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Lichen Mineral Studies — Currently Clarified or Confused?

D.H. BROWN
Department of Botany, The University, Woodland Road, Bristol, BS8 1UG, UK

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Abstract

A critical review of lichen mineral studies is presented. Emphasis is placed on laboratory studies that discriminate between extracellular exchangeable binding and intracellular uptake of metals, biomonitoring studies and the significance of trapped particulate matter, and the role of biogenic metal-rich crystals in rock-weathering studies. Cross-fertilisation of ideas from such studies is recommended in order to avoid the acceptance of partly verified hypotheses. New data are presented on the influence of thallus age and morphology on metal uptake.

Keywords: metal uptake, extracellular and intracellular sites, trapping particulate matter, biogenic crystals, morphology and age

1. Introduction

"Lichen mineral studies" is an expression that will convey different meanings to researchers depending upon their particular interests. Thus a laboratory worker might view the subject in terms of the exchangeable uptake of cations according to predictable physico-chemical laws, emphasizing the cell wall as a major cation binding site, or consider the quantitatively smaller, trans-membrane carrier-mediated uptake of metals to intracellular sites and their metabolic consequences. Field workers using lichens as biomonitors stress the occurrence of particles derived from factories, mine sites or automobiles,

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whereas those interested in phenomena such as rock weathering may highlight the occurrence of biologically formed extracellular metal-rich crystals. Regrettably, inadequate cross-fertilisation of ideas occurs between these disciplines.

In this article certain aspects of mineral studies are critically reviewed, in order to encourage researchers to attempt to test or verify hypotheses directly rather than relying upon extrapolation and assumption from other studies. Examples are quoted that present the diversity of conclusions, and their choice reflects a laboratory worker's knowledge of the literature. Some new data are introduced.

2. Cellular Location of Elements

The majority of early studies on metal uptake by lichens emphasize the fact that most uptake is by a cation exchange process to extracellular sites, presumed to be in the cell walls and on the outer surface of the cell membrane (Brown, 1976; Nieboer et al., 1978; Boileau et al., 1985a). This high cation exchange capacity has frequently been used to explain enhanced levels of minerals, especially heavy metals, in both bryophytes and lichens. Cell death can increase such uptake, presumably by exposing suitable binding sites previously protected by the cell membrane (Nieboer et al., 1976; Richardson et al., 1985). The chemical nature of these negatively-charged exchange sites is still the subject of speculation (Richardson et al., 1985). Resolution of this point may contribute to our understanding of why different species bind different quantities of metals (e.g. Richardson and Nieboer, 1983; Brown and Beckett, 1983; Brown, 1987), and permit more reliable predictions to be made of binding capacity and binding affinity. Uncertainty exists as to the relative contribution made by each symbiont within a lichen to cation binding, although thallus layers have shown a range of uptake capacities in closely related species (Asta and Garrec, 1980; Goyal and Seaward, 1981; Richardson and Nieboer, 1983).

The predictable replacement of one element by another on extracellular exchange sites has been used as the basis for a sequential elution procedure (Beckett and Brown, 1984a; Brown and Buck, 1985; Brown and Wells, 1988). After cation exchange, generally using nickel or lead as the displacing agent, intracellular elements can be recovered by treating samples with acid to rupture the cell membrane and release elements from within the cell. This technique has been used, for example, to determine the effect of desiccation on the maintenance of intracellular metal levels (Buck and Brown, 1979), cadmium uptake kinetics, interactions with other cations (Beckett and Brown, 1984b; Brown and Avalos, 1990), and movement of heavy metals from the cell wall to

the cell interior (Brown and Beckett, 1985). The latter observation suggests that the cell wall, rather than being a device to protect the cell interior from toxic elements, may potentially act as a reservoir for such metals.

Toxicity of heavy metals to lichens has been assessed by short-term laboratory experiments (Boileau et al., 1985b). Observations suggest that cyanobacterial lichens are more sensitive than chlorophycean lichens to heavy metals (Brown and Beckett, 1983), that specific metal tolerance may be induced in the laboratory (Beckett and Brown, 1983) and that populations of *Peltigera* spp. on abandoned mine sites may possess tolerance due to reduced intracellular uptake of toxic metals (Beckett and Brown, 1984b), although the latter requires further investigation (Brown and Avalos, 1990). Damage to cell membranes can cause loss of soluble intracellular chemicals (Buck and Brown, 1979). Garty et al. (1985a) showed that chlorophyll damage correlated with metal uptake when lichens were transplanted to polluted areas. The recovery of soluble elements in incubation media or washing solutions has been used as a measure of cellular damage by metals in the laboratory (Puckett, 1976), or air pollution in the field (Alebic-Juretic and Arko-Pijevac, 1989), but these can be underestimates due to cations becoming bound to the cell wall exchange sites during the release process (Buck and Brown, 1979).

3. Biomonitoring and Trapping Particulate Matter

Lichens appear to be efficient at trapping particulate matter from the environment. Thus, with distance from particle emission sources, declines have been reported in ash content (Richardson and Nieboer, 1980), and a variety of metals, including mercury (Bargagli et al., 1987a, 1989), uranium and lead (e.g. Beckett et al., 1982), and iron and titanium (e.g. Nieboer et al., 1982; Looney et al., 1985). Distribution patterns are not always identical for all elements and species (e.g. Thompson et al., 1987). Analyses of iron, titanium, aluminium and silicon have all been used as measures of particulate matter in the form of soil, rock or factory emissions (Addison and Puckett, 1980; Bosserman and Hagner, 1981; Moser et al., 1983; Puckett, 1985, Vestergaard et al., 1986; Bargagli et al., 1989), with the presumption that they are relatively insoluble and, for the latter three, are assumed to be non-essential elements. Although Gough et al. (1988) showed a correlation between titanium and ash content in the terricolous lichen *Parmelia chlorochroa*, they failed to detect such a correlation with the epiphytes *Hypogymnia enteromorpha* and *Usnea* spp.

Linear correlations between the iron and titanium concentrations in lichens have been used to reinforce the concept of trapping of unmodified soil particles. They have been extended to suggest that similar correlations between iron,

titanium, aluminium, or silicon and other elements imply a common particulate origin (e.g. Nieboer et al., 1978). However, in the same article, it was shown that extrapolation of the relationship between iron and titanium content to zero titanium showed a positive iron content in the lichen, which was suggested to be the quantity of this essential element required by the plant. Whether the iron was derived from the partial dissolution of soil particles trapped in the lichen, or from an entirely different source was not established, but it raises the possibility that metal-rich particles may not be entirely inert within the lichen. No attempt appears to have been made to test this possibility directly.

Washing lichens with water before analysis often, but not invariably, decreases the recovery of heavy metals (Lawrey and Rudolph, 1975; Brown, 1976; Lawrey and Hale, 1981, 1985). Gough and Erdman (1977) showed that washing removed contaminating particles from the surface of rhizinae. It is concluded that such losses represent removal of surface particulate matter, although most experiments failed to monitor for loss of intracellular soluble elements in order to distinguish particulate release from desiccation-induced damage (Buck and Brown, 1979). There have been relatively few reports demonstrating the chemical nature of particles trapped within lichens (Garty et al., 1979; Galun et al., 1984; Olmez et al., 1985), but these show that metal-rich particles can reach the interior of the thallus, thereby making release by washing difficult. Bargagli et al. (1987a) concluded, after a sequence of homogenisation, centrifugation and digestion of organic material, that, with *Parmelia sulcata* from Mt. Amiata, the presence of aluminium may have been due to soil particles but that mercury was acquired as volatile mercury that had become associated with organic matter. The same lichen from Mt. Etna may contain soil-derived mercury-rich soil particles (Bargagli et al., 1989). As the usual exponential decline in mercury content with distance was seen in both studies, these papers emphasize that caution must be shown when generalising about metal acquisition processes.

Factory emissions come in a range of particle sizes and compositions, especially where metals are surface deposited on such particles. The relationships between the efficiency of particle entrapment, size of particle and form of the acceptor have been considered for other groups of plants (e.g. Clough, 1975; Little, 1979; Brown, 1984). Schuepp (1984) used an unidentified, fruticose, nickel-plated lichen (sometimes with wax infilling of interstitial spaces) and nickel-wire roughness (wire) to show that such porous surfaces acquired more submicron-size aerosol by convective deposition than did flat surfaces. Garty et al. (1985b) coated *Ramalina duriaei* with various polymers and found that some decreased copper and nickel uptake, but not lead uptake, during transplant experiments. In a comparison of lichen chemistry and air-borne particles,

Olmez et al. (1985) concluded that foliose epiphytic *Parmelia* spp. preferentially trapped larger-sized particles, probably by dry deposition or impaction rather than rainfall. Garty (1985) and Garty and Ammann (1987) considered that a high coefficient of variation between lichen samples for their metal concentration was indicative of the entrapment of large particles. However, the low coefficient of variation reported for zinc may reflect its status as an essential element that is generally found in higher concentrations than the more variable (but also essential) copper and manganese and (assumed non-essential) chromium and nickel.

Correlations between atmospheric deposition (which includes both wet and dry deposition) and lichen composition have been attempted occasionally (e.g. Andersen et al., 1978; Pilegaard, 1979; Olmez et al., 1985; Vestergaard et al., 1986). Vestergaard et al. (1986) considered that poor correlation between bulk precipitation and lichen chemistry close to an emission source reflected a change in particle size distribution. Other studies have compared lichen composition with annual deposition data (Herzig et al., 1989). Uptake by transplanted lichens was relatively rapid (Pilegaard, 1979; Deruelle, 1984; Bartòk, 1988). Such studies appear to assume that metal uptake is a one-way process: once acquired metals are never released. Decreases in lichen heavy metal concentrations have been reported when particulate emissions from power plants and a foundry were reduced (Showman and Hendricks, 1989). However, because the age of the lichens sampled after controls were introduced was not stated, it is not clear whether only recently formed tissue was analysed or whether actual loss of metal occurred. Deruelle (1984) showed that lead acquired by lichens transplanted to sites contaminated with automobile exhaust was lost within months when they were returned to their original uncontaminated site.

Field radio-isotopic studies are amongst the few where consideration is given to the biological residence time of an element (reflecting thallus growth and redistribution within the thallus). Differences between elements probably relate to the solubility of trapped particles, meteorological conditions at the site investigated, and expectations about the biological behaviour of comparable physiological elements (e.g. Ellis and Smith, 1987). However, it is not known, for example, whether ^{210}Pb (or its daughter product ^{310}Po) is initially acquired in the form of particulate matter (Ellis and Smith, 1987) is then dissolved to behave as a cation (Schwartzman et al., 1987), nor has this been tested experimentally.

Using various, more or less detailed, computational procedures many workers have concluded that it is possible to establish the nature of the source of individual elements in lichens (Saeki et al., 1977; Puckett and Finegan, 1980;

Bosserman and Hagner, 1981; de Bruin et al., 1986; Jenkins, 1987). These reports tend to imply that the lichen is incapable of modifying or controlling the quantity or balance of elements it acquires. Variations occur in the potassium to calcium ratio in different epiphytic species but, although the actual amounts may differ, within a species this ratio is fairly constant, irrespective of the tree species involved (Kuziel, 1973). Lichens are known to modify the chemistry of rainfall as it passes over them (Lang et al., 1976; Crittenden, 1983, 1989), although the actual results may have been modified by the use of incomplete lichen thalli and/or desiccation-induced damage. Puckett (1985) found that potassium and magnesium concentrations were correlated within the lichen but not in the incident precipitation and that seasonal variation in the aluminium and potassium concentrations in lichens and precipitation did not coincide. It was suggested that the latter observation may reflect the different responses of lichens to metals in rain and snow; snow-melt may wash off more elements than it introduces. Crittenden (1983, 1989) showed that the concentration of elements is rapidly reduced during rainfall events. How the lichen reacts to this changing concentration is unknown, but most researchers use average chemical values for rain without taking account of the dynamic situation which exists. The enhanced accumulation with increasing altitude that occurs with some, but not all, elements (Kwapulinski et al., 1985a, 1985b; Bargagli et al., 1989) may be related to greater rainfall and wash-out of particles dispersed over long distances.

While interspecies calibrations have been reported between lichens and other plants (Folkeson, 1979), metal uptake by lichens does not invariably correspond with the patterns shown by other monitoring systems, e.g. bark (Laaksovirta et al., 1976) and pine needles (Bargagli et al., 1987b). This may partly reflect differences in particle-trapping ability (Puckett and Finegan, 1980), but some note must be taken of the possibility of lichens removing minerals from their substratum. Although Kabata-Pendias et al. (1989) reported significant correlations between lichen zinc and total and extractable zinc in soils, this still does not preclude zinc uptake being due to soil-particle trapping. Kovàcs-Làng and Verseghy (1974) noted that the potassium and calcium contents of terricolous lichens varied during the year, being generally higher during the autumn and winter, but found no correlation between lichen concentration and the water-soluble soil elements, despite comparable seasonal changes. For many elements, epiphyte chemistry has been significantly correlated with surface and underlying bark chemistry (de Bruin and Hachenitz, 1986) and lichen hyphae have been shown to penetrate as far as xylem elements in trees (Ascaso, 1985). Unfortunately statistical correlations only show numerical relationships between two features and not that there are direct biological relationships. The

selectivity of element uptake to the cell wall and cell interior shown in laboratory experiments often appears to be overlooked in field studies in which the lichen is treated almost as a passive single unit.

4. Rock Weathering and Biogenic Particles

Lichens alter the chemistry of rocks on, or in, which they are growing (Kerr and Zavada, 1989). This process can either involve dissolution and loss of specific elements or, more regularly reported, concentration of elements in specifically generated chemicals. Thus biogenic oxalates containing either calcium, magnesium, copper or manganese have been reported using X-ray diffraction or visualised by scanning electron microscopy (Jones and Wilson, 1986; Jones, 1988). Most studies have investigated crustose lichens but, since Erdman et al. (1977) found calcium oxalate in *Parmelia chlorochroa*, biogenic crystals should be sought amongst the particulate matter present in samples used for biomonitoring. Buck and Brown (1979) postulated the occurrence of calcium oxalate crystals in epiphytes from dry habitats to account for the very variable calcium analyses in such plants.

Lichen phenolic substances have often been proposed as suitable agents for rock weathering due to their metal chelating abilities (Rundel, 1978). Ascaso (1985) reviewed the possibility of lichen acids causing release of elements from rock and the formation of clay minerals. Others have questioned the quantitative significance of these processes in nature, both from direct observation and because of the low solubility of lichen phenolics (Jones and Wilson, 1986). Recently copper-norstictic acid (Purvis et al., 1987) and copper-psoromic acid (Purvis et al., 1990) have been identified in crustose lichens from copper-rich substrata. These have been suggested to contribute to the heavy metal tolerance of the lichen involved but, as not all species in such habitats contain these complexes and copper is an essential element, this cannot be a universal extracellularly developed tolerance mechanism. It is also notable that acetone treatment of lichens, which removes phenolic lichen acids and probably damages cell membranes, leads to enhanced, rather than reduced, metal uptake (Brown, 1976; Richardson et al., 1985).

5. Influence of age and morphology of lichen thalli

Elevated metal concentrations in central, older, parts of foliose lichen thalli have been attributed to slow and prolonged mineral uptake (Schutte, 1977; Hale and Lawrey, 1985; Bargagli, 1989). Higher concentrations of divalent metals in older parts of *Cladonia* thalli could also be related to the longevity

of the tissue (Pakarinen, 1985; Brown, 1987). If metal uptake is in the form of insoluble particles, then this relationship could be a reasonable explanation, especially if particles can penetrate through cortical layers into the thallus interior. However, the above discussion suggests that equilibration to new metal levels can be achieved relatively rapidly in both the laboratory (section 2) and the field (section 3).

It is possible that higher metal concentrations in older tissue may reflect a greater cation exchange capacity in older parts of the thallus. Somewhat surprisingly, there do not appear to be any reports of age-related uptake of soluble cations. Table 1 shows the results of one such experiment where 6 mm discs of rhizinae-free *Peltigera membranacea* (collected from a calcareous woodland, at Goblin Combe, Avon) were bubbled in deionised water or 0.01 M zinc sulphate for 60 min, before subjecting them to the sequential elution procedure (Beckett and Brown, 1984a). "Young" discs were taken from within 1 cm of the lobe margin and "old" discs 5 cm from the lobe margin. The results show that untreated field samples contain higher concentrations of zinc and calcium in older tissues. The slightly lower concentrations of magnesium and potassium in older tissues may reflect minor cell senescence with loss of intracellular ions and the exposure of additional cation exchange sites (see section 2). High and variable levels of calcium in the acid fraction may represent particulate material or calcium oxalate crystals rather than strictly intracellular metals. For both zinc and calcium, field samples showed approximately the same metal concentrations on the extracellular exchange sites and in the intracellular fraction.

Following zinc treatment, substantial zinc uptake occurred at the exchange sites, with loss of pre-existing wall-bound divalent cations (Table 1). As a consequence of using high zinc concentrations some release of intracellular potassium occurred, which was recovered in the washing solutions and from the exchange sites. Greater zinc uptake occurred in the older discs, mostly to the cell wall exchange sites, but some also to the cell interior. This experiment shows that while older tissue of *P. membranacea* may contain elevated metal levels, these may be particulate. Addition of saturating levels of zinc showed that the old tissue has, compared to the young, a higher cation exchange capacity. How much of an individual exchangeable metal is present in field material must reflect the composition of the last solution to bathe the thallus, the route of acquisition by a particular tissue, and the affinity of sites in tissues of different age for the available elements.

The role of morphology in metal acquisition is a seriously under-investigated topic. Nash and Sommerfield (1981) suggested that morphological form may account for some variation in element composition. Goyal and Seaward (1982a)

Table 1. Location of elements in samples of two different ages from untreated and zinc-treated *Peltigera membranacea*

Condition		Concentration in cellular fractions ($\mu g\ g^{-1}$)			
		Inter-cellular	Extracellular exchangeable	Intra-cellular	Total[1]
Zinc					
Untreated	young[2]	7	46	23	76±22
	old	6	56	83	145±6
Treated[3]	young	591	2809	181	3581±101
	old	641	4542	254	5437±211
Calcium					
Untreated	young	96	1785	1057	2938±555
	old	58	2495	2105	4658±1626
Treated	young	36	604	1125	1765±1394
	old	71	384	550	1005±574
Magnesium					
Untreated	young	41	278	895	1214±61
	old	20	261	537	818±107
Treated	young	1	100	1038	1139±178
	old	1	65	346	412±42
Potassium					
Untreated	young	105	216	5002	5323±526
	old	93	60	4825	4978±859
Treated	young	453	305	4972	5730±1636
	old	168	204	3949	4321±90

[1] Mean ± standard deviation (n=3).
[2] Discs cut 1 cm (young) or 5 cm (old) from thallus margin.
[3] Bubbled for 60 min in deionised water (untreated) or 0.01 M zinc sulphate (treated).

suggested that differences in tissue dimensions may have been induced by exposure to heavy metals. However, some of the reported changes may reflect responses to other stresses, such as desiccation (Snelgar and Green, 1981), experienced in different metal-contaminated habitats. Goyal and Seaward (1981) reported highest metal levels in the rhizinae of field samples of *Peltigera* collected from metal-rich sites, where, despite washing, particulate contamination within the fungal mass was still possible. Subsequently Goyal and Seaward (1982b) experimentally verified that rhizinae acquired higher total concentrations of metals than did thallus discs without rhizinae.

Table 2 shows the results of a comparable experiment to that reported in

Table 2. Location of elements in discs and rhizinae of untreated and zinc-treated *Peltigera membranacea*

Condition		Quantity in cellular fractions (μg sample^{-1})				(μg g^{-1})
		Inter-cellular	Extracellular exchangeable	Intra-cellular	Total	Total[1]
Zinc						
Untreated[1]	Disc[3]	0.59	0.87	0.49	1.95	115±20
	Rhizinae	0.10	0.21	1.54	1.85	1085±585
Treated[2]	Disc	2.48	14.16	4.21	20.85	1345±280
	Rhizinae	7.40	50.48	0.60	58.48	33565±4780
Calcium						
Untreated	Disc	1.30	31.81	5.32	38.43	2720±135
	Rhizinae	2.99	5.14	9.07	17.20	9845±3735
Magnesium						
Untreated	Disc	0.86	5.67	4.05	10.58	610±25
	Rhizinae	0.54	0.94	0.42	1.90	1050±190
Potassium						
Untreated	Disc	3.29	0.99	81.51	85.79	4845±875
	Rhizinae	8.62	4.62	3.56	16.80	9545±3360

[1] Mean ± standard deviation (n=3).
[2] See Table 1 for explanation of conditions
[3] Discs cut 3 cm from thallus margin.

Table 1 but where intact discs cut 3 cm from the margin were treated with water or a zinc solution and subsequently, after separation into rhizinae and discs, assayed by the sequential elution procedure. Because of the difficulty of obtaining reliable weights for the small mass of rhizinae, data are mainly presented as zinc (μg) per sample. Rhizinae represented approximately 10% of the total disc weight. This data cannot, therefore, be directly compared with that of Goyal and Seaward (1981, 1982b) but does, however, show the relative proportions of zinc in the two fractions. Total metal concentrations are also included to permit such direct comparisons.

Field samples contained, on a weight per sample basis, almost 50% of the zinc in the rhizinae, which increased to 73% after zinc treatment (Table 2). For field samples rhizinae contained, as a percentage of the intact disc, calcium 31%, magnesium 14%, and potassium 18%. Field samples of rhizinae had high levels of zinc in the "intracellular" fraction but this could partly represent trapped particulate matter. After zinc treatment the low level of zinc in the intracellular fraction of the rhizinae may reflect the loss of soluble cell

constituents, viz. potassium, possibly as a result of desiccation of the rhizinae before starting the sequential elution sequence. The smaller percentage loss of potassium from the discs suggests that they are less damaged by handling. Following zinc treatment, zinc was mostly located on the cell wall exchange sits of the rhizinae. The results show that rhizinae can represent a major site for exchangeably binding zinc but, in these samples from a relatively uncontaminated site, this property is apparently not fully utilised.

6. Conclusions

The present discussion has attempted to demonstrate some of the areas of lichen mineral studies where one group of researchers may consider definite statements can be made while other groups may see uncertainty. For example, laboratory studies involving the location of elements in different cellular fractions by the sequential elution procedure is adequate unless measurable particulate contamination occurs. Metal-rich particles may become trapped by lichens, especially where particulate emissions occur, but final metal concentrations, and therefore discussions on metal origin, must take into account the possibility of partial particle dissolution and redistribution of elements onto extracellular exchange sites, into the cell or re-disposition as organic crystals. Material bound to exchange sites is susceptible to relatively rapid removal when environmental conditions change, i.e. as a consequence of meteorological changes during the year. Lichen mineral studies are a highly complex and dynamic activity, deserving fuller investigation in order to improve the use of these plants as precise, quantitative, and predictive biomonitors of the environment.

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