c. 0.5-2mm diam., plane-convex becoming frequently verrucose and subdivided into further smaller areolae. Apothecia 0.4-1.0(-1.5)mm diam., innate, matt black, occasionally with green, pruinose margins, at first concave, becoming flattened.

Thecium (45-)55-65µm high, colourless. Epithecium c. 12µm dark green-black, K+green colour intensifying. Asci clavate, 36-45x11-15µm. Spores oblong-ellipsoid (7-)9-11x4.5-6µm. Paraphyses simple, c. 2µm thick with slightly swollen apices (2.5-3µm), conglutinate, not separating in K. Hypothecium upper part (45-70µm) colourless, lower part pale brown, hyphae unorientated. Exciple

well developed, edge concolorous with epithecium, gradually becoming colourless within and towards the hypothecium, K+red crystals (norstictic acid) frequently produced.

Chemistry: Thallus surface K+red (crystals), Pd+ yellow, C-, KC-, I+b. TLC: norstictic acid.

Distribution: Material corresponding to the copper-rich ecotype of Lecidea lactea is known from Norway, Sweden, Finland, Austria and possibly Novaya Zemlya. Material examined is listed below. L. lactea is a widely distributed species, occurring throughout the holoarctic and also occurs in Nepal (Hertel 1977).

Comment: In its typical form Lecidea lactea has an areolate thallus reacting K+red, consisting of ± even, flattened areoles with innate black apothecia. The copper-rich ecotype of L. lactea (Plate 11A) was originally described as L. theiodes from Saltdalen, Norway (Sommerfelt 1826). Subsequently, Arnold (1878) collected similar material in Austria which he identified as a variety of L. lactea, this material was subsequently described as L. theiodes var. reperta (Vainio 1883). A further variety of Finnish origin was also described by Vainio, L. theiodes var kuusamoensis (Vainio 1883). Hertel (1977) recognized that L. theiodes scarcely differed in anatomy from L. lactea. The reason for the unusual greenish coloration became apparent when the surface of listed material below was investigated by EPMA and found to contain copper (this study and Purvis 1984). The uneven, verrucose nature of the areoles typical of the type of L. theiodes is a variable phenomenon, though is more common in the Cu-rich ecotype than in specimens of L.

lactea, which are not Cu-rich. However, non-Cu-rich specimens of L. lactea have been observed to have a similar verrucose nature, as in the case of the specimen from Sweden, Härjedalen, Funnäsdalsberget, 4 June 1857 Th. M. Fries, (UPS!) Interestingly, at site 3, Gjersvik (section 4.2.3.a) normal grey-white material of L. lactea is present, together with the ecotype. However, whilst the ecotype is strongly verrucose, the non-Cu-rich material is not. The reasons for the development of the verrucosity are unknown. Evidently, it is a character of little taxonomic value.

Lecidea lactea, unlike either L. inops or Aspicilia subsorediza, is not a pioneer species and usually occurs on more stable surfaces such as boulders and rock-outcrops, where it may grow on either vertical or horizontal surfaces in moderately sunny situations.

Selected specimens of Cu-rich ecotype examined

Austria: Tirol, Ötztaler Alpen, Gurgl, an einem Glimmerfelsen im Geröll gegenüber dem Ort Gurgl im Ötztal, August 1878 Arnold. (as L. lactea var?) [M, TUR (hb. Vainio 24641)].
Finland: Kuusamo, Kuusamon Kunta, Vaskikallio. In rupe syenitica in regione abietina. 1877 Vainio (as L. theiodes var reperta) [TUR (hb. Vainio 24642)] and (as L. theiodes var Kuusamoënsis) [TUR (hb. Vainio 2463)] Norway: Nord Trøndelag, Gjersvik, UTM: VM 254937 (map 1924 IV), an abandoned copper mine, c. 450m, 7 August 1983, Purvis (BM, several collections), Sør Trøndelag, Røros ($11^{o}23'$E: $62^{o}35'$N), Kvintushögda copper mine (disused), spoil heaps, c. 10km NE. of Røros, c. 860m, 8 July 1984, Purvis (BM), Olav's gruva, c. 11km NE.

Røros, UTM: 314 473 (map 1720 III), c. 850m, 9 July 1984, Purvis (BM). Sweden, Härjedalen. Tännäs parish, Mt Gruvvålen (SW. of Mt Mittåkläppen), the old copper mine near Lake Glimsjön, 920m. 17 August 1983, Purvis and Santesson (BM).

5.12. Lecidea lulensis (Hellbom) Stitzenb. (Copper-rich ecotype)

Ind. Lich. Hyperb. (1876): 43. Type: Sweden, Lule Lappmark, Tarren, Tjurvingjarka 1864 P.J. Hellbom (UPS-not seen), Sweden, Lule Lappmark P.J. Hellbom (BM!-paratype). Vainio, Acta Soc. F. Fl. Fenn. 57 (2): 199-200 (1934). Hertel, Mitt. bot. StSamml. munch. 12: 465-466 (1976).

Thallus crustose, pale yellow-green, consisting of small, typically convex areolae, c. 0.1 - 0.2(-0.5)mm diam., forming at first ± circular, small, c. 1cm diam., uneven colonies, often coalescing into a large continuous crust, c. 5cm diam. usually preceded by a black prothallus.

Apothecia black, sessile, flat to slightly concave, 0.2-0.6mm diam., usually concentrated in centre of thallus, apothecial margin occasionally with a pale pruina, concolorous with thallus. Thecium 40-60µm high, colourless. Epithecium green-black. Asci clavate to saccate, 22-30x11-14µm. Spores oblong-ellipsoid, (7-)8-10x4-6µm. Paraphyses simple, c. 2µm thick with slightly swollen apices (to 3µm), conglutinate, not separating in K.Hypothecium colourless. Exciple dark green-olive, concolorous with epithecium.

Chemistry: Thallus surface K+red, Pd+yellow, C-, KC-, I-.

TLC: norstictic acid.

Distribution: Lecidea lulensis has been reported from Norway and Sweden (Santesson 1984), Spitzbergen and Franz-Josef-Land (Hertel & Ullrich 1976) and appears to have an essentially arctic and subarctic distribution. L. lulensis has been incorrectly recorded for the British Isles, although the species probably occurs there in suitable habitats. Apart from collections made at Gjersvik during this study, material corresponding to the Cu-rich ecotype of L. lulensis is only known from one further locality: Norway, Finnmark, Alta, Mt. Sakkubadni, near Kvenvika, UTM EC 80 60 (map 1834 I), W.-facing slope, c. 100m, 14 June 1984, Timdal 4302 (O!).

Comment: Lecidea lulensis is a small and rather inconspicuous species, characterized by the minute, whitish grey, ± convex areoles reacting K+red and the frequent, plane, black apothecia. L. lulensis is morphologically and anatomically rather similar to Lecidea leucophaea and has been considered a form of this species by Fries (1874). At Gjersvik, L. lulensis was observed to favour steep and underhanging rock surfaces, together with Acarospora chlorophana, Lecidella bullata and Sporastatio polyspora. On Spitzbergen, Hertel & Ullrich (1976) also discovered Lecidea lulensis on underhangs accompanied by several lichens, including Lecidella bullata and Sporastatia testudinea. Creveld (1981) considers Lecidea lulensis to be typical of the Rhizocarpetum alpicolae and to occur on low boulders with a thick snow cover in winter.

5.13. Lecidella bullata Körber (copper-rich ecotype)

Parerga Lich. (1861): 200. Type: Riesengebirge, "am Basalt der kleinen Schneegrube", G.W. Körber (L - not seen; Koerb. Lich. sel. Germ. 252, Topotypus (BM!). Hertel, Khumbu Himal. 6: 319, 321-323 (1977).

Lecidea mesotropiza Nyl. Flora, 56:20 (1873); Th. Fr. Lich. Scand. II, 458 (1874); Vain. Acta Soc. F. Fl. Fenn. 57 (2), 192 (1934); type: Scotland, on walls, Hill of Ardo near Aberdeen, 1872, J.M. Crombie (BM!) [TLC: atranorin, psoromic acid, 2'demethyl-psoromic acid + zeorin].

Thallus crustose, moderately thick, white to grey-white, verrucose, consisting of irregular, convex, occasionally bullate granules to c. 1.5mm diam. Apothecia c. 1-1.5mm diam., adnate, typically black and covered in a conspicuous bright green pruina, at first plane with a prominent black margin, later becoming convex with margin excluded and occasionally sublobulate to 3mm diam.

Thecium (56-)70-90µm high, colourless. Epithecium well defined, c. 15µm high, consisting of numerous granules (birefringent under crossed polars), drab brown, disappearing in K when a green coloration is evident. Asci clavate, (45-) 55-60 x 9-11(-14). Spores oblong, (6-)9-11 x 4.5-5.5. Paraphyses simple, c. 2µm thick (in K) with slightly swollen apices, conglutinate, partially separating in K. Subhymenium colourless, hyphae unorientated c. 90-140µm. Exciple dark brown usually subtending beneath the subhypothecium. Hypothecium occluded with

granules (birefringent under crossed polars) c. 15µm diam. (LKB), disappearing in K. The hypothecial area is variable in extent to 0.5mm high and is typically bright yellow-green in reflected light.

Chemistry Thallus surface K + pale yellow, C-, KC-, Pd + pale yellow. [TLC: atranorin and zeorin]. Discocarp Pd + bright yellow-orange [TLC: atranorin, zeorin, psoromic acid and 2'-demethylpsoromic acid, the last two acids restricted to the epithecium and hypothecial regions.].

Distribution: Lecidella bullata is a widely distributed species. It is known from the arctic, antarctic, Scandinavia, Scotland the Sudeten Mountains, Poland, the Alps, USSR, Canada, Japan and the Himalayas. Distribution maps are given in Hertel (1968) [Europe], (1975) [Europe] and Hertel & Ullrich (1976) [World]. The Gjersvik locality is the only known record for the Cu-rich ecotype of Lecidella bullata. it does not appear to have been described previously as a distinct species.

Comment: Lecidella bullata is a variable species reflected in the large number of synonyms, notably: Lecidea bullosa Zahlbr., L. alboradiata B. de Lesd., L. contorta Bagl. et Car., L. formosa Bagl. et Car., L. lacticolor Arnold, L. mesotropiza Nyl., L. nuoljae H. Magn., L. subdita Nyl., L. nansenii Lynge and L. subtesselata Nyl. The synonymy of this species is discussed in several papers by Hertel (Hertel 1968, 1970, 1971, 1977, 1981).

At Gjersvik, in this study, this species was observed to colonize steep, precipitous rock surfaces and underhangs. Hertel

describes this species as occurring in similar situations at Finse, Norway (Hertel 1975) and also at Spitzbergen (Hertel & Ullrich 1976). However, a contrasting habitat is that in Britain, where Lecidella bullata has been considered to be a typical component of the snow-patch communities in the Cairngorms (Gilbert & Fox 1985).

A characteristic feature of Lecidella bullata is the bluish grey pruina of the fruits which is usually conspicuous, contrasting with the white colour of the thallus. However, the apothecia in the Cu-rich ecotype from Gjersvik have an unusual greenish pruina. In addition, the hypothecial area has a similar anomalous colour (Plate 19A). The Cu-rich nature of both these areas has been confirmed by EPMA (section 6.2.2). The chemistry of Lecidella bullata has been investigated by Leuckert & Hertel (1969) who examined 29 specimens by TLC and identified the constituents atranorin and usually psoromic acid. Likewise, the specimens of Lecidella bullata from Gjersvik have been shown to contain these compounds and in addition a derivative of psoromic acid, 2'O-demethylpsoromic acid and zeorin. However, in these specimens the psoromic acid and derivative are restricted to the exciple and hypothecial areas (section 6.2.2). They are absent from the thallus. The implications of this discovery are discussed in section 6.2.4.

5.14. Psilolechia leprosa sp. nov.

(Plate 9B)

Thallus leprosus, albido-viridulus. Algae viridis cellulis 6-9µm

diam., Apothecia immarginata, convexo-hemisphaerica, mox tuberculata, pallida carnea -violacea -fusca, 0.1-0.5mm diam.,aut ad 1.6mm diam. ubi tuberculata. Hymenium c. 30µm altum, hyalinum aut pallidum stramineum. Ascosporae dacryoideae aut ovoideae, simplices aut interdum 1-septatae, 4.5-6.3 (-7.2) x 1.3 -1.8 µm. Paraphyses ramosae et interdum anastomosantes, septatae et articulatae, crassae 1.3-2µm, apicibus interdum leviter incrassatis ad 3µm latis et haud pigmentiferis. Hypothecium c. 50-70µm altum, hyalinum aut pallidum stramineum, (K-) Excipulum indistinctum. Pycnidia ignota. Thallus et apothecia C+rubra (acidum gyrophoricum).

Typus: Norvegia, Meridies Trøndelag, prope Røros, Olavsfodina, in muro lapideo ad lapidem cuprum continentam, alt. c. 850m, 9.VII.1984 O.W.Purvis (BM-holotypus)

Thallus leprose, thin to moderately thick (<1.5mm), typically greenish white, white or bluish white (due to copper oxalate crystals) consisting of fine granules c. 0.02mm diam., forming a continuous, scurfy or cracked-areolate crust. Phycobiont not micareoid, cells in clusters and tightly bound by short-celled hyphae but haustoria not observed, clusters interconnected by filamentous hyphae c. 1.5-2µm wide. Phycobiont cells ± globose c. 7-8 x 6-9µm.

Apothecia convex-hemispherical and immarginate from the beginning, frequently becoming tuberculate, pallid flesh-coloured-pale brown with a violet tinge in older examples, 0.1-0.5mm diam., or to 1.6mm diam. when turberculate. Hymenium (22-) 27-35µm tall, dilute straw or hyaline. Asci cyclindrical-clavate, 25-30 x

5-9(-11)µm 8-spored. Spores dacryoid or ovoid, simple or occasionally 1-septate, 4.5-6.3 (-7.2)x1.3-1.8µm. Paraphyses numerous, usually branched, sometimes anastromosing, distinctly septate and appearing ± articulated in LKB, stout, 1.3-2µm wide; apices sometimes ± clavate and up to 3µm wide, walls not pigmented. Hypothecium c. 50-70µm tall, hyaline or pale straw (K-). Excipulum indistinct, of radiating hyphae that protrude as loose, hyaline hyphae c. 2.2µm wide and up to 60µm long.

Pycnidia not seen.

Chemistry: Thallus and Apothecia: K-, C+red, Pd-, UV-. TLC: gyrophoric acid.

Habitat and distribution: Psilolechia leprosa occurs on dry underhangs, shaded rock surfaces and protected ledges in Norway, Sweden and Iceland, where it is a characteristic lichen of copper-rich, particularly Basic, often slightly calcareous substrata.

Comment: This characteristic lichen was first drawn to my attention by Santesson, at lake Glimsjön, Ramundberget (section 4.4.3.c). This material was, however, sterile. Subsequently, similar and fertile material was collected in Greenland: Julianehåb dist., Karamuit, 60°43'N., 45°56'W., 50m alt., growing in deep shade in an entrance to a copper mine, 31/vii/1980, Alstrup 80575 (not seen) which was recognized as a new species of Psilolechia (Coppins, in litt.). Unfortunately, this material was insufficient for a good type specimen. Better material was discovered during the

present study, and also by Tønsberg, allowing this species to be more fully described. Because of the leprose nature of its thallus, the epithet leprosa was chosen.

Hitherto, only two species of Psilolechia had been recognized in Europe, notably Psilolechia lucida and P. clavulifera. With the exception of pigmentation, sections of the ascocarps of P. lucida and P. clavulifera have been shown to possess virtually identical anatomical features (Coppins 1983). Likewise, the new species Psilolechia leprosa shares similarities with these species. A comparison of the three species is given in Table 13. As is evident from the table, P. leprosa is a distinctive species and readily separated from both P. lucida and P. clavulifera by pigmentation, chemistry and ecology.

It is notable that in Iceland, Sweden and Norway, Psilolechia leprosa has been found on Cu-rich substrata, in similar dry and shaded environments. The mineralogical environment of the specimen collected by Tønsberg is, however, unknown. Certainly the species has a high tolerance for Cu mineralization, as at Ramundberget it frequently overgrows secondary copper minerals. In addition to the type material, the substrata of all specimens examined (see below) contain demonstrable carbonate (probably calcite) by dil. HCl. Psilolechia leprosa has not been observed to colonize iron sulphide-rich substrata, characterized by a low pH environment. Evidently Psilolechia leprosa may occur on similar substrata to that of Lecidea inops and associated species, though colonizes different niches. However, since this species is known from so few collections, further field study is required in order to determine

Table 13. Comparison between Pailolechia leprosa, P. lucida and P. clavulifera

	Pailolechia leprosa	P. lucida*	P. clavulifera+
Thallus	Greenish white, white or bluish, leprose forming a scurfy crust	Yellowish green, leprose forming a scurfy crust	Whitish or greenish white, forming a scurfy, granular crust
Phycobiont	Protococcoid, ± globose c. 7-8x6-9µm	As for P. leprosa	Cf. Stichococcus
Apothecia	Convex-hemispherical and immarginate, often tuberculate, pallid, flesh-coloured to pale brown with violet tinge	Convex-hemispherical and immarginate, lemon yellow to flesh-coloured	Convex-hemispherical and immarginate, rarely tuberculate, grey-black with bluish tinge, base of apothecia with a dense white rim
Thecium	(22-)27-35µm high, dilute straw or hyaline	c. 30µm high	28-35µm high, dilute straw to dilute greenish
Epithecium	Colourless or dilute straw	Yellow	Dilute greenish
Spores	As for P. clavulifera 4.5-6.3(-7.2)x1.3-1.8µm	As for P. clavulifera 3-7x1-3µm	Dacryoid or ovoid, simple, occasionally 1-septate 3-6x(1-)1.2-1.7(-2)µm
Paraphyses	As for P. clavulifera	As for P. clavulifera	Stout, c.1.5-2µm wide, with clavate apices (to 3µm) usually branched, distinctly septate and appearing ± articulated
Hypothecium	C. 50-70µm tall, hyaline or pale straw	C. 50-70µm tall, hyaline	C. 50-70µm tall, hyaline or dilute greenish
Exciple	As for P. clavulifera	As for P. clavulifera	Indistinct, of radiating hyphae that protrude as loose hyaline hyphae c. 2µm wide, 50µm long
Chemistry	Gyrophoric acid (C+ red)	Two races exist. 1 Rhizocarpic acid + atranorin. 2 Calycin + lepraric acid, (both C-)	No chemistry (C-)
Habitat	On dry underhangs and protected ledges in shaded situations, tolerating Cu-rich substrata	On protected, mostly shaded vertical surfaces or underhangs of rocks with low levels of $CaCO_3$	On roots, stones and consolidated soil of underhangs on banks, or root systems of upended trees
Distribution	Norway, Sweden, Iceland	Widely distributed, throughout Europe. Occurs also in Tasmania and Hawaii	Britain, Finland, Germany Czechoslovakia

Characters for P. lucida* and P. clavulifera+ based on James in Poelt & Vězda (1981):254 and Coppins (1983):201-203.

its precise ecological requirements and phytosociology.

Additional Specimens examined

Sweden, Härjedalen: Tännäs parish, Mt Gruvvålen (SW. of Mt Mittåkläppen), the old copper mine near Lake Glimsjön, 920m. On very shaded, vertical, Cu-rich rocks. 22.VII.1975. Santesson 26307 (UPS). Norway, Hordaland, Os, 300-400m S. of Gåssand, along the brook from Krokvatn. On shaded, schistose rocky wall. 40-45m UTM LM 0584 (1215 IV) 20.V.1984 Tønsberg 8751 dupl. (BG)

5.15. Rhizocarpon birgittae Magnusson.

Bot. Not. (1945): 308. Type: Sweden, Jämtland, Åre, Storlien, Finnröja, near Enan, 700m, 13 January 1945, B. Magnusson (UPS!)

Thallus crustose, white-grey-fawn, consisting of thin, scattered areoles, c. 0.4-0.5mm diam. Apothecia sessile, 0.14-0.5 (-1.0)mm, black, usually concave with a thin, raised margin.

Thecium (70-) 90-100 (-120) µm high, colourless. Epithecium drab green-olive, K+green. Asci clavate, 70-100 x 30-34µm. Spores oblong-ellipsoid, green-brown, muriform, (18-) 22-26 (-32)x(9-) 10-12 (-14)µm, 8 per ascus. Paraphyses conglutinate, anastomosing, c. 2µm thick. Hypothecium dark brown to purplish-black, K ± purple. Exciple well developed c. 50µm thick, concolorous with hypothecium, K+purple.

Chemistry: Thallus surface K-, C-, KC-, Pd-, I-. No chemistry

detectable by TLC.

Distribution: Rhizocarpon birgittae has previously been recorded only from Jämtland and Torne Lappmark in Sweden. Material collected from Gjersvik in the present study represents a new lichen record for Norway.

Comment: Rhizocarpon birgittae appears to be characterized by its I- thallus, the coloured, muriform spores and an exciple and hypothecium which react K+purple. However, this species is considered by Santesson (1984) as "somewhat doubtful". Magnusson (loc.cit.) suggests that it is close to R. permodestum Arnold. Further work is required to establish the authenticity of R. birgittae. It is illustrated in Plate 13B.

Magnusson's daughter Birgit discovered this species when she collected some pebbles during January 1945 from high ground near Storlien, Jämtland. These sites were extremely exposed, there being no protective snow cover (Magnusson 1945). An earlier collection from Torne Lappmark, par. Jukkasjärvi, Passistjårrok 1919 E. Vrang (UPS!) was associated with Tremolecia atrata, Polysporina lapponica and Huilia tuberculosa. During the present survey, material has been collected from cupriferous substrata at Gjersvik and Røros, where it is the principal brown Rhizocarpon. However, from the earlier collections made by Vrang and Birgit it appears that Rhizocarpon birgittae is not restricted to rocks bearing copper minerals. An alternative explanation accounting for its distribution is that this species has a low competitive ability, which might explain its occurrence in inhospitable environments,

including exposed situations at altitude and substrata containing high levels of copper. However, this cannot be the only explanation, since during the survey it was noted that Rhizocarpon birgittae was absent on rocks with high contents of iron sulphides poorly colonized by other lichens. It would seem likely therefore, that Rhizocarpon birgittae has some specific tolerance mechanism explaining its ability to colonize cupriferous substrata.

5.16. Rhizocarpon furfurosum Magnusson & Poelt

In Verh. zool. -bot. Ges. Wien 95: 110 (1955); type: Österreich, Hohe Tauer, Großarltal, Schwarze Wand, an steilen Felsflächen eines Kupferhaltigen Gesteins bei ± 1700m, July 1955, J. Poelt(not seen).

Rhizocarpon obscuratum (Ach.) Mass. f. granulosum Schade in Sber. Abh. naturw. Ges. Isis Dresd. 158 (1933).

Thallus crustose, thin to moderately thick, forming small radiating colonies, at first scabrid, becoming overall scurfy sorediate with prominent cracking into well defined areoles. Thallus cream-pale-fawn (sheltered, shaded situations) to violaceous deep brown (exposed sites), preceded by a paler or pale grey radiating prothallus. Apothecia rare, usually absent, sessile, black, with a roughened, flattened disc and prominent thalline margin. Epithecium black-brown. Spores (3-septate) sub-muriform, colourless (to pale brown), 14-24 x 7-12 µm, up to 8 cells in optical section.

Chemistry: I-, C- K+yellow, PD+orange. Stictic acid and

cryptostictic acid by TLC, constictic acid absent.

Distribution: Hitherto this species has only been recorded from the mining areas in the Harz, Erzgebirge, Schwarzwald and Eastern Alps where it is local. A further British,fertile collection has recently been collected: V.C.44, Carmarthen: SE. of Lampeter, Ogofau Gold Mines, 22/66-40-, locally abundant on sheltered, ± vertical rocks, July 1984, B.J. Coppins & R.G. Woods (Coppins 10273) (BM!, E!). Rhizocarpon furfurosum was designated a characteristic species of the Acarosporion sinopicae (Wirth 1972). It was recorded from Norway by Creveld (1981), but this record is not confirmed by Santesson (1984). R. furfurosum is an easily overlooked species characterized by its almost continuous, purple-brown, scurfy-cracked thallus with paler areas when abraded and pale grey margin which is often ± fimbriate. Superficially the species resembles markedly sorediate specimens of certain Opegrapha spp., for example O. gyrocarpa and O. zonata, but differs from these both in its phycobiont and chemistry. The species is locally common at the Coniston site A where older parts of the thallus are readily colonized by Lecanora handelii and L. epanora. At site C Rhizocarpon furfurosum is present only as small, scattered areoles which are occasionally sorediate, a demonstration of the extreme variability found in this species.

5.17. Stereocaulon symphycheilum Lamb

Bot. Notiser 114: 271-274; type: Sweden, Lycksele Lappmark, par. Tarna, Hemavan (Björkfors), Syterbäcken, reg. subalp., alt. 450-480 m.s.m., on rocks beside river, 1959, V. Ahmadjian, 26 (FH,

holotype; UPS isotype, not seen).

Pseudopodetia sparingly branched, dorsiventrally flattened, ± prostrate to 1.5cm high, firmly attached to rock. Phyllocladia on upper side of pseudopodetium, grey-green, often concave with a grey-white, wavy and swollen margin. Soralia terminal, capitate. Tomentum lacking. Cephalodia dark brown to black with roughened surface (Stigonema), commonly on the undersurface of the pseudopodetia and on the substratum between basal phyllocladia. Apothecia terminal, rare.

Chemistry: C-, K-, Pd- or weakly yellow. Atranorin and lobaric acid by TLC.

Distribution: In Scandinavia Stereocaulon symphycheilum is considered to be typically a high mountain species, rare but probably overlooked (Krog et al. 1980). It has been reported elsewhere from Canada (Quebec), USA (Alaska) and USSR (Kamtchatka) but seems to be absent from the Alps and central Europe. The material collected (BM) from secondary copper minerals at Black Scar Workings is poorly developed, lacking well-defined terminal soralia. However, the characteristic phyllocladia with the darkened centres and the presence of lobaric acid and atranorin (PD-or weakly yellow) confirm the identity of this species. It is most likely to be confused with Stereocaulon vesuvianum which tends to be more erect and contains stictic acid and atranorin (PD+ orange). Additionally, S. symphycheilum often has basal, ± flattened phyllocladia which may bear soredia and are also frequently interspersed by cephalodia, these features are absent in S. vesuvianum. S.

symphycheilum may possibly have been overlooked in suitable habitats particularly where the pseudopodetia are not well developed, even though basal phyllocladia are present. In this state this species bears a resemblance to S. leucophaeopsis, particularly as both taxa contain lobaric acid. However, they may be distinguished by the more convex areole-like phyllocladia in S. leucophaeopsis whereas in S. symphycheilum they are thinner, more flattened and elevated squamule-like.

5.18. Toninia leucophaeopsis and Bilimbia tornensis

The Toninia leucophaeopsis complex includes two species, T. leucophaeopsis s. str. and Bilimbia tornensis. The latter species was included as a synonym of the former by Santesson (1984). However, detailed examination of these two closely related taxa reveals consistent differences, especially in their chemistries, spores and ecology (see Table 14) which are sufficient for the delimitation of two distinct taxa.

Lecidea leucophaeopsis was described by Nylander (loc. cit.) and transferred to Toninia by Th. Fries (loc. cit.), a present position which must be considered anomalous and untenable. Unlike other indisputable species of Toninia, both T. leucophaeopsis and Bilimbia tornensis have a distinctive chemistry of lobaric and stictic acids respectively. As these metabolites occur widely in certain sections of Sterecaulon, e.g. section Denudata Jatta (Lamb 1977), it seemed the two species under discussion might better be placed in Stereocaulon, even though they both lack pseudopodetia and cephalodia. Other characters which lend support to this

Table 14. Comparison between Stereocaulon leucophaeopsis and S. tornensis

Stereocaulon leucophaeopsis	Stereocaulon tornensis
Thallus areoles spreading, <1mm diam., with slightly tumid margins, darker central area remaining conspicuous especially when wet	Thallus areoles small, <0.5mm diam., with tumid, raised margins, darker central area small, sometimes obliterated even when wet
Soralia, when present, usually confined to the margins of the areoles	Soralia, when present, involving the whole surface of an areole
Thecium (80-)90-110µm high	Thecium 60-85(-100)µm high
Spores (25-)30-38(-40)x6-7µm rarely fusiform but often ± sub-clavate with one end ± tapered	Spores (18-)21-25(-30)x5-8µm regularly fusiform with equally rounded apices
T.L.C. atranorin, lobaric acid	T.L.C. atranorin, stictic and cryptostictic acids
On ± basic usually metalliferous rocks, rich in Cu, Mn, Pb & Zn, occasionally on calcareous substrata (lacking mineralization?). Absent from FeS_2-rich rocks	On pebbles in humid situations occasionally on FeS_2-rich rocks, but apparently absent from ± basic Cu-rich rocks and other heavily mineralized substrata
Rare and very local in western and central Norway, Sweden and central Europe; widespread but very local in hilly, mainly western areas in Britain	Widespread but rather local in the mountains of Norway and Sweden, Jan Mayen island. Recently recorded from Ben Lawers Britain

(Morphological and anatomical details contributed by P.W. James)

transfer are to be found in the thallus morphology, a tendency to form soralia, apothecial anatomy and in the choice of substratum.

In their form and anatomy, the areole-like structures of the thallus of Toninia leucophaeopsis and Bilimbia tornensis closely resemble the basal phyllocladia of the primary thallus of Stereocaulon vesuvianum and S. symphycheilum, having a somewhat tumid, pale or whitish margin and a plane to depressed, dark grey central area. This development is particularly apparent in Toninia leucophaeopsis; in Bilimbia tornensis the swollen margins tend to all but obliterate the darker central area of the areoles. Both species may become sorediate; in Toninia leucophaeopsis only the margins of the areoles are usually involved and such specimens then resemble an undescribed pseudopodetia-less species of Stereocaulon from Tasmania [Kantvilas & James, no. 384/81 (BM!)]. In Bilimbia tornensis individual areoles may dissolve into convex, finely granular soralia, somewhat resembling those of the apices of pseudopodetia of Stereocaulon pileatum. Soralia are of rather erratic appearance in both species, a feature in common with several species of Stereocaulon; soralia are probably unknown in Toninia.

The anatomy of the apothecia of Toninia leucophaeopsis and Bilimbia tornensis is very similar and resembles that of certain Stereocaulon spp., such as S. vesuvianum, S. lavicola and S. vulcani [in Sect. Denudata subsect. Denudata (Lamb 1977)]. All have simple, brown-capitate paraphyses, a well defined straw-coloured to brown hypothecium and septate, elongate-fusiform spores which are, like those of Toninia leucophaeopsis, sometimes attenuated towards

one end. In T. leucophaeopsis and Bilimbia tornensis the hypothecium is dark brown, opaque, K-, and lies above a paler brown area which extends into the excipulum proprium which is K+ rufous to red. A similar development has been observed in the immature fruits of Stereocaulon vesuvianum var. symphycheiloides Lamb (Vězda: Lich. sel.exs. 1281, BM!). True cephalodia appear to be absent in both species although blue-green algae are often abundantly present between the areoles.

In Britain Toninia leucophaeopsis is a local species but occurs on a wide range of predominantly Basic, metalliferous substrata rich in manganese, lead, zinc and copper minerals, but also occasionally on calcareous substrata. T. leucophaeopsis occurs in Scandinavia and central Europe in similar habitats. In contrast, Bilimbia tornensis is only known from Scandinavia and one British locality, notably in Scotland: V.C. 88, Breadalbane, Ben Lawers, c. 250m SE. of summit, 27/ 636 412 on small stones in turf area of late snow lie, 1160m, 16 June 1985, Coppins 10985 (E!, BM!). It is interesting to note that in Scandinavia B. tornensis is typically found on some small stones in gravelly soil in moist, north-facing situations and it may also occur in the vicinity of late snow patches where it can be locally abundant. Bilimbia tornensis does not occur in the more toxic, heavily mineralized substrata where Toninia leucophaeopsis frequently occurs. Bilimbia tornensis bears no similarity to Lecidea calcariella Nyl., Type: Fennia, Regio aboënsis, Pargas (=Parainen), Ersby, 1872, Fr. Elfvring (H-Nyl 18344!), as was indicated by Magnusson (1952); the specimen is on calcite.

From this evidence Mr. James and myself consider Toninia leucophaeopsis and Bilimbia tornensis to be distinct species both of which should be included in the genus Stereocaulon. The relevant new combinations are:

Stereocaulon leucophaeopsis (Nyl.) P. James & Purvis comb. nov.

Lecidea leucophaeopsis Nyl., Flora Jena 56: 20 (1873). Type: Scotland, Mid Perth, Ben Lawers, on walls, alt. 2500 ft., September 1871, J.M. Crombie (BM - holotype!) [TLC: lobaric acid and atranorin]. - Toninia leucophaeopsis (Nyl.) Th. Fr., Lich. Scand. 2: 334 (1874).

Bilimbia cambrica Wheldon, J. Bot., Lond. 58: 15 (1920). - Toninia cambrica (Wheldon) W. Watson J. Bot., Lond. 71: 329 (1933); type: on rocks of volcanic ash on Snowdon, above 3000 ft, Wheldon (BM!) [TLC.: lobaric acid and atranorin].

Stereocaulon tornensis (Magnusson) P. James & Purvis comb. nov.

Bilimbia tornensis Magnusson, Ark. Bot. 2: 144 (1952) Type: Sweden, Torne Lappmark, Jukkasjärvi par., Vassitjåkko towards Vassijaure, 1180m, July 1950, E. Dahl (UPS -isotypus!) [TLC: stictic acid and atranorin].

Toninia leucophaeopsis f. farinosa Havaas, Univ. Bergen Årb. 12: 20 (1954). 'Exsiccatum: Havaas Lich. norv. occ. 250 (BM!) [TLC: stictic acid and atranorin].

CHAPTER 6. OBSERVATIONS ON METAL UPTAKE AND WEATHERING BY LICHENS WITH SPECIAL REFERENCE TO CUPRIFEROUS SUBSTRATA

6.1. Introduction

The aim of section 6.2 is to account for the special green coloration observed in several copper-rich lichens or ecotypes containing norstictic acid, which occur on cupriferous substrata. The species considered include *Acarospora smaragdula*, *Aspicilia alpina*, *A. myrini*, *A.* cf. *simoënsis*, *A. subsorediza*, *Buellia aethalea*, *Lecidea lactea*, *L. lulensis*, *L. swartzioidea* (= *L. lactea*?) and *L. umbonella*. Because of the association of copper with norstictic acid in these lichens, it was tentatively suggested that complexing of copper by norstictic acid could occur (Purvis *et al.* 1985, see appendix). However, in order to ascertain whether or not such a complex is present in the lichens, it is necessary to make a comparison by X-ray diffraction and infra-red spectroscopy of the lichen material and a synthetic norstictic acid complex of known composition. A Cu-norstictic acid complex has been prepared by Dr J.A. Elix according to the method outlined in section 6.2.1.d and this has enabled a comparison to be made.

During this study, other lichens have been discovered at Gjersvik and Røros which do not contain norstictic acid, but can become partly green in colour when growing on cupriferous substrata (section 6.2.2). Yet other lichens have been found which do not become yellow-green in colour when growing on these substrata (section 6.2.3).

Two lichens have been observed to cause a discoloration of the rock surface, notably Aspicilia mashiginensis overgrowing a thin surface precipitate of a secondary copper mineral and Lecidea lactea colonizing the Ultrabasic rock dunite. These phenomena are briefly considered in section 6.3.

Several techniques have been employed in this study, including the use of polarized light in optical microscopy, morphological examination by SEM, qualitative analyses by EPMA, quantitative analyses by ICP and also XRD and IR analyses, according to the methods outlined in chapter 2.

6.2. Metal uptake by specific lichens in copper-rich environments

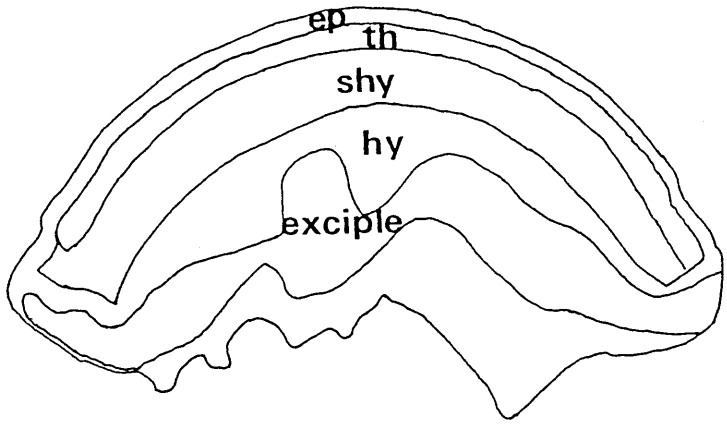
6.2.1. Cu-rich lichens containing norstictic acid

6.2.1.a Observation of lichen sections in polarized light

The upper cortex, ranging from 15 to 30μm thick in sections of the Cu-rich ecotypes of Acarospora smaragdula, Aspicilia alpina and Lecidea lactea, typically appears as a distinct, brownish to yellowish green band (birefringent) between crossed polars (Plate 14). In contrast, the rest of the lichen sections, in particular the algal zone, remains in extinction (uniform darkness), though the medullary region may show some slight birefringence and appear brownish grey between crossed polars. When the polars are crossed the planes of vibration of the analyser and polariser are at right angles to each other. Extinction occurs (uniform darkness) unless

PLATE 14.

The use of polarized light as an indication of crystallinity in sections of the Cu-rich ecotypes of Lecidella bullata (Gjersvik) and Acarospora smaragdula (Alstrup 77899). See accompanying diagram to identify specific apothecial regions discussed.



A. Apothecial section of Lecidella bullata in transmitted, plane polarized light. Scale = c. 400µm. Note the dark hypothecium (hy) and epithecium (ep).

B. Thallus section of Acarospora smaragdula in transmitted, plane polarized light. Scale = c. 120µm. Note the dark appearance; the section is thick.

C. View as A, between crossed polars. Note the birefringent hypothecium (hy) and epithecium (ep) whereas the thecium (th) and subhymenium (shy) are in extinction.

D. View as B, between crossed polars. Note the cortex (1) which appears as a strongly birefringent band.

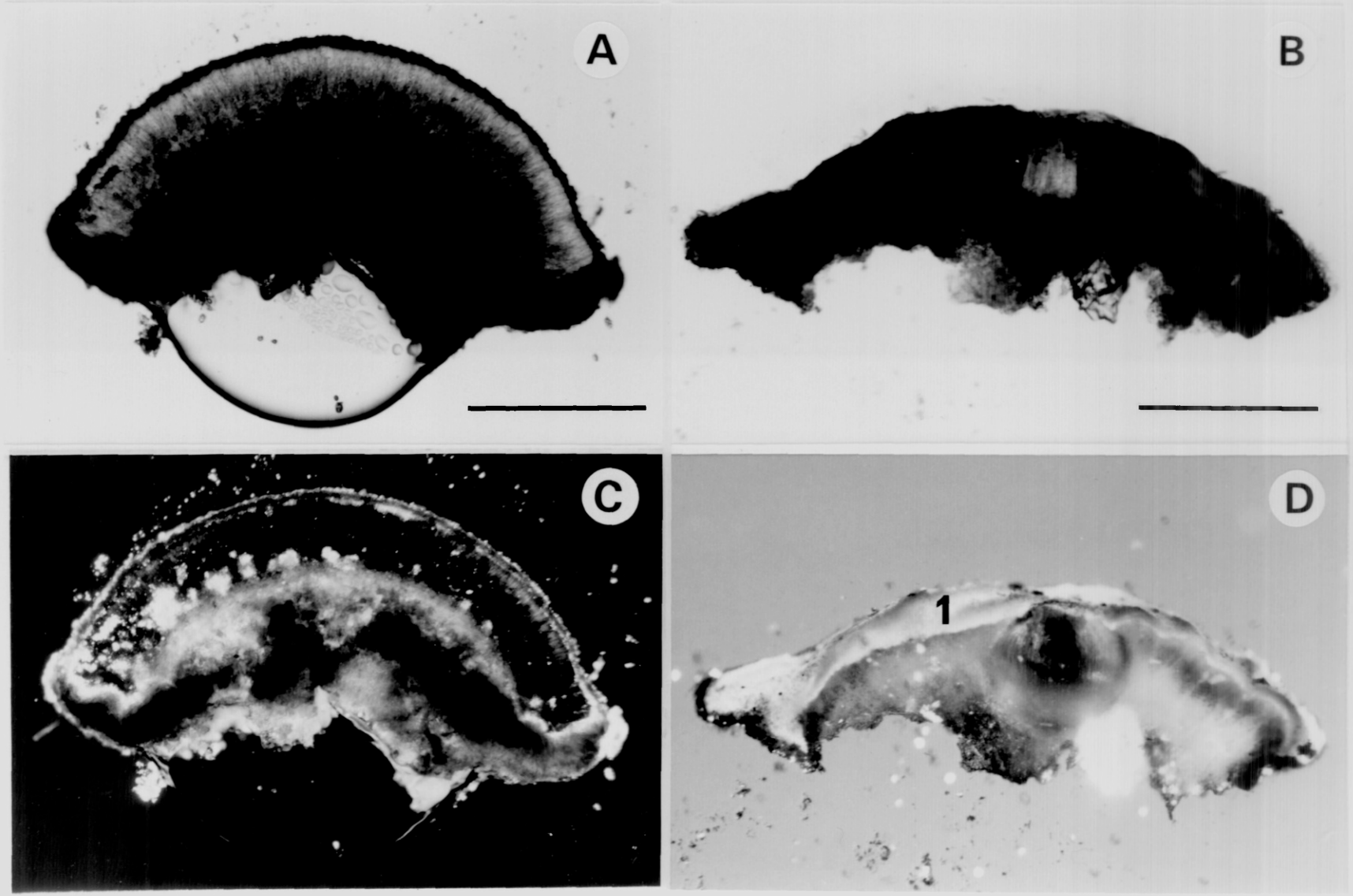
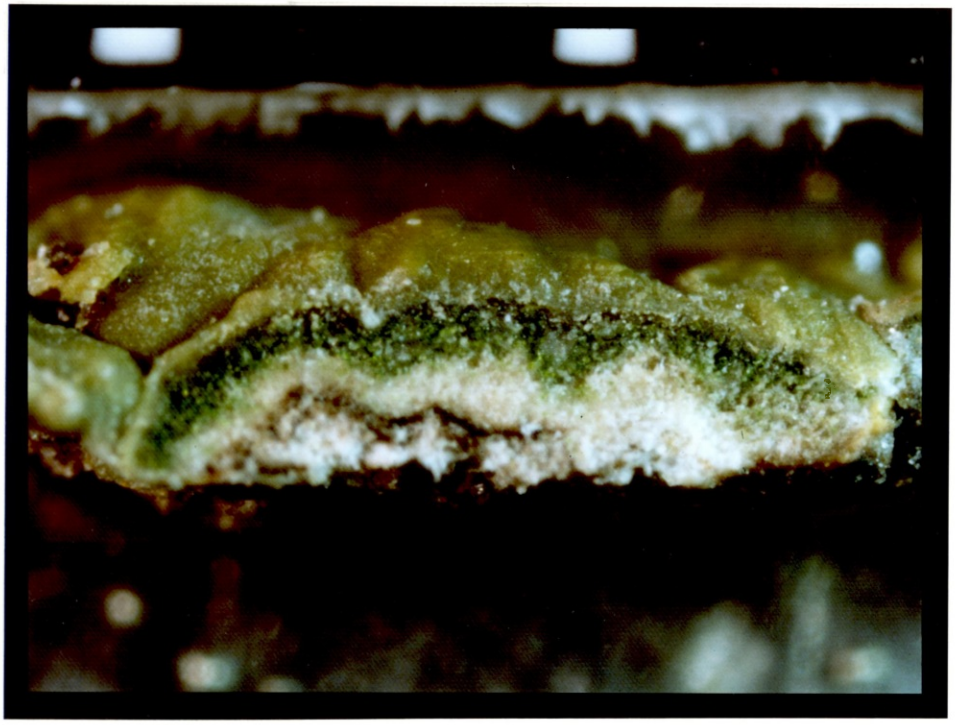

A
B
C
D
1

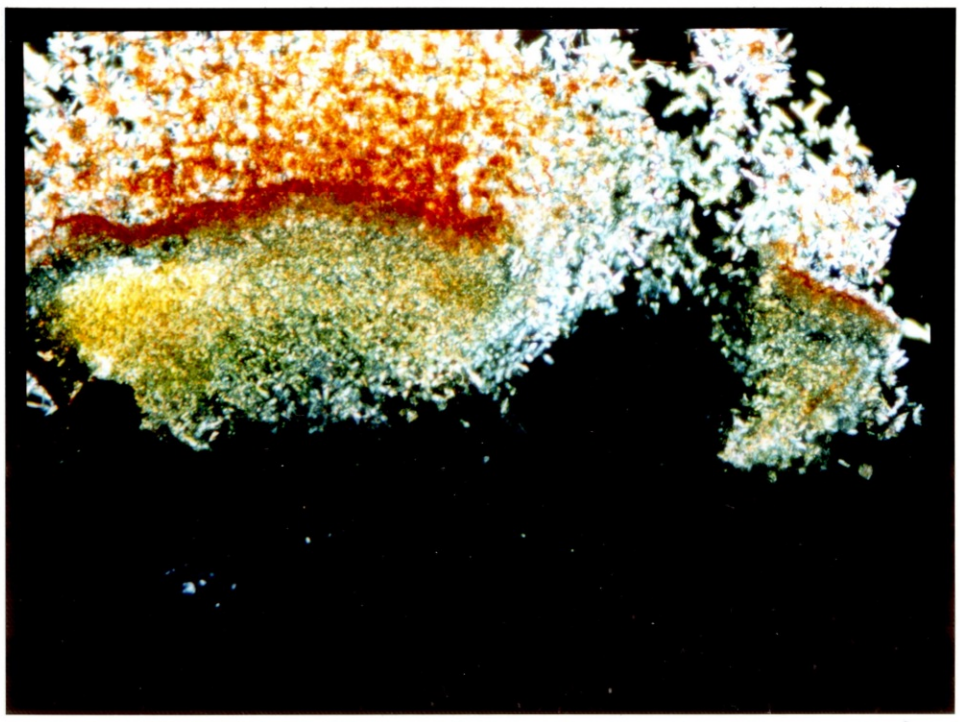
PLATE 15.

A. Section of Cu-rich ecotype of Acarospora smaragdula (Alstrup 77899) in reflected light. Note the surface pale green Cu-rich cortex with thicker, darker green algal layer below. Scale in mm.

B. Squashed section of above in KOH, transmitted light between crossed polars. Note the needle-shaped crystals arising from the cortex which has turned red. Scale = 200µm.



A



B

the field is occupied by an anisotropic mineral which has a regular structure, but which does not crystallize in the isometric system. In the upper cortex of the lichens, interference colours are produced as a result of birefringence and interference between the two rays of light which emerge from the analyser. By this means, it is demonstrable that the cortical region in the Cu-rich ecotypes is crystalline and anisotropic. On the basis of the less obvious interference colours observed in the same lichens collected from substrata lacking Cu, it is evident that the cortical region in the Cu-rich ecotypes is more crystalline than the cortices of lichens from substrata lacking copper.

Sections of both the Cu-rich ecotypes and the non-Cu-rich examples were irrigated with KOH which caused the cortex to turn bright red and red, acicular crystals form in this area alone (Plate 15B). The formation of this complex demonstrates that norstictic acid is restricted to the upper cortex of these lichens.

6.2.1.b Morphological examination of lichens in the SEM

Specimens of Acarospora smaragdula, Aspicilia alpina and Lecidea lactea, including both Cu-rich ecotypes and examples from non-cupriferous substrata were fractured to expose in section the lichen cortex and medulla and sputter-coated with Au/Pd. At low magnifications (<1000x), the cortex of all the lichens is weakly cellular (prosoplectenchymatous) in nature and has a sharp boundary with the underlying algal zone and medulla (Plates 16A, C and 17A). At higher magnifications c. 10,000x, the matrix surrounding the hyphae within the upper cortex of the Cu-rich ecotypes appears very

PLATE 16.

SEM micrographs of cortices of Cu-rich and non-Cu-rich Acarospora smaragdula.

A. T.S. of thallus, non-Cu-rich material (James, Tiree Golf Course 9.4.1983, BM). Scale = 75µm. Note upper, well-delimited, dense cortex (1) with more lax tissues beneath.

B. Close-up of cortex in A. Scale = 2.31µm. Note poorly defined crystals (norstictic acid) surrounding hyphal lumena.

C. T.S. of cortex (1) and algal zone (2), Cu-rich material (Alstrup 77899). Scale = 30µm. Note similarity with A.

D. Close-up of cortex in C immediately below thallus surface. Scale = 3µm. Note the uneven, ± botryoidal appearance.

E. Close-up of a cortical hypha in C coated with extracellular, elongated crystals (Cu-norstictic acid complex?). Scale = 3µm.

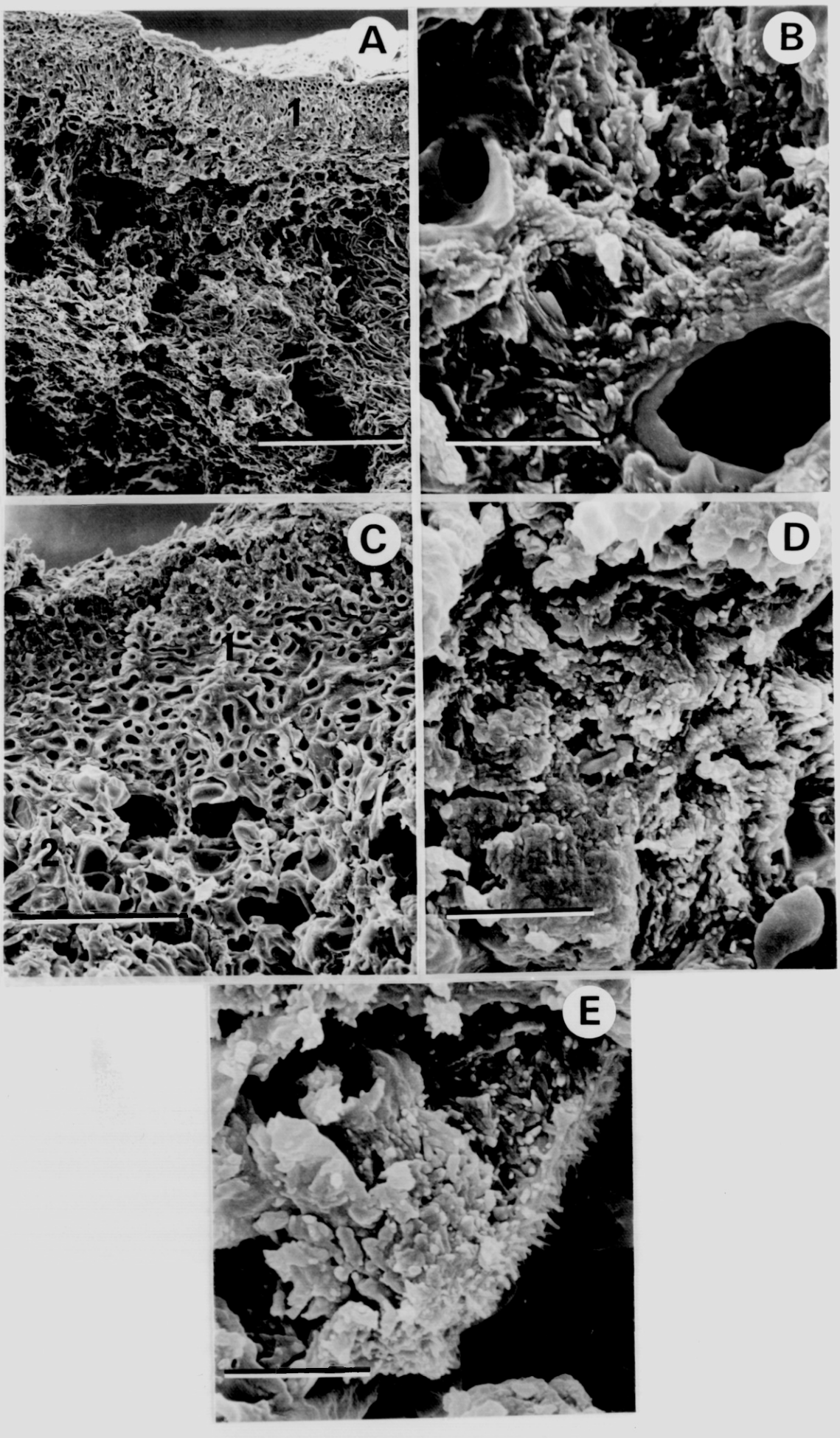

A
1
B
C
1
2
D
E

PLATE 17.

SEM micrographs of Cu-rich Aspicilia alpina, Lecidea lactea and non-Cu-rich Aspicilia alpina.

A. T.S. of cortex (1) and algal zone (2) of Cu-rich A. alpina (Ramundberget). Scale = 20μm. Note dense nature of cortex.

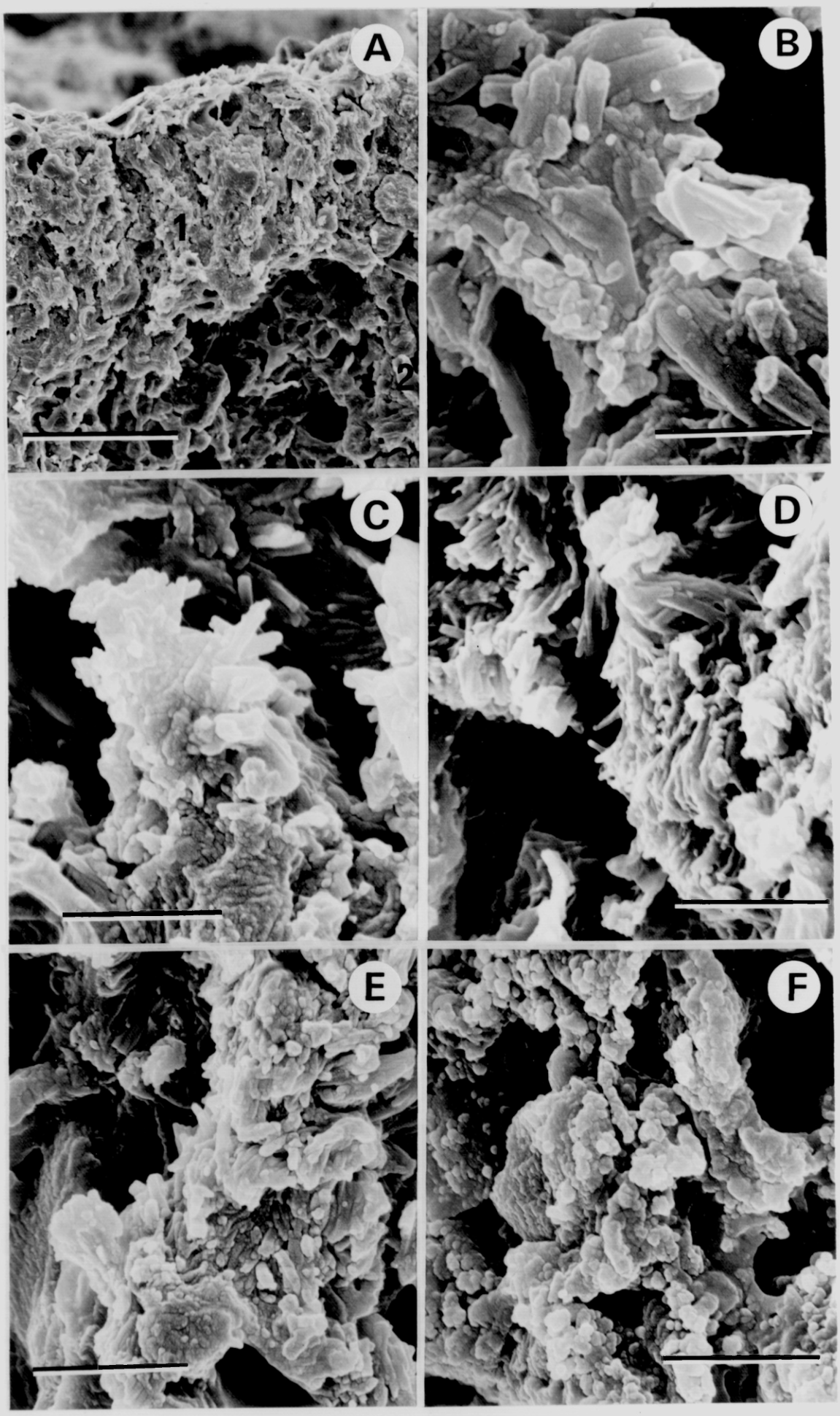
B. Close-up of cortical crystals (Cu-norstictic acid complex?) in A. Scale = 1.5μm. Note their predominantly anhedral, tabular appearance.

C. Close-up of cortical crystals (Cu-norstictic acid complex?) in A. Scale = 2μm. Note that some crystals appear elongated, others ± plate-like.

D. Close-up of cortical crystals (norstictic acid) in non-Cu-rich A. alpina (Ramundberget). Scale = 1.5μm. Note the anhedral crystals have a tendency to be elongated.

E. Close-up of cortex of Cu-rich L. lactea (Gjersvik). Scale = 3μm. Note the variety of crystal morphology.

F. Close-up of pruina on the exciple of Cu-rich L. lactea (Røros). See Plate 11A. Scale = 2.31μm. Note the ± botryoidal appearance.


A
1
2
B
C
D
E
F

uneven and often ± botryoidal (e.g. Plate 16D). The green pruina observed on the exciple of Cu-rich Lecidea lactea is similarly botryoidal (Plate 17F). Occasionally thin, c. 0.1μm thick, elongated crystals are apparent within the cortices of these lichens (Plates 16E, 17C and E). In other cases, anhedral, tabular crystals (<1.5μm diam) or even thin, plate-like crystals may occur in the same section (Plates 17B, C and E). Thus, whilst the cortex of the Cu-rich ecotypes contains abundant crystalline material, the form and aggregation are very variable. In contrast, the cortices of specimens of the same lichens from non-cupriferous substrata are less obviously crystalline, thus confirming the observations made in polarized light. However, this is a variable feature and abundant, typically anhedral crystals with a tendency to be elongated, have been observed in the cortex of a specimen of Aspicilia alpina from Ramundberget (Plate 17D). In the absence of other evidence (see below), since norstictic acid is known to be localized in the cortex of these lichens (section 6.2.1.a), it would be reasonable to assume that the cortical crystals observed in these lichens are of norstictic acid. Owing to the poorly defined nature of the crystals occurring in the cortices of the Cu-rich and non-Cu-rich examples of Acarospora smaragdula, Aspicilia alpina and Lecidea lactea, it is difficult to comment on the significance of their morphology. It is interesting to note that the crystals of norstictic acid in Usnea strigosa growing in culture have a predominantly plate-like morphology (Ahmadjian & Jacobs 1985) which was rare in the norstictic acid-containing lichens examined in this study. However, it is well known that the crystal habit of a mineral species is determined by a large number of environmental factors. Therefore, variation in habit should not

necessarily be taken to infer a different chemical composition.

Large crystals, c. 5μm diam. of calcium oxalate are widespread in most specimens of Acarospora smaragdula, Aspicilia alpina and Lecidea lactea examined, which are responsible for the slight birefringence noted under crossed polars (section 6.2.1.a). Plate-like crystals of copper oxalate have also been found in Lecidea lactea, but not in Acarospora smaragdula or Aspicilia alpina (Purvis 1984, see appendix).

6.2.1.c Electron probe microanalysis of lichen thalli

Lecidea lactea collected from Gjersvik at site 3 (section 4.2.3.a) was sectioned together with its immediate substratum, embedded in an epoxy resin, ground and polished to a flat surface and carbon-coated. Almost one complete areole and part of another areole of L. lactea are visible in the back-scattered electron image shown in Plate 18A. The image shows areas of contrast indicative of differences in composition. The majority of the medulla has a higher average atomic number than other regions of the lichen thallus. In addition, the rock substratum has a higher average atomic number than the cortex and upper medullary regions of the main areole. The paler medullary area visible in the back-scattered electron image is pale blue in colour (Plate 19B) and confirmation of the copper-rich nature of this area was obtained by X-ray mapping (Plate 18B). Lesser amounts of Si, which is mainly confined to the underlying substratum, were also detected in the medulla (Plate 18D) together with Ca (Plate 18C). The copper present within the medulla has been shown to be in the form of

PLATE 18.

Back-scattered images (A & E) and X-ray maps (B-D) of Cu-rich Lecidea lactea (Gjersvik) embedded in resin. See Plate 19B. Scale = 250μm.

A. T.S. of almost an entire areole (1) in contact with the underlying rock substratum (2). Note the difference in contrast within the areole.

B. Cu Kα X-ray distribution map of area shown in E. Note the concentration of Cu within the lichen thallus.

C. Ca Kα X-ray distribution map of area shown in E. Note the localization of Ca within the lichen thallus.

D. Si Kα X-ray distribution map of area shown in E. Note the predominant localization of Si within the rock substratum and particles within the lichen.

E. Close-up of lichen medulla and underlying rock substratum shown in A. Scale = 100μm. Note the correspondance of areas of high contrast with the X-ray distribution maps in B-D.

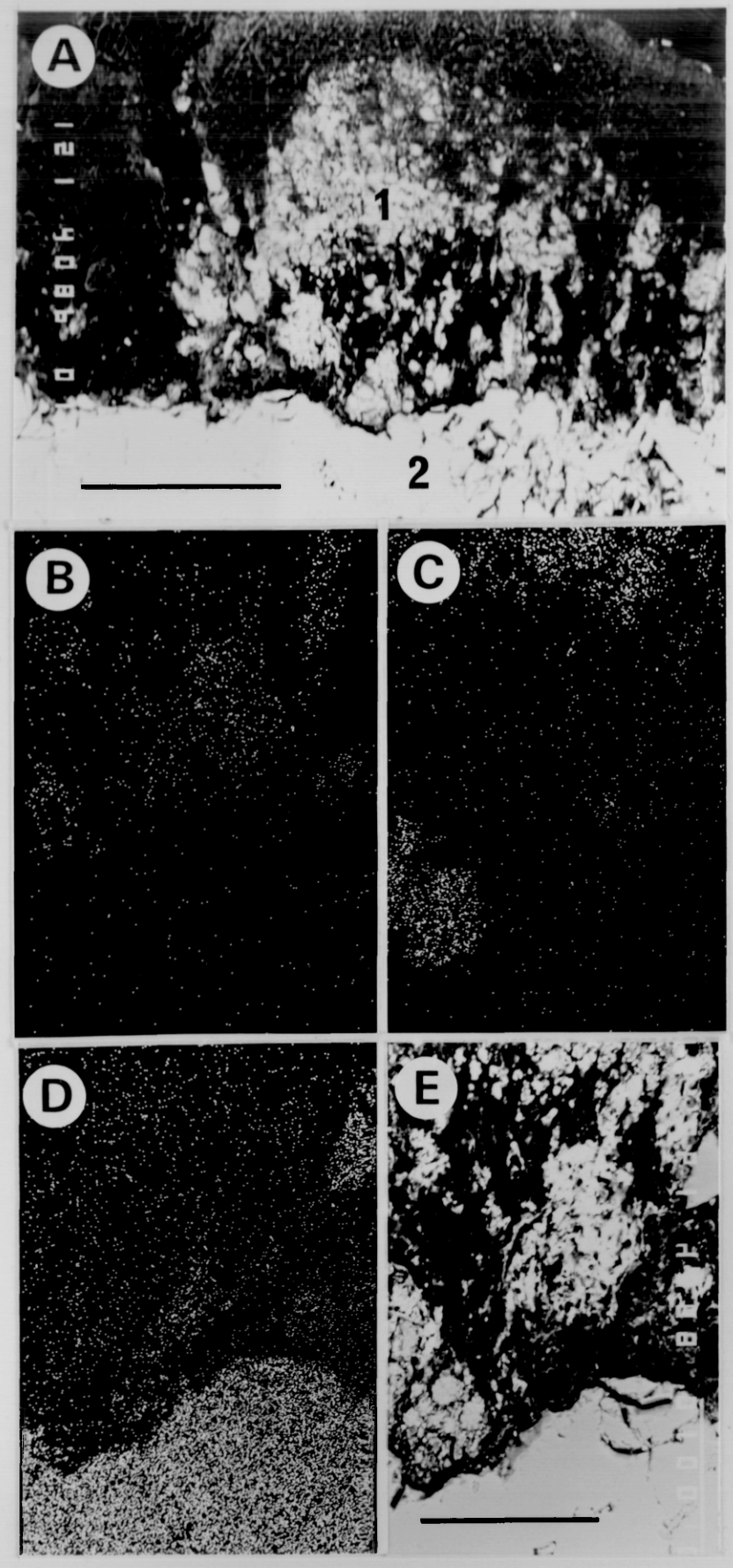

A
1
2
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E

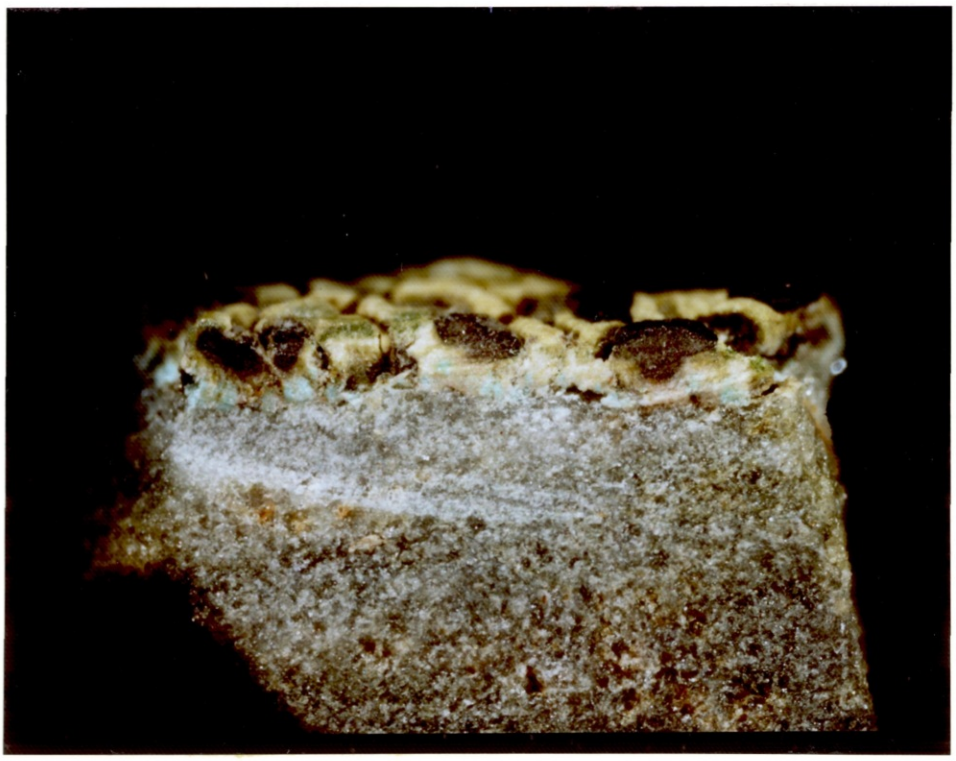
PLATE 19.

A. Section of an apothecium of Cu-rich Lecidella bullata (Gjersvik) in reflected light. Scale = 0.5mm. Note surface green, Cu-rich pruina and green, Cu-rich internal area (hypothecium). In contrast, the underlying thallus is white in colour.

B. Section of Cu-rich Lecidea lactea (Gjersvik) and substratum. Scale = 3mm. Note blue-green inclusions of copper oxalate at rock-lichen interface within the medulla.



A



B

copper oxalate and the calcium as calcium oxalate (whewellite) (Purvis 1984). The presence of silica within the lichen is partly due to the incorporation of siliceous fragments, largely quartz and also probably due to a small amount of redistribution during the grinding and polishing procedure.

There is also a slight difference in average atomic number between the cortex, c. 15μm thick and the underlying upper part of the medulla (Plate 18A). However, the cortex is not so bright as the major part of the medulla. Confirmation of the Cu-rich nature of the cortex, accounting for the difference in contrast in the back-scattered electron image, was obtained by spot analyses using EPMA. X-ray mapping studies with the Jeol 733 failed to demonstrate a localization of copper in this area, unlike in the case of the medulla rich in copper oxalate. This observation indicates that the level of copper in the cortex is substantially less than that occurring in the medulla and below the detection limits for X-ray mapping using the Jeol 733 microprobe.

As in the case of Lecidea lactea, the cortex in copper-rich ecotypes of Aspicilia alpina and Acarospora smaragdula is also Cu-rich, though copper oxalate was not detected in these species.

6.2.1.d Synthesis of a Cu-norstictic acid complex

A complex has been prepared by Dr J.A. Elix with a purity sufficient to allow comparison with natural materials derived from the cortices of several Cu-rich lichens. The complex was prepared

(Elix in litt.) by reaction between $Cu(CH_3COO)_2.H_2O$ and norstictic acid in the molar ratio 1:2 in warm N,N dimethylformamide (dmf). The reaction was not immediate, but overnight a low yield of a yellow-green, solid precipitate was formed. This was cleaned by washing with dmf and then with ether. Crystallinity was demonstrated by XRD. Analysis of the precipitate indicated a formula $Cu_2L_3.dmf$ where L = norstictic acid. Calculated for $Cu_2(C_{54}H_{32}O_{27}).C_3H_7NO$ C, 52.2; H, 3.0; N, 1.1; Cu,9.7. Found: C,49.3; H,3.2; N, 1.8; Cu, 9.8%.

The colour, analyses and IR spectrum obtained by Elix are consistent with the identification of the Cu complex as $Cu_2L_3.dmf$. Further work will be required to completely define the nature of the complex. It is possible that the synthetic complex is a mixture of several complexes of different structure or else some sort of polymeric complex. It is, however, unlikely to contain free norstictic acid. An attempt to prepare the complex using $CuCl_2.2H_2O$ was unsuccessful. The explanation for this is believed to lie in the need to deprotonate the phenolic groups before co-ordination.

6.2.1.e Infrared spectroscopy of Cu-rich lichen surfaces

Infrared spectra were obtained from scrapings of the thallus surface of the Cu-rich ecotype of *Acarospora smaragdula* (holotype of *A. isortoqensis*) and *Lecidea lactea* (coll. Gjersvik, site 3, section 4.2.3.a), using as standards, pure norstictic acid supplied by Dr J.A. Elix and a synthetic copper-norstictic acid complex (section 6.2.1.d). The spectra were recorded using the KBr disc technique over the range 4000-200 cm^{-1}. The significant region for

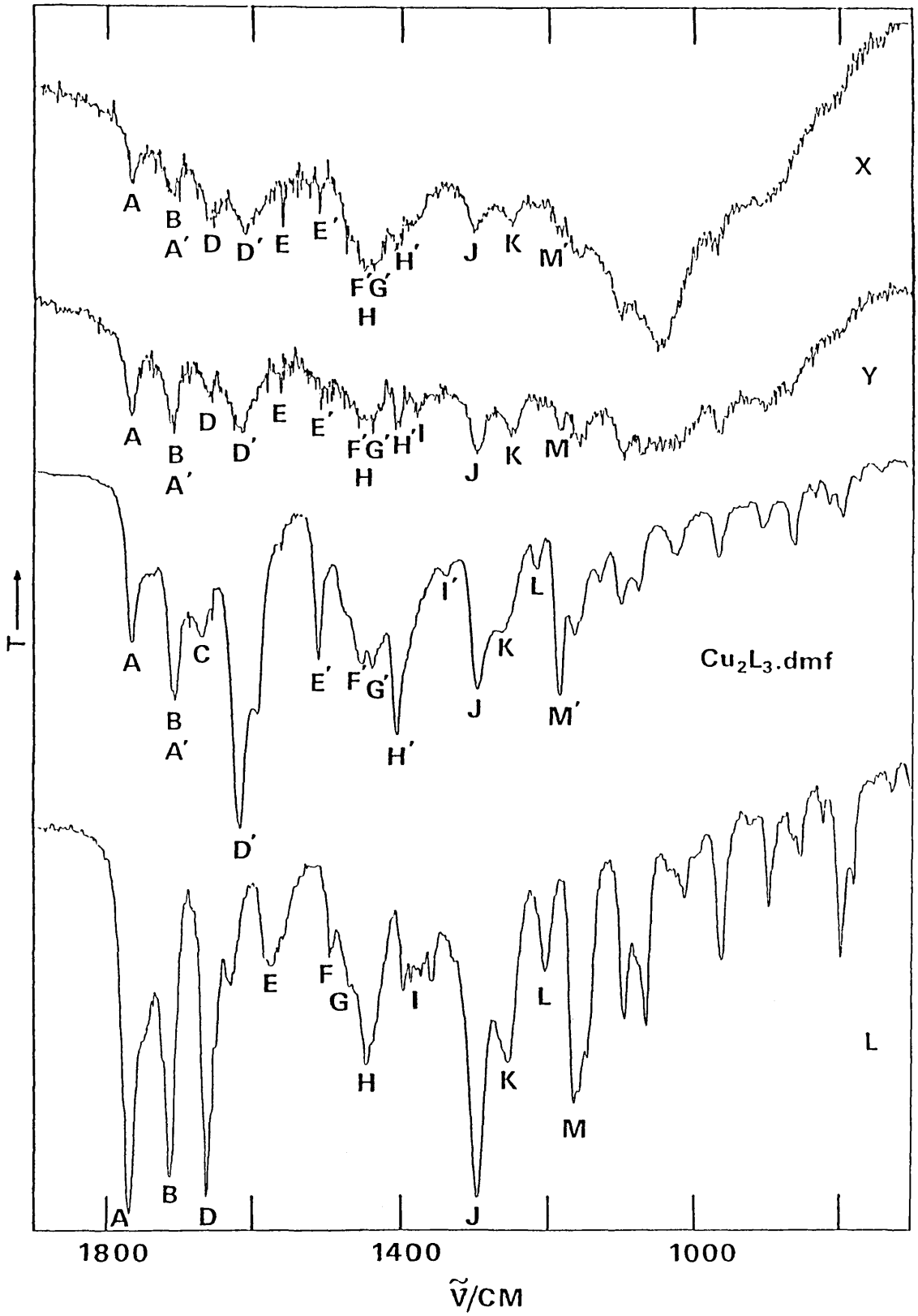


Fig. 4. IR absorbance spectra of norstictic acid (L), a synthetic Cu-norstictic acid complex (Cu_2L_3.dmf) and material from the Cu-rich cortices of the lichens X=Acarospora smaragdula (Alstrup 77899) and Y=Lecidea lactea (Gjersvik).

Table 15. A comparsion of IR absorbance values over region 1165-1770 cm^{-1} of L=norstictic acid, a synthetic complex Cu_2L_3.dmf, and material from the Cu-rich cortices of X=L. lactea and Y=A. smaragdula. Absorbance is quantified as s=strong, m=medium, w=weak or as sh=shoulder. Peaks correspond to those indicated in spectra, (Fig. 4.) the suffix ' indicates a possible shift in the complex from the value in L.

Peak	L	Cu_2L_3.dmf	X	Y
A	1770 s	1770 m	1770 m	1770 m
A'		1710 s	1710 s	1710 s
B	1715 s	1710 s	1710 s	1710 s
C	-	1670 w	-	-
D	1665 s		1660 m	1660 s
	1630 sh			
D'		1620 s	1615 s	1615 s
E	1575 m		1580 w	
	1565 sh			
	1560 sh		1560 w	1560 w
E'		1510 m	1510 w	1510 w
F	1495 sh			
G	1475 sh			
			1460 w	
F'		1455 w		
				1450 s
H	1445 m			
G'		1440 w	1440 w	
H'		1405 s	1405 m	1405 w
	1400 w			
	1385 w			
I			1380 w	
	1375 w			
	1360 w			
I'		1335 w		
J	1300 s	1295 s	1300 m	1300 w
K	1255 m	1260 sh	1250 m	1250 w
L	1205 m	1210 w		
M	1165 s	1180 s	1180 m	1180 w

comparative purposes, from 1800-800 cm^{-1} is shown in Fig. 4 and the absorbance values are tabulated in Table 15.

The IR spectra of the two lichen samples are weak, owing to the limited material available for analysis. However, in spite of the poor resolution, the spectra of both lichens are similar and also share similarities with the spectra of both the copper complex and norstictic acid. On the basis of similarity alone, peaks D', H' and possibly E', which are absent from norstictic acid but present in Cu_2L_3.dmf and the lichens, strongly suggest complexing of Cu by norstictic acid in the lichen samples. However, it is necessary to explain the significance of the IR bands and shifts to positively demonstrate the complexing of Cu by norstictic acid in these lichens. This has been possible by reference to data on absorbance values in the literature and also particularly from information supplied by Dr Elix.

Absorption bands due to the carbonyl region occur at 1780-1600 cm^{-1} in a variety of depsides and depsidones (Rao *et al.* 1967). Elix has suggested (diagram in litt.) that some of the C=O groups, probably the aldehyde and lactol carbonyls with adjacent OH groups in the benzene ring (Fig. 5) will be involved in the bonding of Cu in the complex. Because of possible variations in structure, it is reasonable to expect differences in the spectra of norstictic acid and Cu_2L_3.dmf to occur in this region. Peak D at 1665 cm^{-1} in L has shifted to 1620 cm^{-1} (D') in Cu_2L_3.dmf. It is believed that this peak corresponds to the aldehyde carbonyl, the absorption of which, according to Rao *et al.* (1967), occurs near 1650-1640 cm^{-1}. Further information may be obtained from an examination of the IR

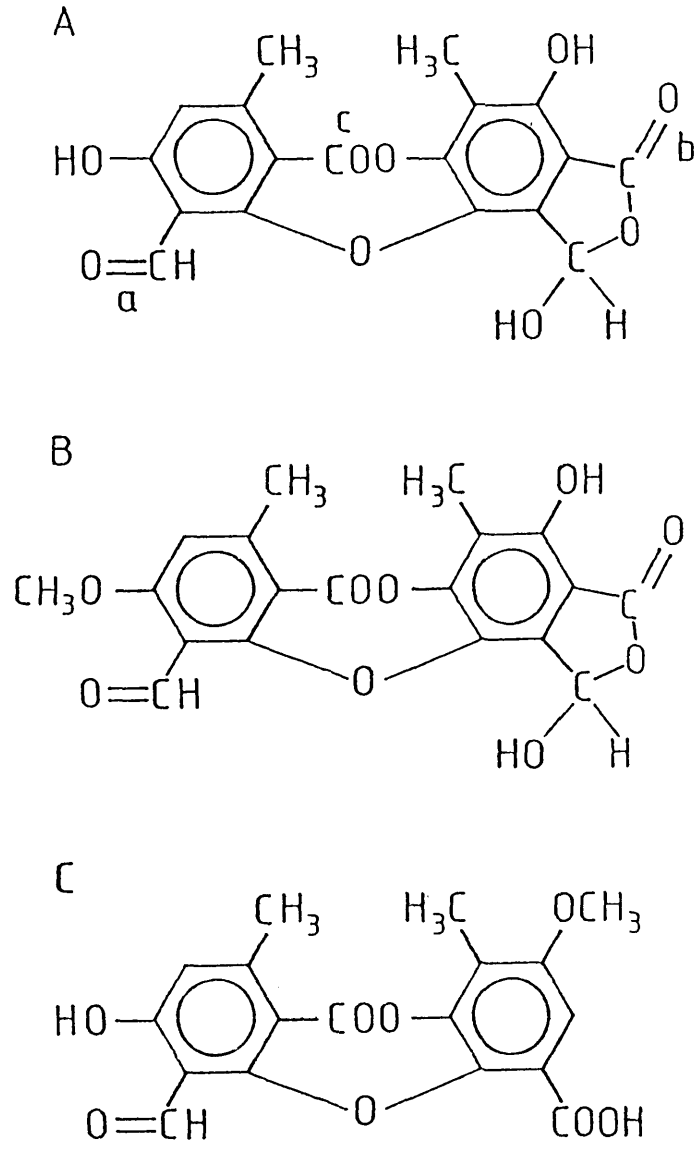


Fig. 5. Structurally related depsidones occurring in some lichens from cupriferous substrata. A=norstictic acid, B=stictic acid and C=psoromic acid. Aldehyde (a), lactol (b) and depsidone (c) carbonyl groups are identified in A.

spectrum of hypostictic acid, since this compound only contains a depsidone and lactol carbonyl group (Elix in litt.). Absorbance bands due to the lactol and depsidone carbonyl groups occur at 1750 cm^{-1} and at 1710 cm^{-1} respectively (Keogh 1978). It is reasonable to assume, therefore, that peak A (1770 cm^{-1}) and peak B (1710 cm^{-1}) correspond to the lactol and depsidone carbonyl groups. In view of these comparisons and the shift of peak D from 1665 cm^{-1} in norstictic acid to 1620 cm^{-1} (D') in Cu_2L_3.dmf, it appears certain that the complexing of Cu by norstictic acid involves the aldehyde carbonyl and adjacent hydroxy group. By analogy, an entirely similar situation exists in the lichen samples (Elix in litt.).

Peaks A (lactol C=O gp) and B (depsidone C=O gp) appear to be unshifted in the complex. However, it is the opinion of Dr Elix that in the complex, Cu_2L_3.dmf the lactol C=O does shift, in part from 1770 cm^{-1} to 1715 cm^{-1}, where it overlaps the depsidone C=O absorbance. The evidence for this is indicated by the relative intensities of the lactol vs depsidone C=O peaks. In free norstictic acid, the lactol peak is more intense than the depsidone, whereas in the complex (and the lichens) it is significantly less intense. This can be interpreted as indicating that at least in some molecules, the lactol carbonyl (and adjacent hydroxy group) are involved in complex formation. A situation involving the complexing of all aldehyde C=O, but only one third of the lactol C=O groups is envisaged (Fig. 6, Elix in litt.).

Looking empirically at the region 1600-1400 cm^{-1}, peak E (1575 cm^{-1}) in norstictic acid appears to have shifted to 1510 cm^{-1}

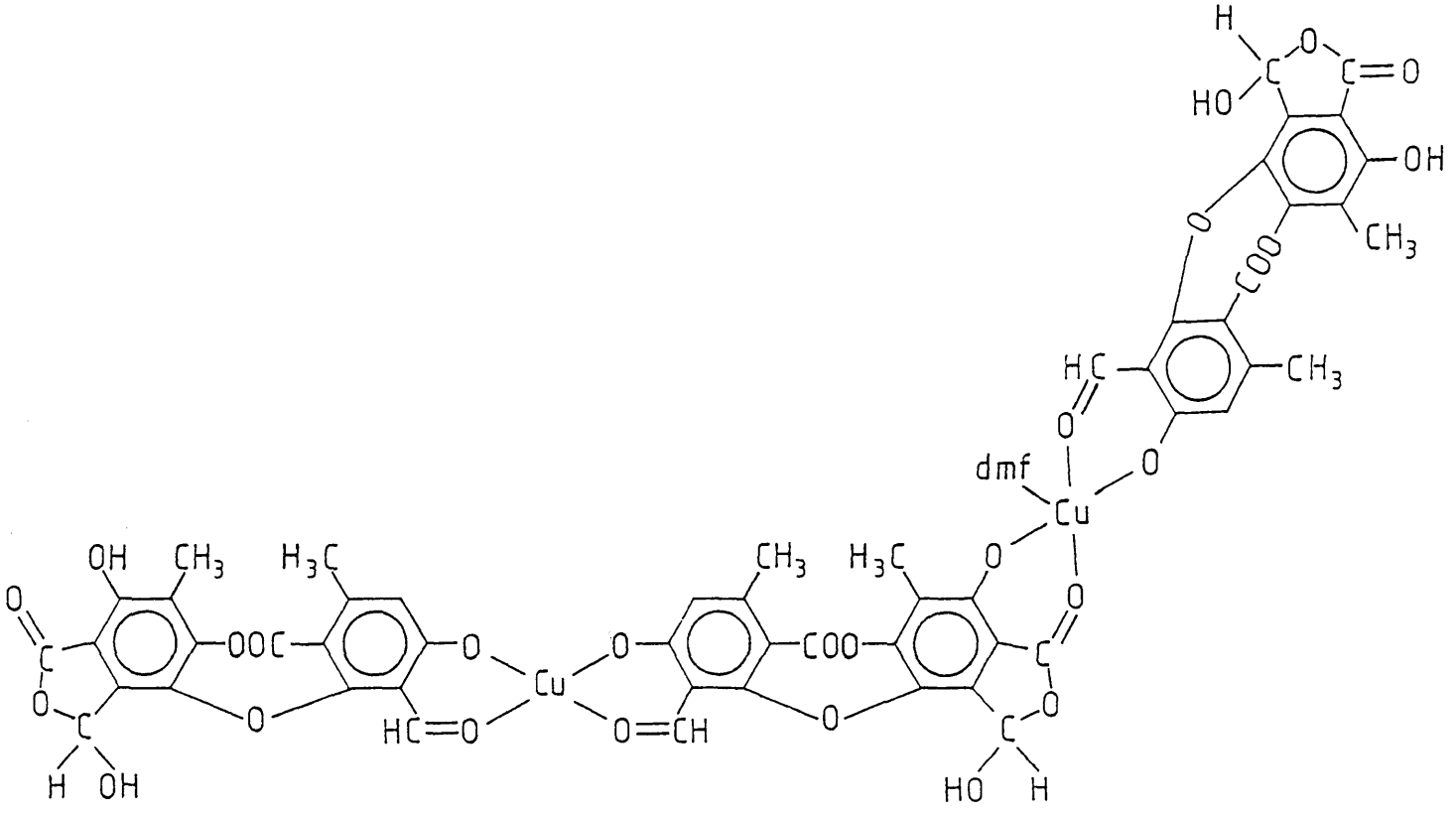


Fig. 6. Proposed structure of synthetic Cu-norstictic acid complex, Cu_2L_3.dmf, where L=norstictic acid and dmf=N,N dimethylformamide (Elix in litt.).

(E') in the complex, and peak H from 1445 cm^{-1} to 1405 cm^{-1} (H'). The other associated smaller peaks F, G and I appear also to have shifted in the complex. Full details of these absorbance values are given in the table. The reasons for these shifts remain to be interpreted.

6.2.1.f X-ray powder diffraction studies of Cu-rich lichen surfaces

Surface scrapings of the Cu-rich, norstictic acid-containing Acarospora smaragdula (A. isortoqensis holotype), Aspicilia alpina (coll. Gjersvik, site 1, section 4.2.3.a), Lecidea lactea (coll. Gjersvik, site 3, section 4.2.3.a) and control samples of norstictic acid supplied by Dr J. A. Elix and a synthetic Cu-norstictic acid complex prepared by Dr Elix (section 6.2.1.d) were studied using XRD. Measurements of the d-spacings and intensities of the patterns obtained are shown in Table 16 (Chisholm in litt.). In addition, data are also provided for the Cu-rich Lecidella bullata from Gjersvik which contains psoromic acid (see section 6.2.2). Caution is required in the interpretation of the powder patterns since it is unlikely that any of the lichen material is pure. Moreover, as there are no standard reference data available for matching d-spacings and intensities of the organic complexes involved, these results cannot be regarded as definitive. Organic phases themselves may be variable in chemistry or structural order. As a consequence, the d-spacings and intensities may themselves be variable and that makes comparison difficult.

With these qualifications Acarospora smaragdula, Aspicilia

Table 16. Summary of powder patterns: d-spacings (d) and intensities (I) of Cu-rich lichen cortices and synthetic materials.
N.B. Because of high diffuse scattering, all intensities are likely to be inaccurate. Chisholm, in litt. 22.7.85

4834		4707		4508		4401		4108		3946		
d	I	d	I	d	I	d	I	d	I	d	I	
11.8	15											
10.5	80					10.8	100			10.5	40	
9.6	45	9.72	100									
						9.0	100			9.3	40	
8.72	100											
		8.55	70	8.43	100			8.38	80	8.43	100	
7.78	15											
7.22	15					7.3	20					
								7.07	80			
		6.84	80	6.90	55					6.90	50	
6.00	10					5.99	15					
		5.44	60	5.45	70	5.38	70	5.55	45	5.46	40	
5.24	45											
		4.98	45									
4.77	30					4.84	wk					
		4.59	50	4.60	30	4.49	45	diffuse scatter		4.55	25	
4.34	25			4.23	35			4.25	25Q			
4.00	55	3.92	50	3.90	45	3.96	25	3.91	40	3.90	50	
3.66	25	3.69	40			3.66	40			3.68	40	
3.51	20							3.52	40			
3.38	65	3.40	75	3.40	40	3.39	45	3.35	100Q	3.40	70	
3.20	10			3.24	wk	3.20	20					
										3.15	15	
3.12	15	3.08	30									
3.04	15			3.01	wk	3.00	20	3.02	35	3.03	35	
Synthetic norstictic acid		Synthetic Cu complex		Acarospora smaragdula		Lecidella bullata		Aspicilia alpina Q = Quartz line		Lecidea lactea		

Diffuse scattering in region from about 5 to 4 Å on all patterns

alpina and Lecidea lactea and Elix's synthetic Cu complex appear to have a compound X in common. Even this is not conclusively established, as the match between the d-spacings is not very good by mineralogical standards. In particular, the strongest line of the synthetic Cu complex is not matched in the lichen material. Because the match is not exact, it follows that if there is a component X in common, that component is variable in its chemistry or structural state. The synthetic Cu-norstictic acid complex is not pure, but most likely to be a mixture of several Cu-norstictic acid complexes (Elix in litt.). X could therefore be one of these complexes (or even a mixture of them) and this would be evidence for the take-up of Cu as a norstictic acid complex, though that evidence is indirect and not wholly corroborated. The powder diffraction pattern of the sample of norstictic acid differs distinctly from that of Elix's Cu complex. The latter does not contain free norstictic acid (confirming Elix's view) as the strong 10.5 Å line of the free acid pattern is not observed on that of the synthetic complex. According to the powder patterns there is no free norstictic acid in the material from Aspicilia alpina or Acarospora smaragdula. The 10.5 and 9.3 Å lines of the Lecidea lactea pattern might come from the norstictic acid, but they could also come from Y of Lecidella bullata or even something else again (Chisholm in litt.).

6.2.1.g A comparison between IR and XRD data

XRD and IR are two complementary analytical methods. XRD is sensitive to the long-range periodic arrangements of atoms in a crystal lattice whereas the IR spectrum yields basic information

on the interatomic bonding. In most cases it can serve as a "fingerprint" to give proof of identity without recourse to other analytical methods, as no two compounds give exactly the same spectrum (Estep-Barnes 1977).

The fundamental differences between these two methods almost certainly account for the relatively poor match obtained between the synthetic complex and lichen material by XRD as compared with the IR results. Thus, it would appear that the absence of the strongest line of the synthetic complex in the lichen material might be explained by a fundamental difference in the arrangement of copper and norstictic acid moieties in the lichen material as compared with that of the complex (Chisholm pers. comm.). The IR spectra confirm that the complexing of Cu by norstictic acid is occurring in the lichens studied and also suggests that free norstictic acid may also be present. Whilst the IR spectrum of Acarospora smaragdula suggests the presence of the free acid, this is, however, unsubstantiated by XRD. This apparent contradiction might simply be explained by its absence in the sample analysed by XRD. TLC investigations of this specimen often failed to detect free norstictic acid. In conclusion, the results obtained by IR and XRD provide firm evidence to support the view, first suggested by field observations, that the critical factor in the formation of green, copper-rich surfaces in particular lichen species, depends on the existence of norstictic acid in the lichen thallus. However, it is desirable, from a chemical point of view, to have a fully characterized synthetic complex of known molecular formula with which to make comparisons.

6.2.2. Green coloration due to Cu in lichens without norstictic acid

Several other lichens have been found in this study including Lecanora polytropa, Lecidea arctogena and Lecidella bullata which contain different lichen acids and which may also become partially green in colour on cupriferous substrata. Lecidea arctogena was only observed once at Gjersvik (section 4.2.3.e), where its surface is stained yellow-green in patches, though the medulla is of a more even, pale green-yellow coloration. Lecidella bullata is locally wdiespread at Gjersvik where it has conspicuous green-yellow pruinose apothecia on a white thallus (Plate 12A). In addition, on sectioning the apothecia, the hypothecium is seen to be of a similar coloration as the surface pruina (Plate 19A). Both Lecidea arctogena and Lecidella bullata contain the depsidone psoromic acid, the latter species containing in addition 2'O demethylpsoromic acid, atranorin and zeorin. However, psoromic acid and its derivative are restricted to the hypothecium and the surface of the apothecia in L. bullata, as demonstrated by the yellow-orange colour reaction of sections with Pd, and further substantiated by TLC investigations. Lecanora polytropa may have dark green apothecia on cupriferous substrata and is fairly widely distributed, though the green colour of the discs is rather uneven (Plate 13A).

The green areas of all 3 lichens have in squashed sections been shown by EPMA to be rich in Cu (Fig. 7) and when examined by transmitted polarized light, interference colours are observed between crossed polars (Plates 14 and 23). In the SEM, the

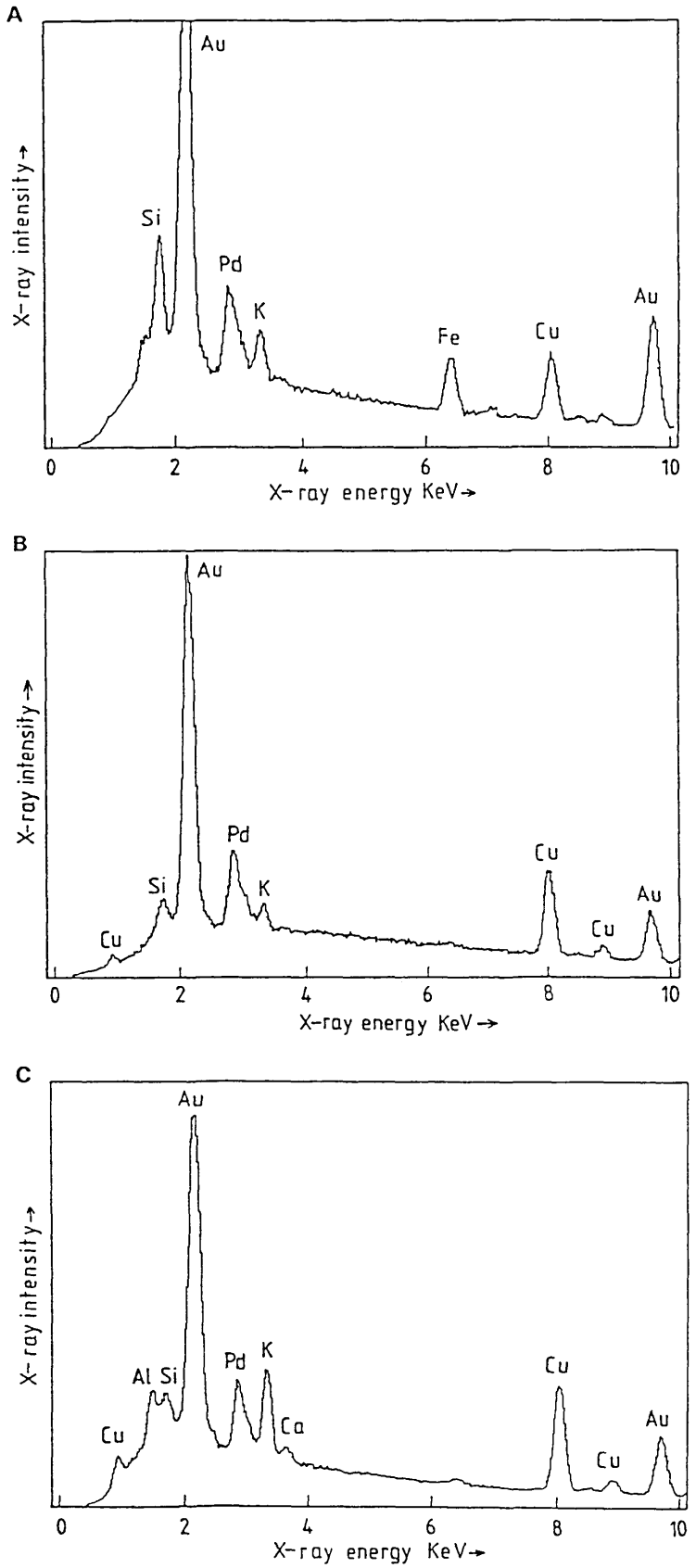


Fig. 7. X-ray spectra of some Cu-rich ecotypes. A. Lecanora polytropa (Røros, Plate 13A): spot analysis of discocarp surface. B. Lecidea arctogena (Gjersvik): spot analysis of thallus surface. C. Lecidella bullata (Gjersvik, Plate 12A): spot analysis of hypothecium. (Au/Pd coated)

PLATE 20.

SEM micrographs of sections of Cu-rich Lecidella bullata (Gjersvik). Secondary electron images are given above and back-scattered electron images below.

A. T.S. of apothecium. Scale = 430µm. Note the lax internal region (hypothecium).

B. Close-up of hypha in section within the hypothecium, encrusted in extracellular crystals (Cu-psoromic acid complex?). Scale = 1.5µm.

C. Close-up of hypha within the hypothecium, bearing numerous thread-like crystals (Cu-psoromic acid complex?). Scale = 2µm.

Note the poor contrast in the back-scattered electon images.

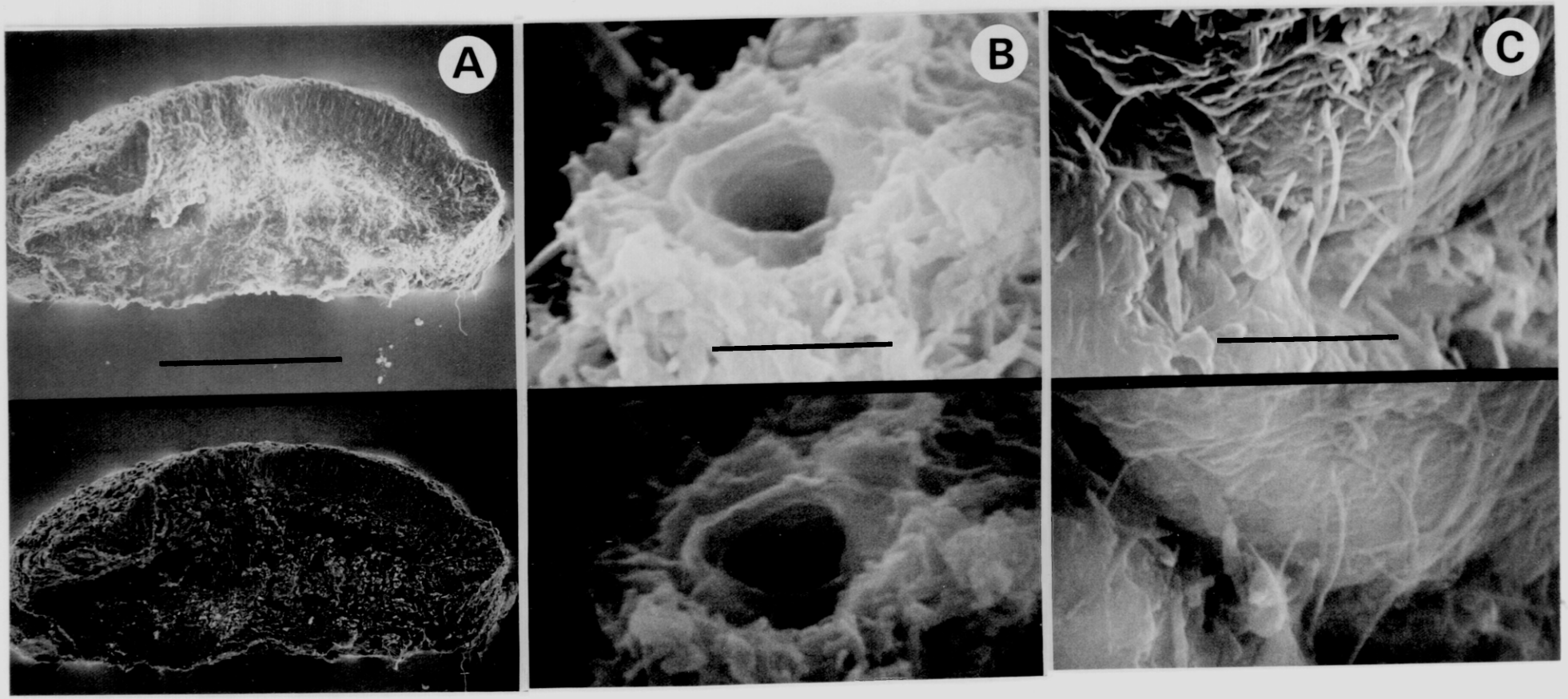

A
B
C

PLATE 21.

SEM micrographs of sections of non-Cu-rich Lecidella bullata (Gilbert, on boulder well into the late snow patch of Margaret's Coffin, Cairngorm, July 1982, BM).

A. T.S. of apothecium. Scale = 250µm. Note the lax internal region (hypothecium) and similarity with Plate 20A.

B. Close-up of hyphae in section within the hypothecium, encrusted in extracellular crystals (mainly psoromic acid). Scale = 1.5µm. cf. Plate 20B.

C. Close-up of thread-like crystals (mainly psoromic acid), coating a hypha in the hypothecium. Scale = 0.6µm, cf. Plate 20C.

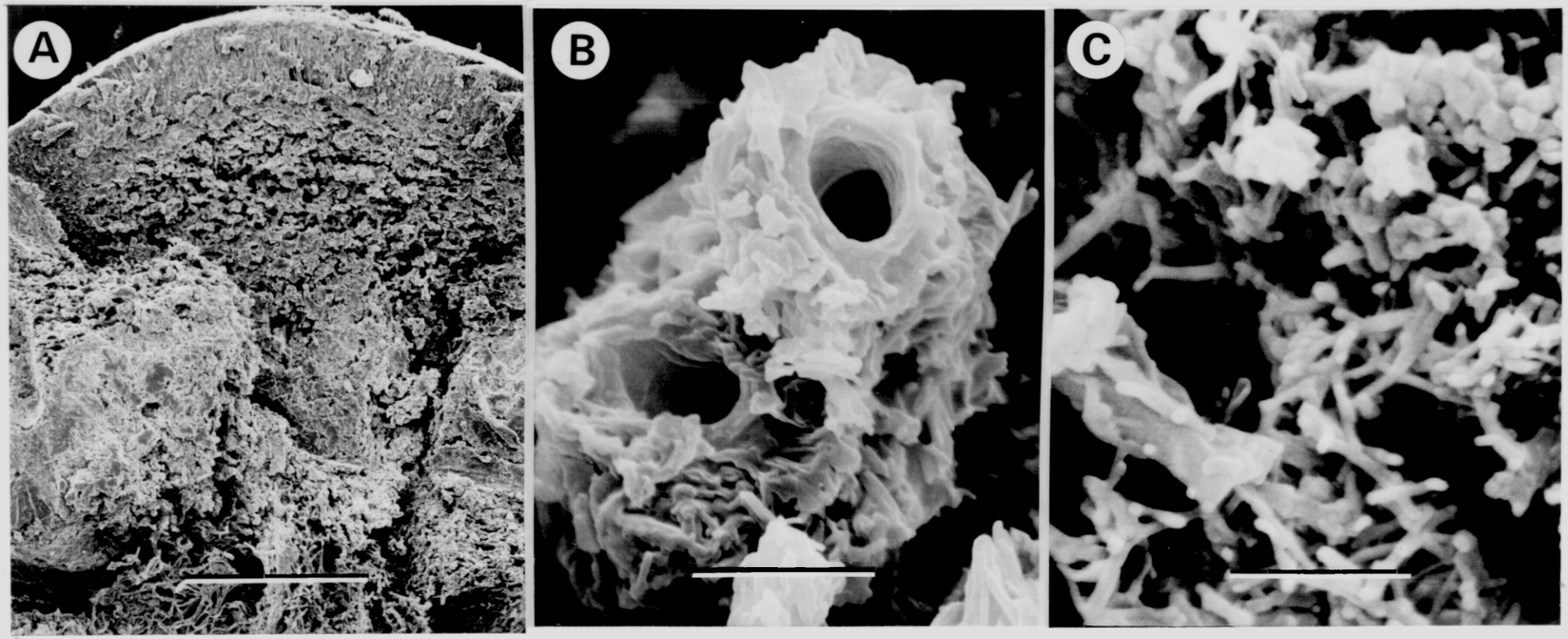

A
B
C

PLATE 22.

SEM micrographs of miscellaneous crystals etc. associated with lichens.

A. Medulla of Acarospora rugulosa (Ramundberget, Plate 10A) containing abundant plate-like crystals of copper oxalate. Scale = 15µm.

B. Close-up of a sectioned, medullary hypha in A, encrusted in extracellular crystals of copper oxalate. Scale = 1.5µm.

C. Crystals of gypsum occurring within Acarospora rugulosa (Gjersvik). Scale = 3µm.

D. Unidentified crystals occurring on apothecial surface of Cu-rich Lecanora polytropa (Røros). Scale = 3µm.

E. Amorphous silica coated in iron oxides, produced as a result of weathering by Lecidea lactea on dunite. Scale in mm.

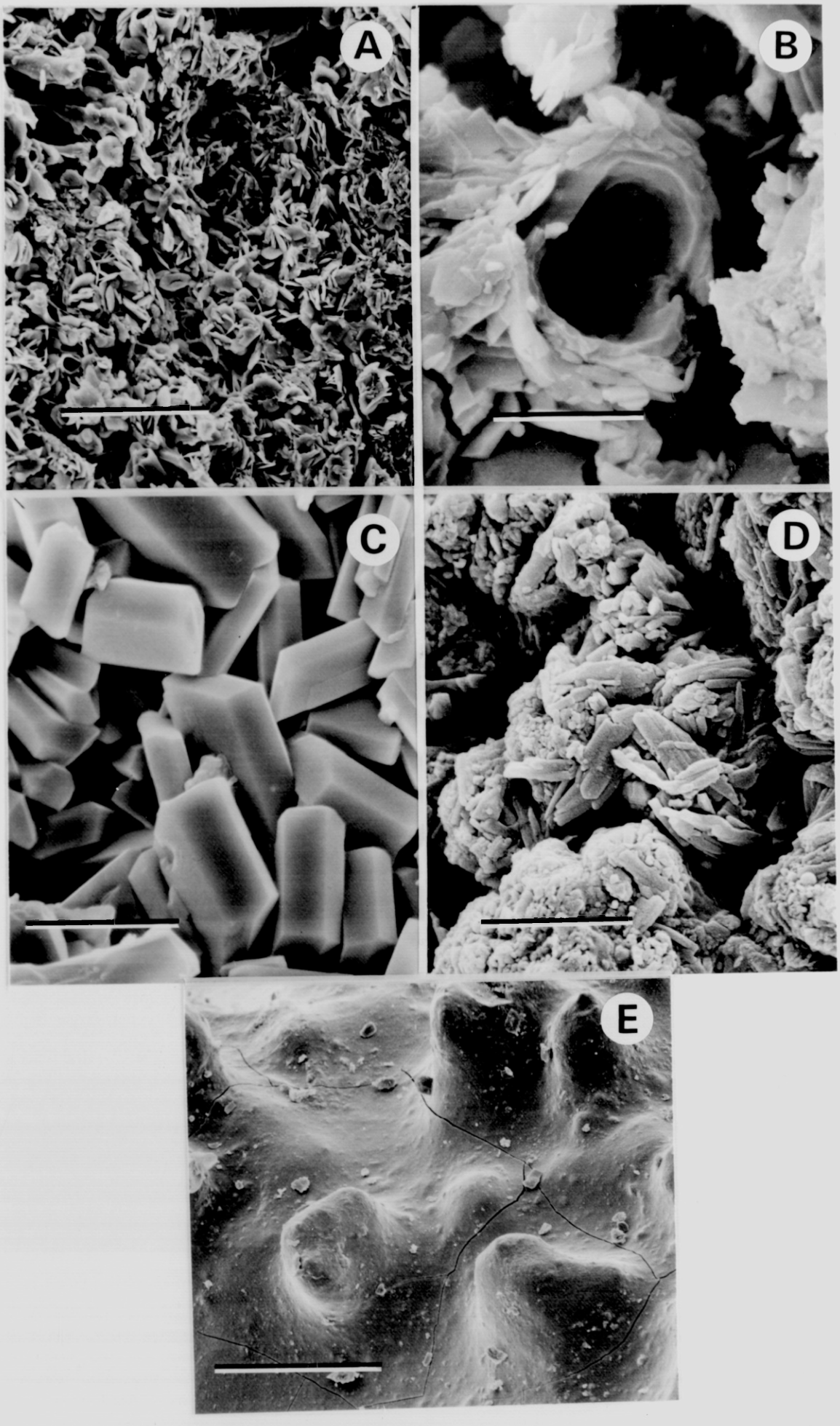
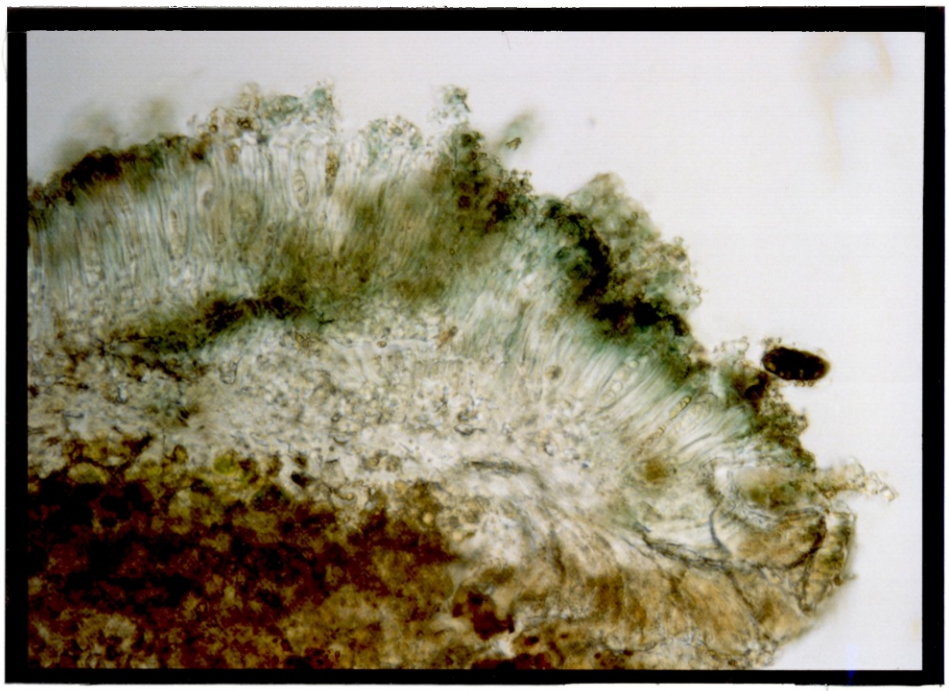

A
B
C
D
E

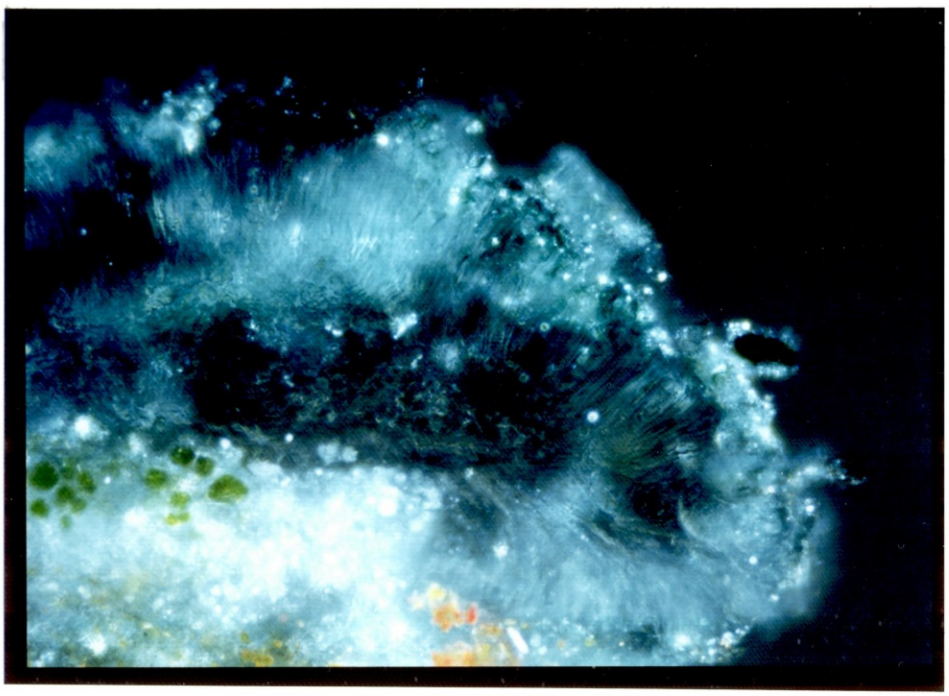
PLATE 23.

A. Squashed apothecial section of Cu-rich Lecanora polytropa (Røros, Plate 13) in transmitted, plane polarized light. Scale = 50μm. Note the green colour of the epithecium.

B. Squashed apothecial section of Cu-rich Lecanora polytropa (Røros) in transmitted light between crossed polars. Scale = 50μm. Note the coincidence of part of the birefringence with that of the green colour in A.



A



B

hypothecium of both Cu-rich and non-Cu-rich examples of Lecidella bullata is seen to consist of loose, randomly orientated hyphae bearing abundant, extracellular, thread-like crystals (Plates 20 and 21), which are poorly developed in the environment of the surface of the apothecia, where they give rise to pruinosity. Similar thread-like crystals have also been observed in the medulla of Lecidea arctogena. The XRD pattern of the hypothecial area of Cu-rich Lecidella bullata is different from those from norstictic acid-containing lichens (Table 16). In particular, the 8.72 Å strong line of norstictic acid is absent (Chisholm in litt.). IR spectra have not been obtained from this material. In Lecanora polytropa, irregular, more or less plate-like crystals have been observed on the apothecial surface in the SEM (Plate 22D) and these areas are rich in Cu, as demonstrated by EPMA using the Hitachi S-530 SEM. In apothecial sections mounted in water, the green coloration of the epithecium soon disappears as a green mist, suggesting that this compound is rather labile (Plate 23A). Its irregular occurrence and uneven nature would further substantiate this.

6.2.3. Lichen species not subject to colour changes on cupriferous substrata

There are several lichens, which although frequently associated with the green Cu-rich ecotypes, do not assume this coloration. These include Acarospora rugulosa (gyrophoric acid), Aspicilia cinereorufescens, A. mashiginensis (cf. constictic acid), Lecidea inops (perlatolic acid), Psilolechia leprosa (gyrophoric acid), Rhizocarpon birgittae and Stereocaulon leucophaeopsis

(atranorin and lobaric acid). Other less frequent associates include Huilia tuberculosa (confluentic acid), Lecidea atrofulva (stictic acid), L. auriculata (confluentic acid), L. lapicida (stictic acid), L. paupercula (stictic acid), Rhizocarpon geographicum (rhizocarpic acid) and Tremolecia atrata.

Two of these lichens, Acarospora rugulosa and Lecidea inops have been found to accumulate extracellular crystals of copper oxalate, which may be very conspicuous within the medulla of these lichens (Purvis 1984, Plate 22A and B). In fact a specimen of L. inops from Ramundberget (Santesson 24576 UPS!) has been found in this study to contain 16.1% Cu dry weight by ICP, corresponding to a copper oxalate content of c. 38%. Sections of Aspicilia mashiginensis collected from Gjersvik (section 4.2.3.c) were examined in the SEM and found to contain abundant crystals of calcium oxalate (Plate 25D), located within the medulla, cortex and even on the surface of the lichen, thus explaining the reason for the white coloration of the specimens. The calcium-rich nature of the crystals was confirmed by EPMA, whilst XRD identified the oxalate as whewellite. ICP analysis of material of this species from Gjersvik gave calcium contents of up to 21% dry weight. This represents a calcium oxalate content of c. 76%. Another specimen of A. mashiginensis overgrowing a copper mineral from Ramundberget (Plate 24A) was also shown to contain abundant calcium oxalate (see X-ray spectra, Fig 8A), though in this instance the oxalate is weddellite (Plate 25C). Copper oxalate was not observed in any specimens of this species.

Examples of Rhizocarpon geographicum collected from the

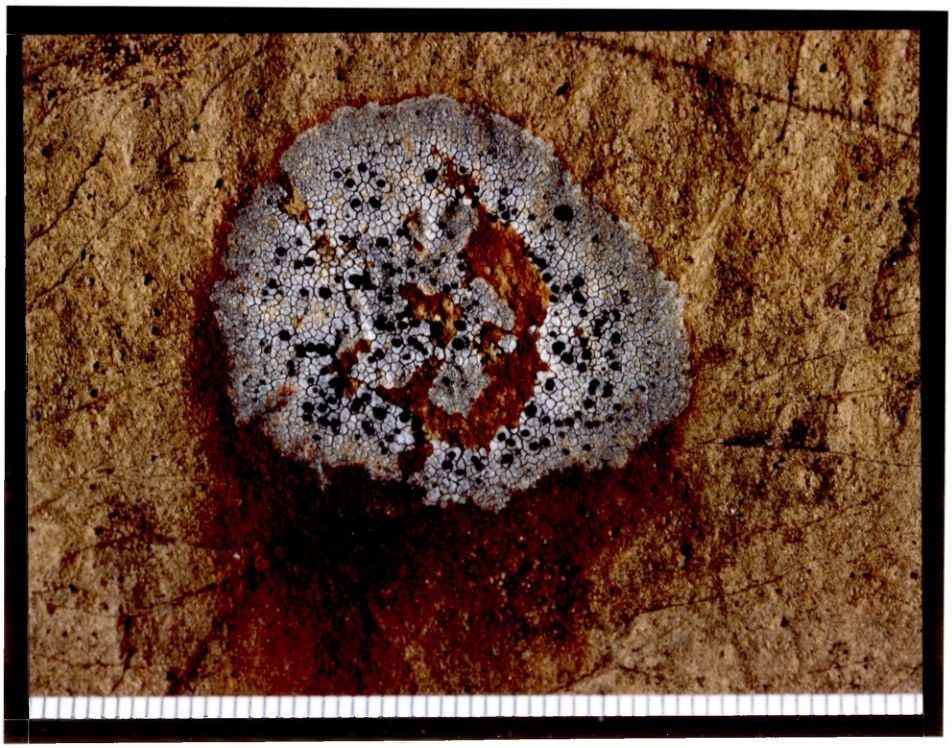
PLATE 24.

A. Aspicilia mashiginensis overgrowing a secondary copper mineral (Santesson 24577). Scale in mm. Note the white edge of the mineral surrounding the main thallus and the smaller thalli.

B. Lecidea lactea growing on dunite, Leka. Scale in mm. Note that the intense ferruginous stain (amorphous silica coated in iron oxides) occurs mainly below the thallus.



A



B

PLATE 25.

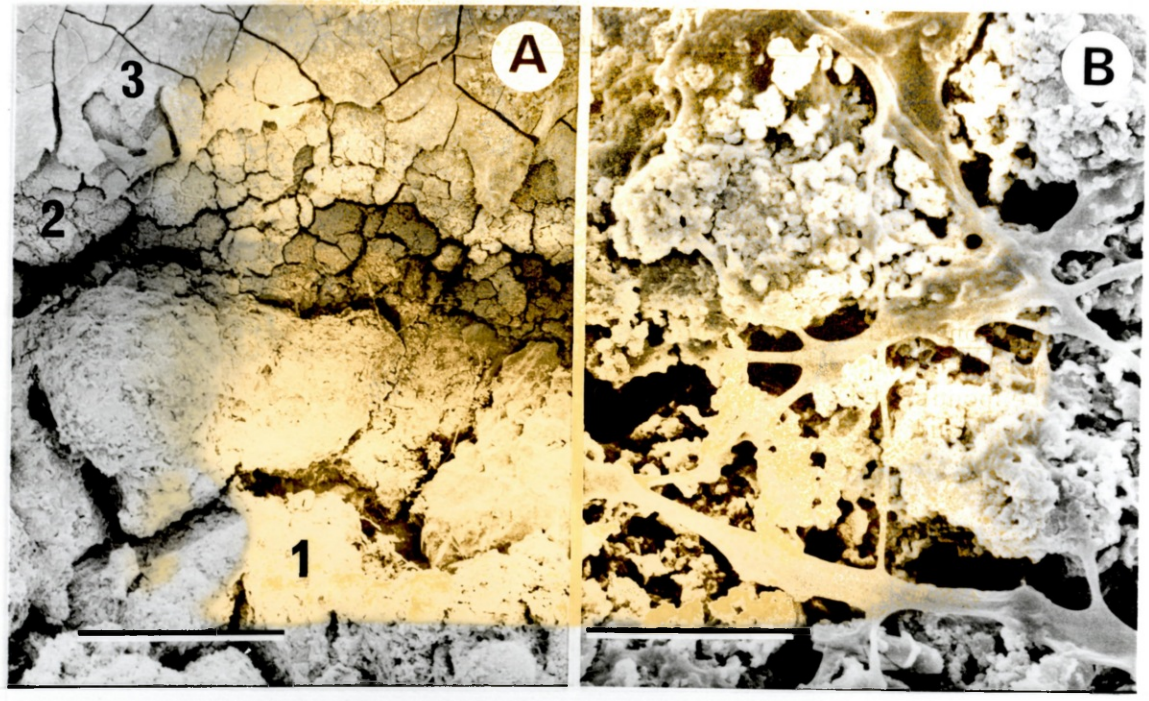
SEM micrographs of Aspicilia mashiginensis.

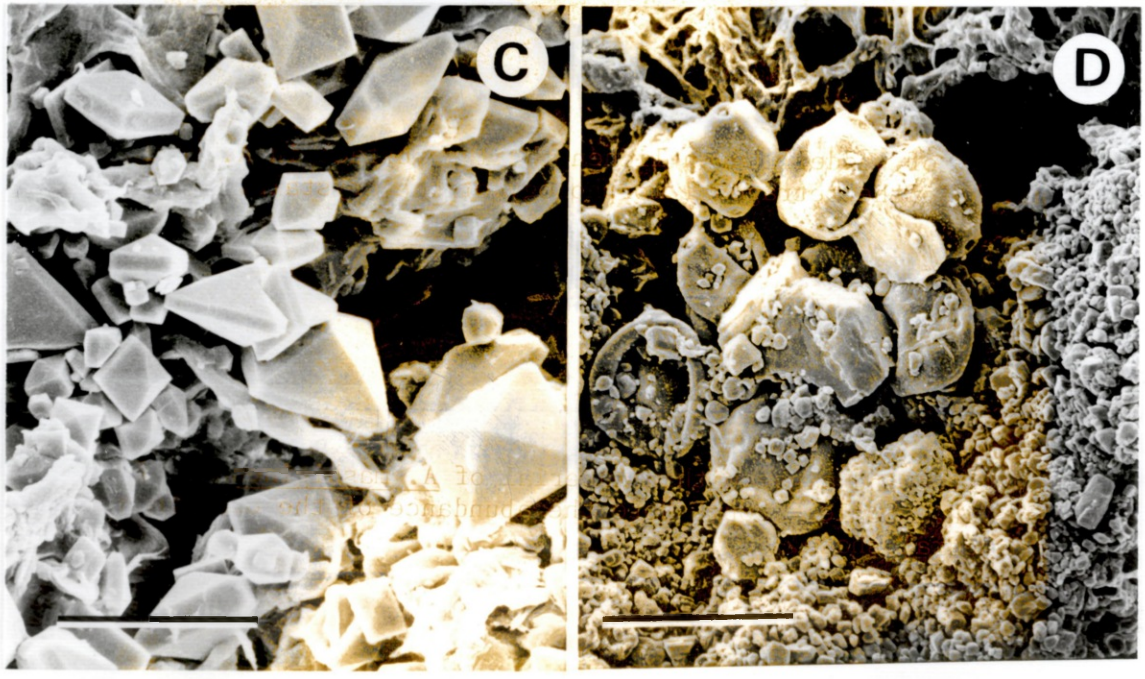
A. Santesson 24577, Plate 24A. General view showing contact between thallus (1) with the blue mineral (3). The white rim corresponds to 2. Scale = 300µm. Note the even, areolate mineral and degraded white rim.

B. Close-up of degraded white rim shown in A. Scale = 8.6µm. Note the ramifying hyphae penetrating the mineral.

C. Close-up of weddellite on lichen thallus surface in A. Scale = 12µm. Note the tetragonal morphology of the crystals.

D. Whewellite and algae within material of A. mashiginensis from Gjersvik. Scale = 30µm. Note the abundance of the oxalate and its ahedral shape.


A
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vicinity of Aspicilia mashiginensis at Gjersvik (Plate 5B) were analysed by ICP and also found to be rich in calcium, (as calcium oxalate) to a maximum of 18.4% Ca dry weight. In this instance, the thallus also contained 0.3% Cu; the lichen was senescent. Neighbouring living thalli similarly contained high contents of Ca (12.3 and 15% Ca dry wt) but substantially lower concentrations of Cu (0.046 and 0.056% Cu dry wt). The form of the Cu present in the lichens in these instances is unknown, but it is possible that the senescent example had been affected by toxic concentrations of this element.

6.2.4. Discussion

The results of the present study demonstrate that lichens are highly selective in their capacity to accumulate copper, as a direct consequence of their biochemistry. Evidence from XRD and IR confirm field and other observations (Purvis et al. 1985) that complexing of copper by norstictic acid, produced by the lichen, is occurring in 3 and probably 9 lichen species. Lecidella bullata and Lecidea arctogena, which may also accumulate Cu, contain psoromic acid which is stucturally similar to norstictic acid (Fig. 5). It is probable that these species contain a Cu-psoromic acid complex, though further chemical evidence is required to confirm this. A dark green example of Lecanora cascadensis, described by Czehura (1977), has been examined and found to contain psoromic and usnic acids. It is conceivable, therefore, that this species could also contain a Cu-psoromic acid complex. However, the nature of the copper compound(s) responsible for the green apothecial coloration in Lecanora polytropa is unknown. It has not been possible to

identify any lichen compounds restricted to this area by TLC. Evidently the chemical factors responsible for the complexing of copper in the lichens are very subtle, since the depsidone stictic acid (Fig. 5), a compound structurally related to norstictic acid is not apparently involved in complexing. Stictic acid occurs in Lecidea lapicida which has been found on several occasions, as at Røros (section 4.6.2.d) without concentrating copper. This would seem to provide further evidence that the aldehyde C=O gp and adjacent OH are important in bonding to Cu; the aldehyde C=O gp is absent in stictic acid, but present in norstictic and psoromic acids.

High contents of both calcium oxalate and copper oxalate have been observed and analysed in a range of lichens from cupriferous substrata. This is perhaps not surprising as both Cu and Ca are available under these conditions (section 4.5) and oxalates are stable at these pH regimes. It is, however, difficult to account for the observation that a lichen e.g. Acarospora rugulosa occurring on brochantite may accumulate abundant copper oxalate, whilst adjacent thalli of Aspicilia mashiginensis accumulate calcium oxalate. It is possible, therefore, that the organism has some control, at least, over the type of deposition of extracellular oxalate precipitates. The mechanism is unexplained.

It is interesting to observe that in the laboratory, the state of hydration of calcium oxalate has been shown to be pH dependent (Franceschi & Horner 1980). It is possible that this observation might explain the occurrence of the different oxalates, whewellite and weddellite in different specimens of the same

species, as in Aspicilia mashiginensis and Acarospora rugulosa (see Purvis 1984). Certainly the nature of the calcium oxalate is not a specific character for a species and crystal morphologies are similar to those which might be expected from a purely chemical precipitation in a test tube. There does not appear, therefore, to be an alteration in crystal morphology mediated by the organism such as has been proposed by Arnott (1982) for certain forest litter fungi. It is widely recognized that the presence of calcium may be beneficial to plants, usually by stabilizing membranes, in environments with high metal contents or other harmful factors, including SO_2 e.g. in algae (Mierle & Stokes 1976), lichens (Nieboer et al. 1979), mosses (Coker 1971, Wilkins 1957) and fungi (Somers 1963, Chester 1965) [see chapter 1]. It would be informative to discover whether or not Ca in the form of calcium oxalate is physiologically useful to the lichens in environments with high levels of toxic metals, and is not merely a chance product of chemical precipitation. It cannot, however, be essential to all lichens growing in environments rich in toxic elements. For instance, Ca was below the level of detection by ICP ($<125\ \mu g g^{-1}$) in a specimen of Acarospora sinopica collected from FeS_2-rich rocks at Gjersvik. Moreover, no crystals of calcium oxalate were observed in SEM studies. Since calcium oxalate is unstable in acidic conditions (Franceschi & Horner 1980) this observation is not surprising, unless of course the lichen itself maintains a high internal pH.

Whilst it is tempting to suggest that the formation of copper oxalate and possible Cu-lichen acid complexes are important factors in avoiding the toxic effects of this element, these cannot be the

only explanations, since several lichens grow in these Cu-rich environments apparently without forming these types of compounds. Evidently there is no universal mechanism by which all lichens may avoid the toxic effects of copper.

6.3. Some observations on the weathering of two substrata by lichen growth

6.3.1. Aspicilia mashiginensis, (Santesson 24577, UPS)

In this specimen the lichen is growing upon a surface layer of a blue mineral which has a more or less microbotryoidal morphology (Plate 24A). Several small, circular lichen colonies are present. An interesting feature of the specimen, is that the mineral in contact with the outer margin of each colony and of the main thallus, has a contrasting white colour. XRD analysis of the blue and white parts of the mineral gave no distinctive pattern and the mineral must therefore be a poorly ordered, amorphous substance. In the SEM, the mineral appears as a cracked-areolate crust (Plate 25A). In contrast, the whitish areas surrounding the lichen colonies is less ordered and clearly represents a degraded state of the blue mineral, caused by the outermost radiating hyphae overgrowing the rock surface and penetrating the blue mineral (Plate 25A and B). EPMA has shown that the blue mineral is rich in Cu, Fe, Al and Si (Fig. 8B). The lichen has high Ca contents, due to calcium oxalate (weddellite) and the parts of the rock lacking the superficial blue precipitate are more Si-rich than other regions. X-ray maps showing the distribution of the K- α rays of Al, Si and Ca are given in Plate 26. The back-scattered electron

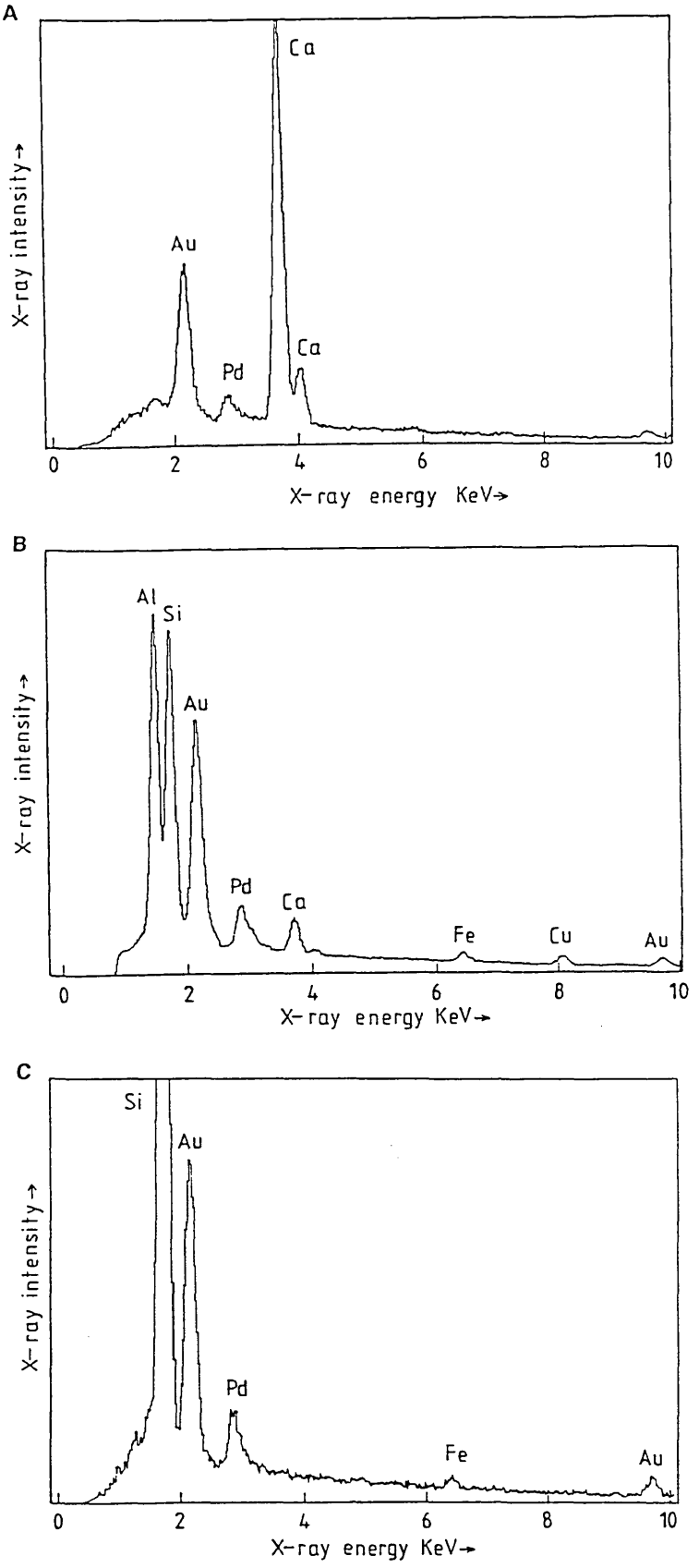


Fig. 8. Miscellaneous X-ray spectra. A. Aspicilia mashiginensis (Santesson 24577, Plate 24A): spot analysis of thallus surface. B. Spot analysis of blue mineral overgrown by A. mashiginensis in A. C. Lecidea lactea (Leka, Plate 24B): spot analysis of ferruginous stain. (Au/Pd coated)

PLATE 26.

Studies on the weathering of a secondary copper mineral by *Aspicilia mashiginensis* (*Santesson* 24577, Plate 24A).

A. Back-scattered electron image of lichen thallus (1), degraded, white rim (2) and blue mineral (3). Scale = 1mm. Note the bright response of the blue mineral.

B. Ca K α X-ray distribution map of area shown in A. Note the localization of Ca in the lichen thallus (calcium oxalate).

C. Si K α X-ray distribution map of area shown in A. Note the abundance of Si on the rock surface and in the blue mineral.

D. Al K α X-ray distribution map of area shown in A. Note that Al is restricted to the blue mineral and the degraded white rim.

A
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B
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D

image in Plate 26A shows a brighter response from the blue mineral, contrasting with that from the degenerate white area and the lichen. The bright response is largely due to its Cu content. Copper is absent from the white rim as shown by EPMA, though Al is present and also some Si.

This specimen provides a visible demonstration of a consequence of lichen growth on a rock surface. It is evident that Cu is liberated from the blue mineral, but is not fixed in the lichen thallus. In contrast, Al which is geochemically relatively immobile is left behind. The fate of the Si is less clear from the X-ray map; some may be removed in solution. A possible explanation for this observation is the action of oxalic acid on the substratum, as has been suggested by Jones et al. (chapter 1) in a number of cases, though this remains to be proven in this instance.

6.3.2. Lecidea lactea on dunite: Norway, Leka, west of Kvaløy, 17 June 1983, Purvis (BM)

On the island of Leka, central Norway, Lecidea lactea was frequently observed surrounded by a conspicuous halo of iron staining where it occurs on dunite surfaces. This is best displayed where it is growing in vertical situations; the ferruginous stain is predominantly found in the area immediately beneath the lichen thallus (Plate 24B). The colour of the iron staining contrasts markedly with the typical 'peanut butter-coloured' surface coloration of the rock surface, in which iron oxides are loosely disseminated throughout the surface crust of supergene serpentinization. In the SEM, the surface of the ferruginous area

appears smooth, but slightly cracked and develops a series of wart-like protuberences. Interestingly, EPMA indicates that this area is dominantly rich in Si with lesser amounts of Fe (Fig. 8C). XRD analysis of the brown material gave no pattern, leading to the conclusion that the main body of the stained surface area was composed of amorphous, colloidal silica, with a proportion of iron oxides. Amorphous silica has often been found in studies on weathering products of lichens (Wilson & Jones 1983) as, for example in the weathering of chrysotile (Jones et al. 1981). In L. lactea from Leka, however, the production of amorphous silica is also accompanied by a thin deposition of Fe^{3+}, providing a further instance of the visible effects of lichen weathering on rock surfaces. It is possible that this phenomenon might be explained by the action of oxalic acid produced by the lichen mycobiont on the rock surface. In this respect, it is interesting to note that according to Proctor & Woodell (1975), Pedro & Bitar (1966a, b) distinguished two important processes by which serpentine rock could be weathered in conditions of free drainage. These depend on whether pure water or water and CO_2 or acetic acid are involved. The first instance corresponds to a laterization process where iron oxides tend to accumulate, silica is removed more rapidly than Mg, and Mg-compounds of a non-silicate type remain in the weathered crust. In the case of leaching by acetic acid, there is a greater removal of Mg compared with silica, which forms free amorphous silica on the rock surface; in addition Fe^{3+} is also resistant to mobilization. This observation provides some evidence suggesting that oxalic acid, also a weak organic acid could have a similar effect to acetic acid, though this remains to be verified.

CHAPTER 7. CONCLUSIONS: USE OF LICHENS AS INDICATORS OF METALLIFEROUS MINERALIZATION

Attention has been given in this study to both geobotanical and biogeochemical aspects of the association of lichens and cupriferous substrata. One result of the geobotanical study has been the identification of the community, the Lecideion inopis, specific for certain copper-bearing rocks in central Scandinavia. This highly specific community is strongly dependent on the mineralogy of the rocks, together with the pH of the environment; the latter parameter itself largely controlled by the mineralogy. The Lecideion inopis is restricted to environments where chalcopyrite or secondary Cu minerals are present, at near neutral to slightly alkaline pH regimes. It does not occur under acidic conditions when high contents of the iron sulphides pyrrhotite and pyrite are present. The new community occurs in a wide variety of habitats, including small stones, boulders and rock outcrops, in sheltered, exposed, moist and dry environments. Lecidea inops is found only within this community and may occur in a number of different habitats. However, the other species present within the community usually have distinct habitat preferences. Thus, for example, a new species Psilolechia leprosa occurs in dry and shaded situations on these substrata. The biological reasons for the restriction of particular species to these cupriferous substrata are unknown. In addition to this new community specific for certain copper-rich substrata, a second community has been observed. This is the Acarosporetum sinopicae specific for iron sulphide-rich substrata (Wirth 1972). Further research in other mineralized areas will undoubtedly lead to the identification of other distinctive

lichen communities characteristic for other metals. It will, however, be necessary to base such studies on an integrated approach (chapter 2).

Concerning the biogeochemical aspect of this study, it is now apparent that crustose lichens vary strikingly in their capacity to accumulate copper. This is a direct result of their biochemistry. In the case of copper, this differential capacity for uptake is obvious, since accumulators may become yellow-green in colour as a result of the concentration of Cu, whilst non-accumulators may not. Some nine, possibly ten norstictic acid-bearing lichens have been found to accumulate Cu and on the basis of XRD and IR data the complexing of Cu with norstictic acid is demonstrated to occur within the cortices of 3 of these lichens. The structurally related psoromic acid also appears to be involved in the complexing of Cu. It appears that the presence of an aldehyde carbonyl group with an adjacent OH group is an important factor in the complexing of Cu by depsidones. Certain lichens may also contain vivid blue inclusions of copper oxalate, accounting for up to 38% dry weight.

These observations are of great interest, since previously neither copper complexes nor lichen acid-metal complexes were reported in lichens. These observations are of importance to both biogeochemists involved in the analysis of lichen material as potential indicators of mineralization and also to all lichen taxonomists. Obviously a random chemical analysis of crustose lichens is unlikely to give much information on rock mineralogy or chemical composition. Moreover, TLC investigations may fail to reveal the presence of a lichen acid if it is complexed by a metal.

It is now particularly important for chemists to establish the precise factors involved in the complexing of metals by lichen acids. It should then be possible to predict the occurrence of further metal-lichen acid complexes in lichens. In this respect the so-called Irving-Williams rules are probably relevant (Irving & Williams 1953). These rules state that the stability of metal-organic complexes is independent of the nature of the co-ordinated ligand or of the number of ligand molecules involved. For divalent cations the order of stability (most stable first) is in the sequence: Pt, Pd, Hg, UO_2, Be, Cu, Ni, Co, Pb, Zn, Cd, Fe, Mn, Ca, Sr and Ba. For monovalent cations the sequence is Ag, Tl, Li, Na, K, Rb and Cs. The corresponding values for trivalent ions are Fe, Ga, Al, Sc, In, Y, Pr, Ce and La (Brooks 1983). It is interesting to note that Cu has a relatively high stability, but is less stable than Pt or Pd. It might be expected therefore, that complexing of Pt or Pd would be most strongly favoured and therefore could have potential use in the location of Pt and Pd deposits. It is probable that a whole range of lichen acid-metal complexes will be discovered in lichens, though most, of course will not be coloured and hence not identifiable in the field. It must be stressed that not all green lichens contain copper and many owe their coloration to specific organic pigments, including rhizocarpic acid. Where possible confusion exists, it is suggested that a spot test specific for copper e.g. rubeanic acid might be usefully employed in the field.

As a result of these studies, it is now possible for a lichenologist to confirm rapidly on the basis of the lichen

communities, whether or not significant copper is present in environments, such as those studied in central Scandinavia, provided the pH of the substratum is not too acid. In many instances this observation is of no practical value to the geologist who would almost certainly either notice secondary deposits of Cu minerals in the environment, or chalcopyrite in rock samples. However, in other instances, particularly where there is a scarcity of natural outcrops and where the cover is relatively thick, it is possible that geobotanical and biogeochemical methods involving the study of lichens might be a useful aid in suggesting sites worthy of further investigation. Lichens are unique as compared with other plants in producing large concentrations of a variety of secondary organic compounds (lichen acids) which may contribute up to c. 30% dry weight of the thallus (Huneck 1973). In this respect, the importance of the interaction of the lichen biochemistry with mineralizing solutions, coupled with the great longevity of lichens (to 10000 years) cannot be ignored. For instance, it is conceivable that where an ore body is concealed at depth and even where geochemical and geophysical signatures are weak, that certain lichens might be able to accumulate, over a period of time, significant concentrations of copper (or other elements) as complexes with particular lichen acids or oxalic acid. In such instances such information might prove invaluable in a pilot study and identify areas worthy of further investigation. It is obvious, however, that further research is required with an emphasis on the study of lichen acids and metal complex formation before this can become practical.

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resembles Dinosaur National Monument in Utah, which differs only in that the skeletons there are more complete.

Once the bone-bed was exposed, there began the time-consuming operation of excavating the individual bones from the hard sandstone. This was not a simple job for every square centimetre of bone surface had to be freed with hammer and chisel. The operation was rendered even more difficult by the higgledy-piggledy manner in which the bones overlay each other; fortunately they were not much crushed. As each bone was cleared, it was photographed, its position recorded, plastered and removed; some of the largest bones had boxes built around them *in situ* and were then plastered into the box. A demonstration of cocooning the fossils in polyurethane foam (which had been donated by Shell Chemicals UK Ltd) was successful and enthusiastically received. In the neighbouring farmyard, carpenters made wooden crates to contain the plastered blocks, duly labelled and packed in straw, and gangs of local workers carried the crates on stout poles down to the nearest road. By the time the British visitors left, some 220 jacketed blocks in 35 crates were awaiting transport back to Beijing. The collection probably includes new species, but preparation will take years to complete.

The success of this venture could not have been achieved without the co-operation so kindly given by Professor Sun Ai-lin, Deputy Director of the Institute of Vertebrate Palaeontology and Palaeoanthropology in Beijing, together with her staff (especially Dong Zhi-ming and Li Jin-ling); by the chief Executive (Li Wen-xing), and other officials of Wangcang County; and by many other Chinese.

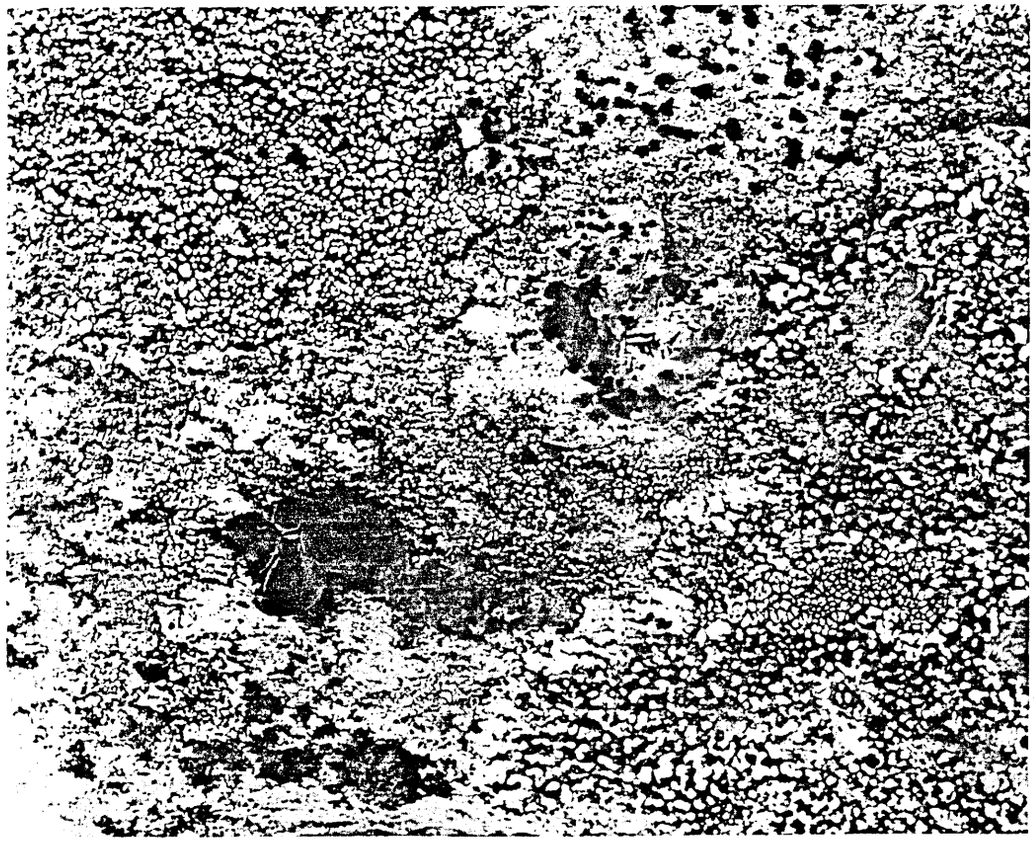
Lichens and mineral exploration

In recent years mineral exploration has reached an unprecedented level due to the ever-increasing demands on the earth's dwindling resources. Plants are assuming significant importance as a rapid and reliable means of detecting mineral deposits. Two major lines of investigation have been developed – *biogeochemical* in which detailed chemical plant analysis gives an indication of the underlying chemical and thereby, indirectly, the mineral content of their habitat; and *geobotanical* where the distribution of indicator plants or communities points to the mineral composition of the soil and underlying rocks. A noteworthy example of an indicator species is the alpine catchfly (*Lychnis alpina*, formerly *Viscaria alpina*); the unique ability of this plant to tolerate exceptionally high soil concentrations of copper, has led to its use in Scandinavia as an indicator of this metal since medieval times. The Viscaria copper mine at Kiruna, Sweden, was named after this species, whose abundance on site first led to the discovery and development of the mine.

Although the role of higher plants in mineral prospecting is fairly well understood and acknowledged, little attention has been paid to lichens in this respect in spite of the fact that they are intimately associated with the rock surface on which they grow, and might therefore be expected to mirror subtle changes in the rock chemistry. Probably the difficulties of correlating rock chemistry with a knowledge of lichen physiology and identification of the species, the latter a particularly difficult problem, have acted as deterrents to detailed research in this field. A studentship in celebration of the Museum's Centenary, funded by British Petroleum and organized by the Museum and the Royal School of Mines, Imperial College of Science and Technology, has enabled research to be started in this potentially important field.

About 18 000 lichens are known. Their plant form – the thallus – is crust- or leaf-like, reaching its highest development in richly branched and tufted structures. Crust lichens are often in very close contact with the substrate on which they grow and can be immersed in it. As a group, lichens are noticeable and attractive as bright splashes of colour on rocks, buildings, and tree trunks; surfaces which are largely inhospitable to most other plants except algae and mosses. Lichens are widely distributed in parts of the world where plant life is poorly developed such as the Arctic and Antarctic, many deserts and alpine regions – all areas of economic potential.

Lichens are unusual compared with most other plants in that they have a capacity to take up and retain significant quantities of metals. Levels of up to 5 per cent total dry weight per lichen of zinc, iron, and lead have been recorded for several species. Furthermore, a special affinity for a particular metal is a feature of some lichens; for instance, *Lecanora vinetorum* only occurs on wooden vine supports periodically sprayed with Bordeaux



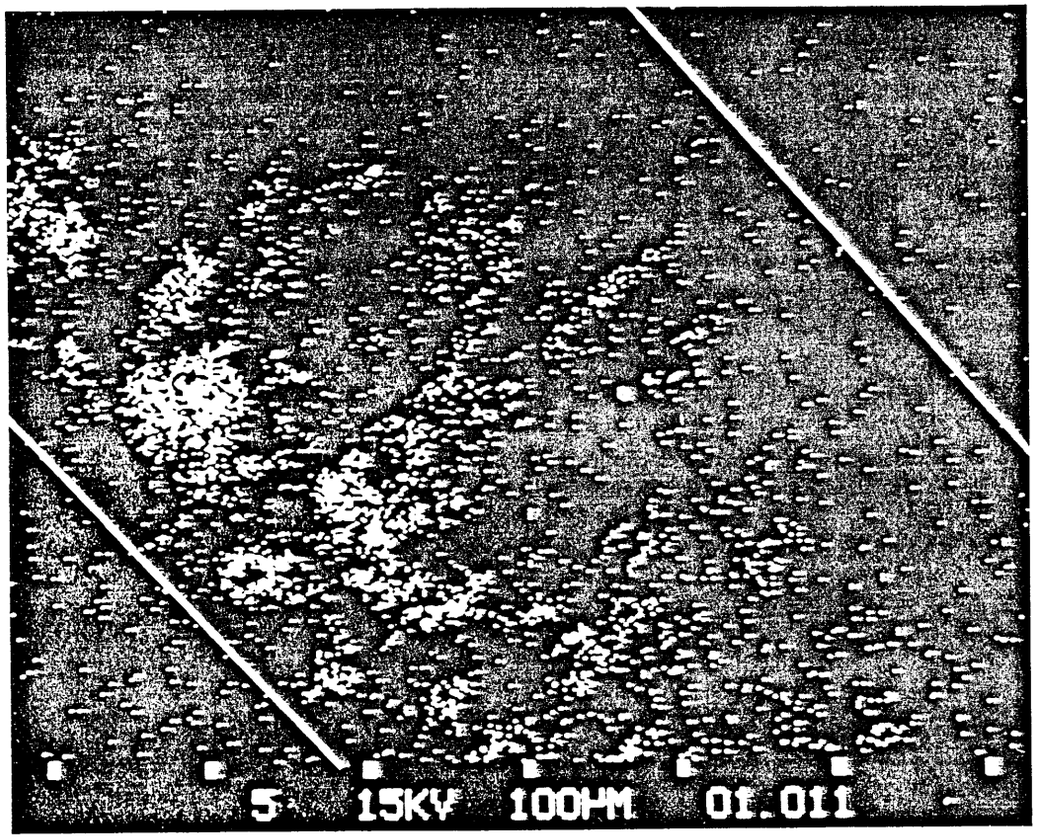
A range of lichens growing on metal-rich rocks in Norway (life-size).

mixture, a fungicide rich in copper. The ability of lichens to take up metals could be of significance in mineral exploration, and has already been widely used in monitoring heavy metal pollution. In the latter as well as in the monitoring of sulphur dioxide and hydrogen fluoride in the atmosphere, the Museum continues to play an important advisory role.

The nature of the relationship between a lichen and its substrate is one of the most contentious and interesting areas of lichen ecology. There is unequivocal visual evidence that lichens form communities composed of particular species which are characteristic of certain rock types. In this context, the proportion of calcium carbonate in a rock has a very significant effect on the distribution of species. Thus, limestone and granite outcrops have very contrasting floras. However, the most striking lichen assemblages occur on rocks that are rich in iron sulphides. The associated lichens are invariably dominated by a suite of crust species which are rust-red in colour due to the deposition of ferric oxide. This discoloration is not necessarily confined to the surface of the lichen and is commonly localized to areas on or within the thallus and fruits, its site being characteristic for the species. It also seems that the nature and availability of iron in rocks is of paramount importance in determining the composition of the associated lichen flora; thus a quartzite-magnetite (iron oxide) rock, supports no 'rusty' lichens, whereas a rock containing iron sulphide may have up to 15 'rusty' species. The acidity of the water associated with the rock surface, together with other physical and chemical considerations, play an important role in determining which community develops.

It has recently been discovered that certain normally grey lichens growing in areas of copper mineralization can assume an anomalous greenish colour due to the accumulation of copper salts in their thalli, as in the case of *Lecidea theiodes* from Gjersvik, Nord Trøndelag, Norway. The accompanying illustration obtained by electron microprobe analysis of a polished section of lichen embedded in resin show a marked concentration of copper (about 6 per cent dry weight) in this species. Subsequently the copper was found to be in the form of hydrated copper oxalate. The lichen thallus was growing in direct contact with quartz which contains no copper; it appears that in this case copper-rich solutions from chalcopyrite-rich veins (copper ore) irrigating the surface of the thallus account for the accumulation, rather than direct uptake from the rock below the lichen. Cross sections of the lichen contain vivid blue inclusions corresponding to the copper salt suggesting that *Lecidea theiodes* has a very high tolerance rate to large concentrations of this metal.

Analysis of lichen and rocks for a range of elements has shown that, in general, the nature of the rock accounts for differences in the metallic compounds within the lichens. Thus, lichens on basic igneous rocks tend to have relatively high contents of chromium, manganese, cobalt and nickel, whereas those on acid igneous rocks often have large accumulations of lead, zinc and cadmium. Very high concentrations of a particular element in lichens seem, for the most part, to be directly correlated with unusually high concentrations of the same element in the rock. However, species of *Umbilicaria* and *Stereocaulon* in which zinc, cadmium, and lead are markedly concentrated from rocks poor in these minerals demonstrate that this is not always so. For example, samples of *Lasallia pustulata* from Finland contained 10 000 parts per million (ppm) of zinc whereas the associated rock contained 300 ppm. Almost all elements studied have been found in



X-ray map (×200) showing the distribution of copper in *Lecidea theiodes*. Note the small amounts of copper in the rock substrate (lower left) and the resin mount (upper right).



Scanning electron microscope image (×6000) showing crystals of copper oxalate associated with fungal hyphae in the blue area within the thallus of *Acarospora montana*.

higher concentrations in lichens than in other plants. It is possible that their slow growth rates, longevity, the unusual affinity for certain elements, and high tolerance levels account for this. Unfortunately, little is known of the tolerance levels of lichens to different metals.

As more evidence becomes available, lichens may become important in geobotanical and biogeochemical surveys, particularly where the mineralization is disseminated, rather than localized in seams or veins. It is clear that a working knowledge of lichen communities and individual 'indicator' species and the range of rock types colonized by them could assist in the delimitation of suitable areas for more conventional methods of mineral exploration. A preliminary rapid survey of lichen populations over wide areas may prove an effective means of identifying limited areas which would repay detailed examination by mineralogists, for the assessment of their economic potential.

Asses and onagers in the ancient world

There are two theories about the donkey and the onager that are accepted as fact by many archaeologists and biologists today. First that the donkey (*Equus asinus*) is the only ungulate to have been domesticated on the African continent having been bred from the wild ass (*Equus africanus*) by the ancient Egyptians. Second that the onager (*Equus hemionus*) was domesticated in ancient Mesopotamia. Recent work, however, indicates that the donkey is as likely to have originated in western Asia as in Egypt, and the onager was never domesticated.

The history of human exploitation of the equids (horse, ass and onager) is more difficult to trace than it is for any other group of livestock because all three species can be made to interbreed, although producing sterile offspring, and the hybrids of all three have been used as draught animals at different periods, from the prehistoric to the present day.

The wild horse (*Equus ferus*) was widespread over Europe and central Asia at the end of the Ice Age. Its numbers dwindled in northern Europe as the climate became temperate but it survived on the plains of southern Russia and it is probable that the first domestication of the horse occurred there in the fourth millennium BC. This was several thousand years later than the earliest domestication of wild animals for livestock husbandry in western Asia. Here the goat, sheep, ox and pig were all well established as the basis for a pastoral economy before 5000 BC, but the wild horse was not a common inhabitant of the Near and Middle East so it was not available for domestication. It is probable that the ox fulfilled the role of draught animal and it was not for another 1000 years that the donkey replaced it.

Because the ass (*E. africanus*) has survived as a wild species in North Africa until the present day, and because it was frequently painted by the ancient Egyptians it was reasonable to assume that it was this civilization that was responsible for the breeding of the donkey as a domestic animal. Similarly an ass-like equid is commonly represented in the art of the Sumerians, the people of ancient Mesopotamia in the third millennium BC, and because the onager has survived as a wild equid in the Middle East today, it was reasonable to assume that it was this ass that was depicted by the Sumerians. The fallacy lay in the assumption that the onager was domesticated.

If the Sumerians had domesticated the onager (*E. hemionus*) it could be expected that the domestic asses of western Asia at the present day would be descended from this ancient stock and therefore they should interbreed freely with onagers. This is not so, however; Asian donkeys will interbreed to produce fertile offspring only with the African wild ass (*E. africanus*).

In collaboration with the Research Laboratory at the British Museum attempts have been made to obtain radiocarbon dates for the skeletal remains of equids in the osteology collections of this Museum to try to establish early dates for the domestication of the ass in Egypt and in western Asia. Some of this material was presented by Sir Flinders Petrie at the beginning of this century, and some of it has been excavated in Iraq within the last five years. The results of these attempts have been unsuccessful so far, however, because subfossil bone that has been preserved in the hot dry conditions of North Africa and Asia loses its collagen, the protein essential for the radiocarbon dating of bone. The oldest osteological material we have of ass from ancient Egypt is a skull from the predynastic site of Badari, excavated by G Brunton & G Caton-Thomson in 1928. Unfortunately this cannot be directly dated as the bone has been coated with paraffin wax, but unless it is an intrusive burial it should date to around 4000 BC, whilst another skull of a ritual burial of an ass from Tarkhan (excavated by Petrie) has been dated on associated cloth to circa 2850 BC (BM–203).

If there were good fossil records for wild ass in North Africa and nowhere else, and if these were the only early dates for ass remains in association with humans then it could be safely assumed that the Egyptians tamed the wild ass (*E. africanus*) and produced the domestic donkey (*E. asinus*), but within recent years the remains of wild ass have been identified by P Ducos from the site of Tell Mureybet in Syria that has been dated to 9000 BC. Furthermore the remains of domestic donkey have now been identified from many archaeological sites, dating from 3000–2400 BC, and ranging right across the Near and Middle East. Previously this material would have been described as domestic onager but it is now agreed amongst archaeozoologists working on this material that the osteological evidence favours the donkey. It therefore seems probable that the ass (*E. africanus*) was living as a wild animal in the Near East as well as in North Africa in the prehistoric period and there can be no certainty that it was the ancient Egyptians rather than the Neolithic peoples of western Asia who bred the first domestic donkeys.

Within recent years a surprisingly large number of entire as well as partial skeletons of equids have been excavated from Sumerian Tell sites in Iraq (ancient Mesopotamia) under the direction of Nicholas Postgate, now of the Faculty of Oriental Studies, University of Cambridge. Due to the kindness of the Department of Antiquities in Iraq, a number of these skeletons, which are third millennium BC in date, have been brought to the Museum for study. This work has been enhanced by the careful interpretation of textual material by Postgate which supports the identifications to species of the skeletons.

Like the ancient Egyptians the Sumerians had an extraordinarily well-ordered society in which list-making on cuneiform tablets seems to have played an important role. It is therefore possible to learn in great detail about how the economy was managed, exactly what animals were used for which purposes, their value, what they were fed on, and how they were kept. From his interpretation of the cuneiform sources Postgate has been able

Lichenologist **16**(2): 197–204 (1984)

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THE OCCURRENCE OF COPPER OXALATE IN LICHENS GROWING ON COPPER SULPHIDE-BEARING ROCKS IN SCANDINAVIA

O. W. PURVIS*

Abstract: Investigation of two sites in the Caledonian allochthon of the central part of the Scandinavian peninsula has shown that several copper tolerant lichens occur on cupriferous substrates. Analysis of the thalli of two of these species, *Acarospora rugulosa* and *Lecidea theiodes*, using atomic absorption spectroscopy, X-ray diffraction, infrared spectroscopy and electron probe microanalysis has revealed that copper occurs at high concentrations (5% Cu dry weight) principally as crystals of copper oxalate (1–5 μm diam) encrusting the fungal hyphae within the medulla.

Introduction

The aim of this preliminary study is to account for the special blue-green coloration and the mineral precipitate recently discovered in certain lichens growing on cupriferous substrates in Scandinavia. One of the most obvious effects of mineralization on the appearance of lichens is the strong rusty coloration of certain species growing on weathered iron-bearing rocks. Lange & Ziegler (1963) have described lichens belonging to the community *Acarosporetum sinopicae* growing on the 400-year-old slags at Okertal, Rammelsberg and at other locations in the Harz Mountains which contained iron in the range of 0·6–5·5% dry weight. There are, however, few published descriptions of the special effects of copper on lichen floras. The most noteworthy of these is an account of the lichen *Lecanora cascadensis* Magnusson growing on copper mineralization at Lights Creek District, Plumas County, California (Czehura 1977). *Lecanora cascadensis* displays a green coloration of the thallus the intensity of which is related to the concentration of copper in the substrate. Dark green samples of *L. cascadensis* contained *c.* 2% wt Cu in the ash. Soils adjacent to the rock on which the lichen was growing contained between 1000 and 2000 ppm Cu. Another relevant example of the association between a lichen and copper is *Lecanora vinetorum* Poelt et Huneck (Poelt & Huneck 1968) which thrives on vine supports sprayed with Bordeaux Mixture, [$CuSO_4.5H_2O(4)$: $CaO(4)$: $H_2O(50)$] and contains 0·5% Cu dry wt. Other species found in association with copper include *Haematomma ventosum* var. *cuprigenum* Poelt which was described by Poelt (1955) growing on cupriferous substrates in the Großarl, Salzburg and it is the opinion of Hertel (pers. comm.) that *Lecidea inops* Th. Fr. (' typus prope cuprifodinas ') grows only on rocks containing copper. In 1978 Santesson collected *Aspicilia alpina* var. *sulphurata* Th.Fr. which was yellow-green in colour, evidently because of the incorporation of copper from the

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rocks on which it was growing, at Ramundberget (Härjedalen County, Sweden); this was distributed as Vězda, *Lich. Sel. Exs.* no. 1549.

Lichen Floras and Sites Investigated

The outcropping rocks in the vicinity of an abandoned mine at Gjersvik (=Gj), Nord Trøndelag, Norway 13°25′E, 64°53′N) at an altitude of 450 m within the *Betula tortuosa* zone support a distinctive flora associated with chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) mineralization which occurs disseminated and in stratiform concentrations in basaltic lavas, and more siliceous volcanic rocks metamorphosed in greenschist facies. A fuller study of the ecology and types of species occurring at this locality is in progress.

During the botanical survey of the mine area, anomalous green-coloured examples of three lichen species were observed, notably, *Aspicilia alpina* (Sommerf.) Arnold, *Aspicilia subsorediza* (Lynge) R. Sant. and *Lecidea theiodes* Sommerf.* *Acarospora rugulosa* Körber, was occasionally observed on secondary deposits of a mixture of atacamite [$Cu_2Cl(OH)_3$] and gypsum ($CaSO_4.2H_2O$). *Aspicilia mashiginensis* (Zahlbr.) Oxner, *Lecidea paupercula* Th. Fr. and *Rhizocarpon birgittae* Magnusson were invariably present as members of the community. The copper content of the three latter species remains to be determined.

A limited survey of a similar habitat was also made at Ramundberget (=R), Härjedalen, Sweden (12°25′E, 62°42′N) at an altitude of 920 m, just above the tree line. Here copper in the form of chalcopyrite occurs in a mixed sequence of volcanic rocks, metamorphosed in upper greenschist to amphibolite facies. *Lecidea inops* Th. Fr. was particularly abundant at this site but it has not been found at Gjersvik. The other lichens which were associated with copper mineralization at Gjersvik were also typically abundant at Ramundberget. Superficial layers of brochantite [$Cu_4(SO_4)(OH)_6$], produced by weathering, support a strong growth of *Acarospora rugulosa* (Fig. 1). Santesson (pers. comm.) is preparing a detailed account of the lichen flora at this site.

Observation and Analysis of Selected Lichen Material

Vivid blue inclusions were seen within the lichen medulla at the rock-lichen interface while examining sections of *Acarospora rugulosa* (R+Gj), *Lecidea lactea* (Gj) and *Lecidea inops* (R) with a ×10 hand lens. The abundance and intensity of coloration of this blue material are variable. In extreme cases almost two-thirds of the cross-section of the thallus consists of the blue phase, for example, in samples of *A. rugulosa* growing on atacamite at Gjersvik and on brochantite at Ramundberget it is readily visible with the naked eye. Specimens of *Lecidea lactea*

*In my opinion *Lecidea theiodes* Sommerf. is a modification of *L. lactea* Flörke ex Schaerer caused by its association with copper-bearing rocks. Qualitative electron microprobe analysis of type material of *L. theiodes* showed the presence of copper in the thallus. The type collection (O) has a strongly verrucose surface and shows a characteristic anomalous green coloration, features which led Sommerfelt to describe it as a new species. The verrucose nature of the thallus is not diagnostic since verrucose examples of *L. lactea* are also known (e.g. Härjedalen: Funnäsdalsberget, 4 June 1857, *Th. M. Fries*, UPS). In addition, the internal anatomy of the ascocarp and chemistry of the thallus (norstictic acid) of *L. theiodes* and *L. lactea* are identical. It is likely, therefore, that *L. theiodes* and *L. lactea* are the same species.

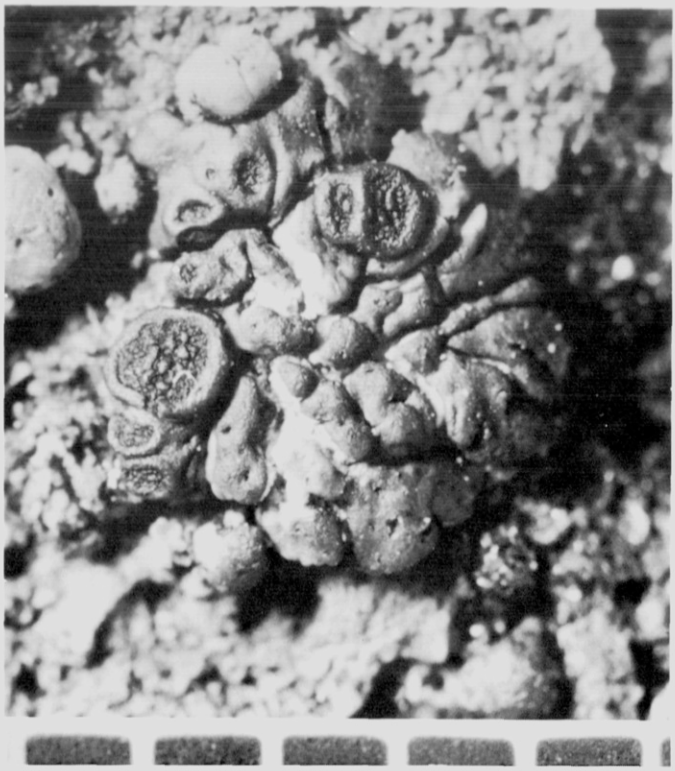
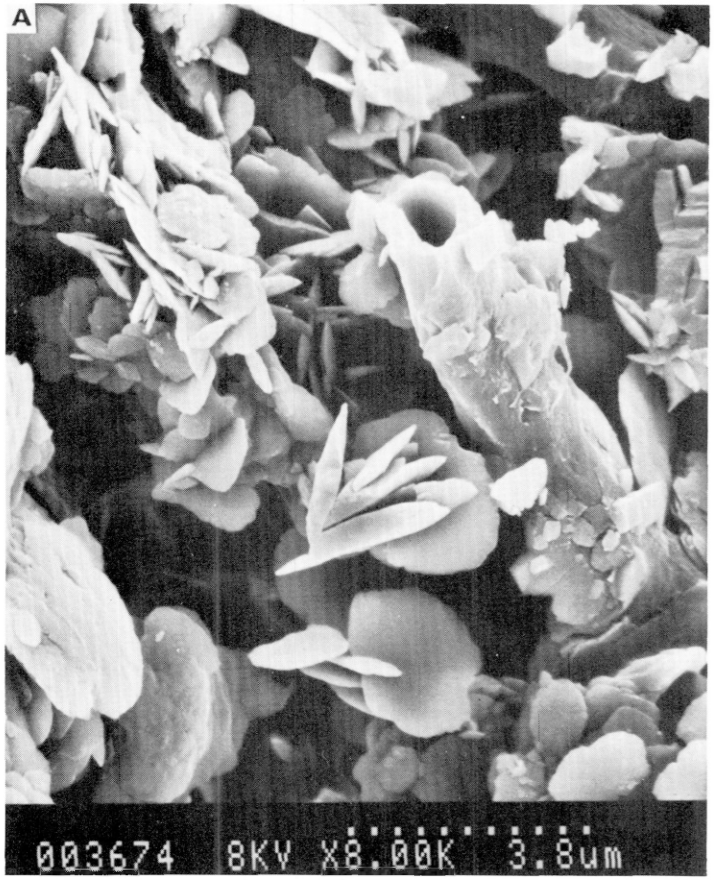


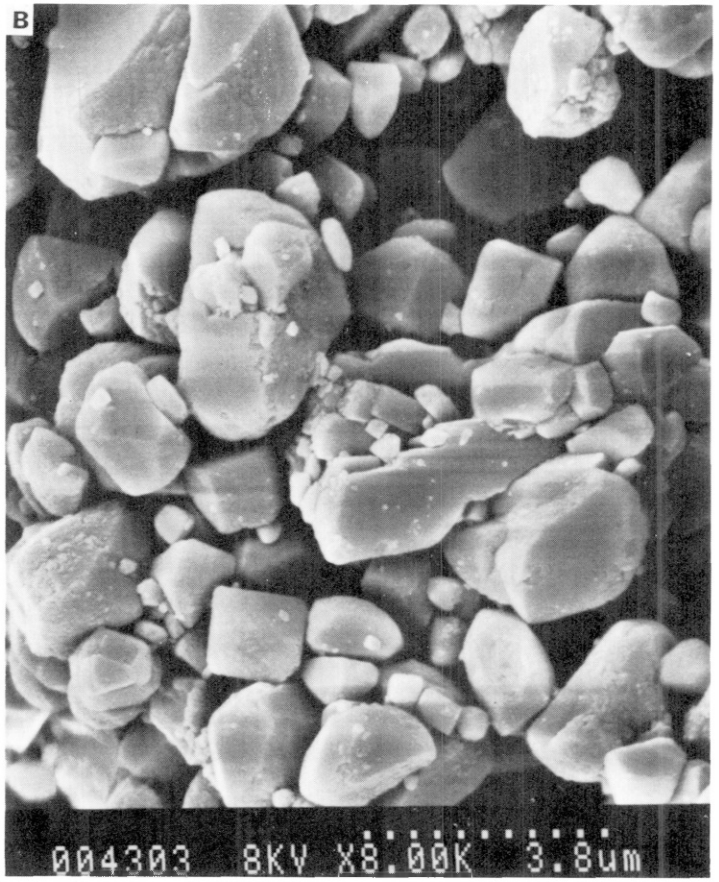
FIG. 1. *Acarospora rugulosa* Körber. This species is frequent at both Ramundberget and Gjersvik growing on cupriferous substrates. 1 scale bar division = 1 mm.

(Gj) have been found with blue inclusions accounting for one-third of the cross-sectional area of the thallus, even when the substrate in direct contact with the lichen is devoid of copper-bearing minerals.

Because these lichens occurred on cupriferous rocks, it was believed that the blue inclusions and the greenish surface colorations could be due to copper salts. Accordingly, the green surfaces and blue inclusions were analysed using the electron probe and the presence of copper was confirmed. A single 5 mg sample including both the white cortex and the blue-coloured medulla of both *Acarospora rugulosa* (R) and *Lecidea lactea* (Gj) were then analysed by atomic absorption spectroscopy to obtain an estimate of the bulk copper content of the thallus. Each sample was hand-picked under a dissecting microscope and then digested in conc. HNO_3. The copper content of the thallus of *A. rugulosa* was found to be 5·9% dry wt and that of *L. lactea* contained 5·3% dry wt.

Sections of *A. rugulosa* and *L. inops* from Ramundberget were examined using the scanning electron microscope (SEM) to determine whether these lichens were modified structurally by their high copper content. In these species the blue areas were seen to consist of an aggregate of plate-like crystals 1–5 μm diam encrusting medullary hyphae (Fig. 2A). At magnifications of 1000–5000 the encrusting


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B
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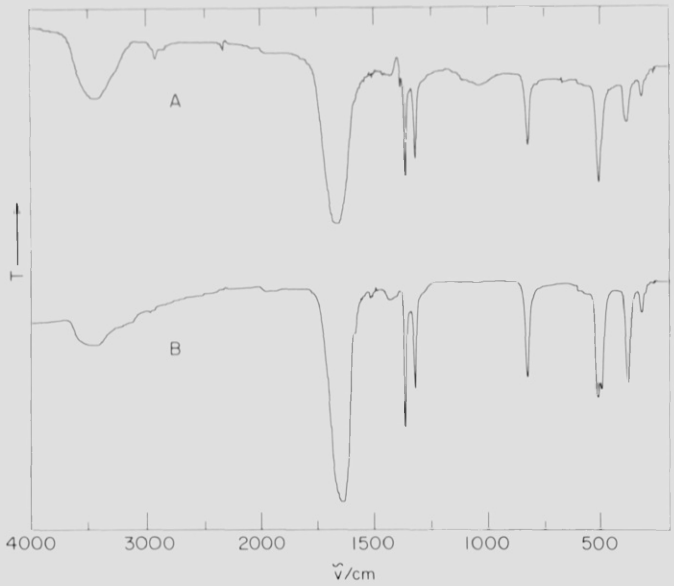


FIG. 3. Infrared spectra of A, blue inclusions within medulla of *Acarospora rugulosa* (R) and B, synthetic copper oxalate prepared by precipitation of copper chloride with oxalic acid. $\tilde{\nu}$ is wavenumber, T is transmission.

crystals are so numerous that it is often difficult to see the hyphae. In samples of *A. rugulosa* from Ramundberget white aggregates occur in which the crystals display a short prismatic habit (Fig. 2B). The white and pale blue materials contained in both *A. rugulosa* (R) and *L. lactea* (Gj) were identified using the infrared spectra obtained from hand-picked material. The spectra were recorded using the KBr disc technique, over the range 4000–200 cm^{-1}. In both instances the white material gave a spectrum characteristic of calcium oxalate monohydrate, whewellite ($CaC_2O_4.H_2O$). The pale blue material was virtually identical to that of a synthetic copper oxalate (Fig. 3) prepared by precipitation from cupric chloride and oxalic acid solutions. Hand-picked pale blue material from *L. inops* (R), *L. lactea* (Gj) and *A. rugulosa* (R + Gj) has been confirmed to be copper (II) oxalate by X-ray diffraction. The microdensitometer traces of powder diffraction photographs shown in Fig. 4 demonstrate that the pale blue material has a pattern similar to that of the synthetic copper (II) oxalate. Measurement of the photographs gives *d*-spacings which agree well with those of $CuC_2O_4.nH_2O$ ($n \sim 0 \cdot 1$), given on Powder Diffraction File Card 21-297 (Joint Committee on Powder Diffraction Standards 1971).

FIG. 2. A, Secondary electron micrograph showing copper oxalate crystals encrusting medullary hyphae within *Acarospora rugulosa* (R) (blue inclusions). B, Secondary electron micrograph showing calcium oxalate (whewellite) crystals within cortex of *Acarospora rugulosa* (R) (white area). Scale bar = 3·8 μm.

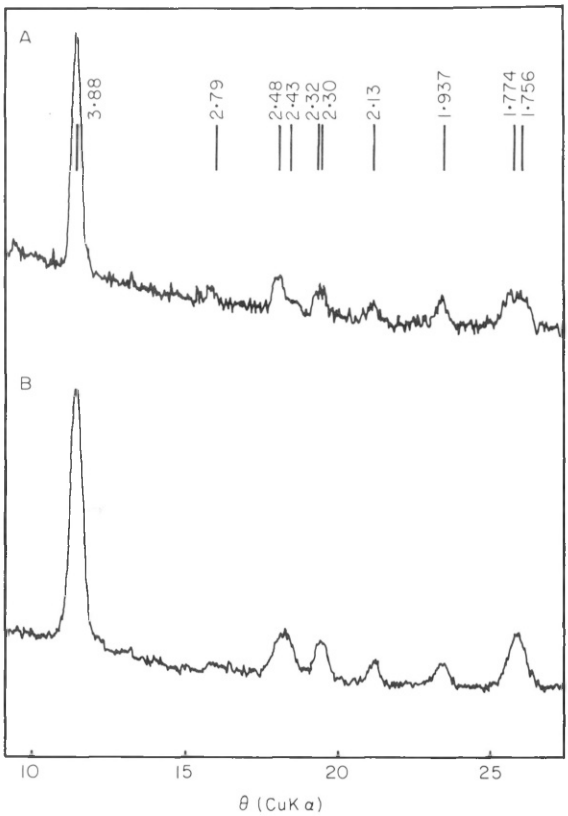


FIG. 4. Microdensitometer traces of powder X-ray diffraction photographs (CuKα radiation). A, Blue material from *Acaraspora rugulosa* (Ramundberget). B, Synthetic copper (II) oxalate. The *d*-spacings for CuC_2O_4. *n* H_2O ($n \sim 0 \cdot 1$) given in the Powder Diffraction File (21–297) are shown on A and the corresponding peak positions are marked.

Using the same procedures the white crystalline material in *A. rugulosa* (R) and *L. lactea* (Gj) has been identified as whewellite ($CaC_2O_4.H_2O$). In *L. inops* (R) and *A. rugulosa* (Gj) similar white material has been shown to consist of weddellite [CaC_2O_4. $(2+x)$ H_2O, $x \leqslant 0 \cdot 5$]. In the case of *A. rugulosa* (Gj) the weddellite is associated with gypsum ($CaSO_4.2H_2O$).

Discussion and Conclusion

Copper sulphide mineralization and associated oxidative products (atacamite and brochantite) in rocks, has been shown to produce visible greenish coloration in lichens growing on them. The copper compounds responsible for this coloration in *Lecidea lactea, Aspicilia alpina* and *Aspicilia subsorediza* have not been specifically identified. Vivid blue inclusions of copper oxalate have been found within

the medulla of *Lecidea lactea, Lecidea inops* and *Acarospora rugulosa*. These features have been observed at both Gjersvik and Ramundberget which both have very similar floras. High concentrations of 5·3% Cu dry wt in *Lecidea lactea* (Gj) and 5·9% Cu dry wt in *Acarospora rugulosa* (R) have been recorded. On the assumption that copper is present only as the oxalate within the latter species, some 15% of the dry wt of *Acarospora rugulosa* (R) will be in the form of copper oxalate. However, it should be stressed that this value would be subject to wide variation since the size and abundance of the blue inclusions are so variable.

It is suspected that precipitation leaches copper from surrounding rocks and the lichen absorbs copper from run-off rather than extracting it directly from its substrate (Czehura 1977). This is confirmed by the observations of the copper form of *Lecidea lactea* growing on copper free quartz veins at Ramundberget surrounded by chalcopyrite-bearing rocks. However, it is also probable that there would be a direct reaction between oxalic acid produced by the mycobiont and copper minerals in the substrate when the lichen thallus is in direct contact with a copper bearing mineral species. Weathering processes in the surface environment will in any case lead to the liberation of copper ions during oxidation of the copper sulphides.

Oxalic acid is a primary product of biochemical processes and in plants it can combine with various elements and compounds to form acid and neutral salts (Franceshi & Homer 1980). Calcium oxalate hydrates, both whewellite ($CaC_2O_4.H_2O$) and weddellite [$CaC_2O_4.(2+x)H_2O$, $x \leqslant 0{\cdot}5$] have been reported in several instances in lichens (e.g. Jones *et al.* 1980). Glushinskite, magnesium oxalate dihydrate, was reported in *Lecanora atra* on serpentinites (Wilson *et al.* 1980, 1981) which undoubtedly reflects the high magnesium content of the underlying rock. It was suggested that magnesium could be substituted by nickel, cobalt, iron, zinc and manganese in the glushinskite structure, thus providing a possible detoxification mechanism to protect the lichen organism from these cations. Evidence was given for iron, nickel and manganese substitution. Copper oxalate is not isomorphous with magnesium oxalate dihydrate nor with the calcium oxalate hydrates (Schmittler 1968). This means that although substitution may be one method of avoiding the effects of toxic elements it is evident that oxalates of a range of elements can form directly as a result of precipitation by reaction with oxalic acid during lichen growth. The nature of the oxalate formed will be dependent upon the cations present in the surrounding medium, which will be determined largely by the mineralogy of the substrate. Thus one might expect to find the relatively insoluble oxalates of metals such as barium, cobalt, lead, manganese, nickel, silver and zinc occurring in lichens growing on mineralized rocks of the appropriate composition.

The precipitation of insoluble salts within the lichen thallus, but external to the protoplast seems to be an effective process by which the lichen organism can avoid the effects of toxic elements. It is evident from this study that significantly high concentrations of copper, up to 5% dry wt, are fixed in the thallus of living lichens as copper oxalate.

I am indebted to Dr J. E. Chisholm for extensive X.R.D. analysis and to Mr G. C. Jones for I.R. and A.A.S. determinations, both of the Department of Mineralogy, British Museum (Natural History). Professor Rolf Santesson is especially thanked for my introduction to the lichen flora at Ramundberget.

The help received from my supervisors Mr P. W. James [British Museum (Natural History)] and Dr C. Halls (Royal School of Mines) is gratefully acknowledged. The management of Grong Gruber A/S and Ing. Arve Hangen are thanked for providing access to the field area and for generous logistical support.

The author gratefully acknowledges receipt of a British Petroleum Ltd funded British Museum (Natural History) Centenary Studentship.

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Accepted for publication 29 *February* 1984

Lichenologist 17(1): 111–116 (1985)

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SHORT COMMUNICATIONS

THE INFLUENCE OF COPPER MINERALIZATION ON *ACAROSPORA SMARAGDULA*

It has recently been reported that certain lichens occurring on copper-rich rocks assume a yellow-green hue due to the accumulation of unidentified copper salts (Czehura 1977, Purvis 1984). These lichens, most of which contain norstictic acid, belong to the genera *Aspicilia, Buellia, Lecanora* and *Lecidea*.

A small, yellow-green species of *Acarospora* with ± rounded, often scattered, flattened squamules and with small, immersed, black-brown discocarps, has recently been collected by O. W. Purvis, as well as by R. Santesson, on chalcopyrite ($CuFeS_2$)-bearing rocks in Scandinavia. At these sites it typically occurred in crevices on steep or vertical rock surfaces together with other lichens characteristic of cupriferous substrata. British material of the same *Acarospora* species has also been collected by O. L. Gilbert from copper-rich epidiorite on Ben Hope, Sutherland. A further collection by B. J. Coppins from this area, that on fence posts evidently treated with a copper-based fungicide, has also been made available to us. All these collections resemble *A. smaragdula* in their morphology and chemistry.

Two new yellow-green species of *Acarospora* have recently been described: *A. isortoqensis* (Alstrup 1981) and *A. undata* (Clauzade *et al.* 1981). *Acarospora undata* was considered by its authors to be very similar to *A. smaragdula* differing only in its green coloration, the concentric fold-like markings on the thallus surface and the abundance of yellowish crystals in the upper cortex (Clauzade *et al.* 1981). In their text there is an inferred affinity of their new species for heavy metals. Atomic absorption spectroscopy of the substrata of *A. isortoqensis* by Alstrup (1984) also suggests a similar affinity of his new species for copper. After comparison, Alstrup (1984) considers *A. undata* and *A. isortoqensis* to be the same species in which case the name *A. isortoqensis* would assume priority. In addition Alstrup reported rhizocarpic acid from his collections.

We consider that both *Acarospora isortoqensis* (including *A. undata*) and our examples of this green *Acarospora* species are modifications of *A. smaragdula* arising through the growth of this species on copper-rich substrata. Initial suspicion as to this relationship arose from field observations in Scotland, where a colour gradation from the normal pale reddish brown hue, through pale yellow to lime-green was observed on several occasions (also noted by Clauzade *et al.* 1981). Confirmation of appreciable amounts of copper on the thallus surface and within the upper cortex was obtained by electron microprobe analysis of all listed specimens, which gave prominent peaks corresponding to the characteristic L_α, K_α and K_β lines for copper (Fig. 1).

Acarospora smaragdula should contain norstictic acid, but only trace quantities could be detected by t.l.c. even after heavy spot loading. However,

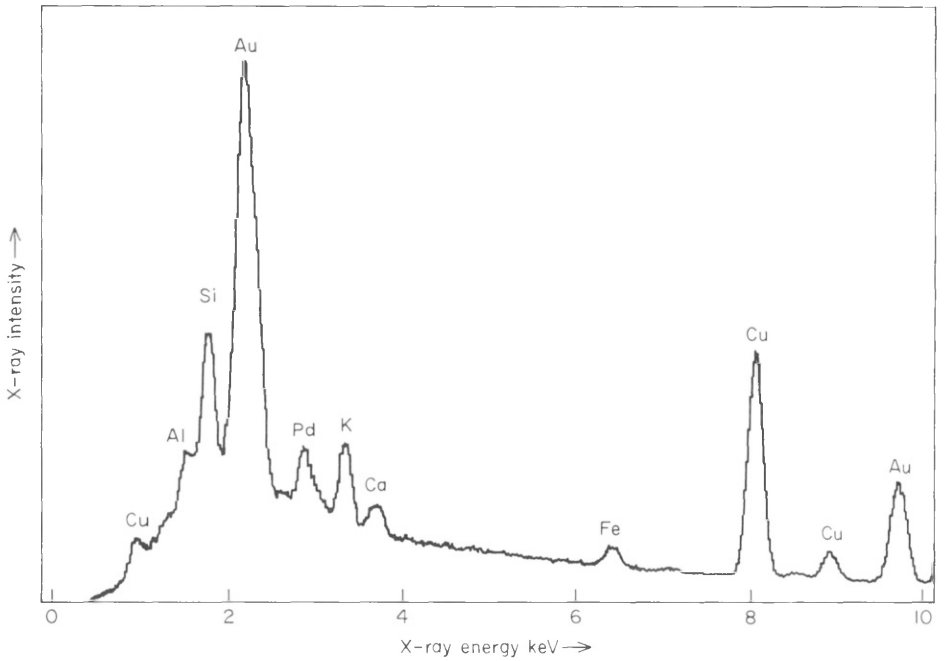


FIG. 1. X-ray spectrum from spot analysis of the thallus surface of the holotype of *Acarospora undata* (Au/Pd coated).

squashes in KOH produced abundant red, needle-shaped crystals indicating the presence of appreciable amounts of this acid. Although rhizocarpic acid, responsible for the yellow-green colour in *Acarospora* subgenus *Xanthothallia*, was recorded by Alstrup (1981, 1984) we could find no evidence of this pigment in any cited material (see below). Clearly the assumed green coloration of the thallus surface of *A. smaragdula* may be compared with that of *Lecidea theiodes*, recently recognized as a modification of *L. lactea* occurring on cupriferous substrata (Purvis 1984). It is particularly interesting to note that the thalli in both *L. lactea* and *Acarospora smaragdula* are unusually verrucose or plicate when growing on copper-rich rocks. This thalline response appears to be a general feature common to many lichen species occurring on cupriferous substrata.

Seven, possibly eight, norstictic acid-containing lichen species which assume a green colour when growing on certain copper-rich rocks are now known, viz. *Acarospora smaragdula, Aspicilia alpina, A. myrini, A. subsorediza, Buellia aethalea, Lecidea lactea, L. lulensis* and *L. swartzioidea* (=*L. lactea*?) and no lichens containing norstictic acid in this particular environment are known which do not change from a grey to a greenish yellow colour.

As a tentative and new hypothesis, one of us (O.W.P.) suggests that the copper compound responsible for the green coloration could be a Cu-norstictic acid complex. Certainly numerous pale yellow (*sic*) crystals surrounding

cortical hyphal tips at the thallus surface and in the upper cortex have been observed in polarized light in sections of *Acarospora smaragdula* (Clauzade *et al.* 1981). Support for such an idea is apparent from the difficulty we had in detecting free norstictic acid by t.l.c.; if the acid is complexed to copper this observation would not be surprising. However, we have shown that norstictic acid is abundantly present by the KOH squashes. KOH, a strong base, could readily dissociate copper from such a complex, allowing the usual formation of red crystals to occur in solution. The chemical feasibility of such a Cu-norstictic acid complex has been confirmed by J. Elix (pers. comm.). Detailed work aimed at positively identifying such a complex is currently in progress.

Other copper compounds occur in lichens; copper oxalate has already been detected in the medulla of several species (Purvis 1984). However, copper oxalate formation and production of the proposed Cu-norstictic acid complex are independent of each other, since these two different substances do not necessarily occur together. A different, dark green coloration has been noted in examples of *Lecanora polytropa* on cupriferous rocks in Greenland (Alstrup & Hansen 1977) and has frequently been seen by us in the same species growing on copper-rich substrata in Scandinavia. This green coloration is due to the presence of a different copper compound; *L. polytropa* does not contain norstictic acid. *Lecanora cascadensis* (Czehura 1977) can also accumulate dark green copper salts.

These observations indicate that taxonomists must pay serious attention to the impact of rock mineralogy on lichens as it can cause obvious colour differences, alterations in morphology and possible changes in chemistry as revealed by t.l.c.

Specimens examined: **Greenland:** Søndre Isortoq, Ivnarssuaq, 65°26′N, 52°11′W, north-facing rock wall, 31 July 1977, *V. Alstrup 77899* (holotype of *Acarospora isortoqensis;* C); Narssaq district, Kangerdluarssuk, west of Grœnseelv, 60°54′N, 45°50′W, 400 m, 25 July 1980 *V. Alstrup 80513* (C); Søndre Isortoq, Igdlut, Kangigdlît, 65°31′N, 52°01′W, 40 m, *V. Alstrup 771438* (C).—**Norway:** Nord Trøndelag, Gjersvik, 13°25′E, 64°53′N, 450 m, 9 August 1983, *O. W. Purvis* (BM, several collections).—**Sweden:** Härjedalen, Tännäs parish, Gruvvålen, Glimsjön, *c.* 2 km NE Ramundbergets fjällgård, 12°25′E, 64°42′N, 920 m, 17 August 1983, *O. W. Purvis & R. Santesson* (BM, several collections).—**British Isles:** Scotland, West Sutherland, v.c. 104, Ben Hope, 29/471487, 500 m, July 1984, *O. L. Gilbert* (BM); Strathnaver, 29/72-49-, on copper-impregnated fence posts, 29 August 1984, *B. J. Coppins* (E).—**West Germany:** Baden, Südschwarzwald, Präg (Kr. Lörrach), auf abgesprengten Felsen an der Straße kurz oberhalb des Ortes, 4 September 1971, *V. Wirth* (holotype of *Acarospora undata*, hb. Wirth).

We are grateful to Dr V. Wirth (Stuttgart) and Dr V. Alstrup (Copenhagen) for the loan of type and other material in their care. Special thanks are due to Professor R. Santesson (Uppsala) for the loan of copper-rich *L. polytropa* and for valuable discussions. Dr J. Elix is thanked for help in providing chemical information. Assistance from Dr C. Halls (Royal School of Mines) is gratefully acknowledged. The management of Grong Gruber A/S and Ing. Arve Haugen are thanked for providing access to the field area at Gjersvik and for generous logistical support.

One of us, O.W.P., gratefully acknowledges receipt of a British Petroleum Ltd British Museum (Natural History) Centenary Studentship.

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PELICOTHALLOS DILCHER, AN OVERLOOKED FOSSIL LICHEN

The fossil record of lichens is meagre and poorly documented. Recognition of a fossil as a lichen depends either upon finding phycobiont and mycobiont preserved together in a thallus or upon finding fungal fruit-bodies or propagules referrable to extant lichen genera. Intact thalli are likely to be met only under conditions of extraordinary preservation since the vegetative portions of lichens, particularly the algae, are typically thin-walled and unpigmented. Characteristic lichen fungi may well be present in fossil assemblages, but have hitherto gone unrecognized.

Among fossil fungi, Cenozoic foliicolous forms are particularly well preserved and well documented. It is reasonable to expect that foliicolous lichens should also be present and identifiable as such in Cenozoic tropical and subtropical floras.

In the course of a review of the literature on Tertiary fungi it became apparent that the genus *Pelicothallos* Dilcher, originally assigned to the family Microthyriaceae (Dilcher 1965), could more plausibly be referred to the extant foliicolous lichen genus *Strigula*.

Pelicothallos, established for the single species *P. villosus* Dilcher, epiphyllous on leaves of *Chrysobalanus* from the Eocene of Tennessee, USA, was originally described as follows. 'Stroma lobed, setose, composed of laterally confluent radiate hyphae. Stroma may be ostiolate and/or may produce stalked conidiophores. Conidiospores round, hyaline; ascospores unknown.' The cells of the 'stroma' (thallus) were described as rugose or granular, with cells 6–12 × 16–43 μm. The thalli bore setae 50–180 × 10 μm, tapering to 2 μm, with blunt apices sometimes bearing spherical spores 16 μm in diameter. In addition the thalli bore several dark fruit-bodies visible as rings 20–30 μm in diameter with a central pore 10–15 μm broad. No spores were associated with these fruit-bodies. No evidence of parasitism on the host was found. The climate of Tennessee in Eocene times, as deduced from the vascular vegetation, was subtropical or tropical and humid. Good photographs of all of the structures described accompany the description.