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Biomechanical and biochemical weathering of lichen-encrusted granite: textural controls on organic–mineral interactions and deposition of silica-rich layers

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Abstract

The crustose lichen *Rhizocarpon geographicum* weathers the Lower Devonian Shap Granite by both biomechanical and biochemical means. Biomechanical weathering is mediated by fungal hyphae that penetrate into the rock via intergranular boundaries at ≥ 0.002–0.003 mm year^{-1}. Once inside the granite, hyphae exploit intragranular pores along cleavage and fracture planes in biotite, alkali and plagioclase feldspar. Grains of biotite exposed at the lichen–granite interface have been fragmented by biomechanical action in <122 years. After an extended period of biomechanical weathering of <10 kyr outcrop surfaces, sub-mm sized fragments of biotite and plagioclase feldspar abound in lower parts of the lichen's thallus. Grains of biomechanically weathered biotite show the clearest evidence for biochemical weathering. Typically, K and Fe are leached from the biotite, but other cations may also be removed, leaving a silica-dominated relic. The silica-rich remains of biotite and possibly also feldspar have been redistributed along the lichen–granite interface forming a silica-rich layer. This silica-rich material also cements fractures and pores beneath the interface. Alkali feldspars from outcrop surfaces have been weathered chemically, as indicated by etch pits on cleavage surfaces and fractures, but it is not obvious that lichen was involved in the dissolution. The etch pits were probably formed during earlier phases of non-biochemical weathering that widened intergranular and intragranular pores, facilitating subsequent access of fungal hyphae into the granite. Despite evidence for biomechanical and biochemical weathering, it is unlikely that colonisation of granite surfaces by *R. geographicum* at Shap significantly enhances their weathering rate relative to bare rock surfaces. The lichen may actually retard weathering by protecting the surface from frost action, binding fragmented mineral grains and depositing 'protective' silica-rich layers.

Keywords: Lichen; Biomechanical weathering; Biochemical weathering; Biotite; Feldspar

1. Introduction

Research into the impact of lichens on rock and mineral weathering has focused on two main aspects of their activity: (i) quantification of the potential role of lichens in the weathering of Ca- and Mg-rich silicate rocks during the late Precambrian and early Palaeozoic (Berner, 1992) and (ii) biodeterioration of building stones and archaeologically important materials (e.g., Seaward, 1988). A central question with regard to both aspects is whether a rock surface that

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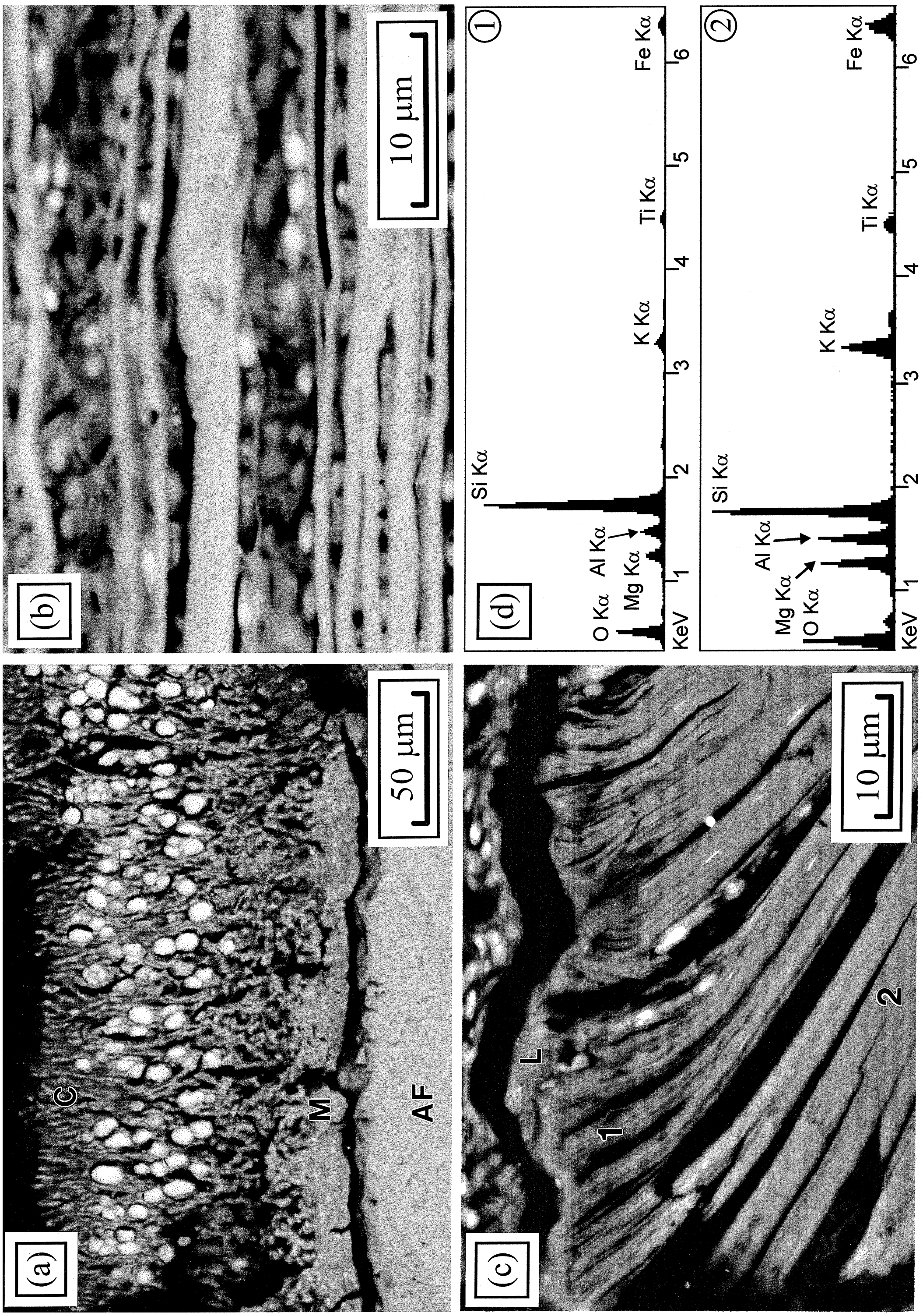
is encrusted by lichens weathers at a slower or a faster rate than an identical but lichen-free surface. For example, before the appearance of vascular land plants in the late Silurian, rock surfaces may have been completely bare, or could have been covered by lichens and algae. From studies of present-day rock surfaces, some workers suggest that the weathering rate of lichen-covered surfaces would have been orders of magnitude greater than bare surfaces (Schwartzman and Volk, 1989; Schwartzman, 1993; Schwartzman et al., 1997). Others, however, state that especially in the longer term, the presence or absence of lichens would have made little difference to overall rates of rock weathering (Berner, 1992; Drever, 1994; Cochran and Berner, 1996).

Lichens are a symbiotic association of two organisms, fungae (the mycobiont) and algae or, rarely, cyanobacteria (the photobiont); the mycobiont and photobiont together form the thallus. There are two mechanisms by which lichens may weather their rock substrate: (i) biomechanical, whereby penetration of the mycobiont beneath the surface leads to fragmentation of the rock and its component minerals and (ii) biochemical, whereby acids or other compounds created directly or indirectly by organic processes etch mineral surfaces or produce changes in the bulk chemical composition of mineral grains (leaching and replacement). These two weathering mechanisms are closely interrelated because biomechanical weathering will increase the surface area/volume ratio of a rock or grain, rendering it more susceptible to biochemical processes (Syers and Iskandar, 1973).

Biomechanical weathering beneath lichens has been recognised for many years and criteria for its identification are firmly established (Fry, 1924, 1927). Lichens are able to mechanically weather their substrate by penetration of fungal hyphae assisted by expansion and contraction of the thallus related to wetting and drying cycles (Syers and Iskandar, 1973). There are three main lines of evidence which can be used to show that a mineral grain within a rock encrusted by lichens has experienced biochemical weathering: (i) etched grain surfaces, (ii) leached/replaced grain interiors and (iii) the presence of weathering products, particularly organic salts such as oxalates, in the vicinity of the lichen–mineral interface. The oxalates most commonly observed are the monohydrate and dihydrate of calcium oxalate, whewellite and weddellite, respectively. Oxalates of other elements, such as the magnesium oxalate dihydrate glushinskite, may be found within lichens encrusting rocks of appropriate chemical composition (see Jones and Wilson, 1985; Wilson, 1995 for comprehensive reviews of evidence for and products of biochemical weathering). The presence of organic salts is the most diagnostic of the three criteria because etching, leaching and replacement can also result from completely inorganic weathering.

Here we describe results of an investigation of mechanisms and rates of biomechanical and biochemical weathering of granite. Of particular interest is the response of different minerals to biomechanical and biochemical action and the presence or otherwise of diagnostic biochemical reaction products. We have studied the Shap Granite, which crops out in northwest England. This granite was selected for a number of reasons. First, its mineralogy and geochemistry have been previously characterised in detail (Grantham, 1928; O'Brien et al., 1985; Caunt, 1986; Lee et al., 1995), allowing an accurate assessment of any changes which may have resulted from biological processes. Secondly, it contains alkali feldspars that behave in a highly regular and predictable manner during natural weathering and can

Fig. 1. Images and analyses of polished transverse sections of the Shap Granite from quarry faces. (a) BSE image of alkali feldspar (AF) encrusted by *R. geographicum*. The outer cortex (C), algal layer (characterised by OsO_4-stained algal cells giving a bright BSE signal) and medullary layer (M) of the thallus are clearly distinguished. Alkali feldspar directly underlying the lichen–mineral interface is apparently unaltered. (b) BSE image of a grain of biotite which has been split into many narrow sheets following penetration of fungal hyphae along its cleavages. The narrowest sheets are ~ 0.5 μm in width. (c) BSE image of a lichen-encrusted biotite grain; the base of the medulla is at the top edge of the image. The grain is encrusted by a thin and discontinuous silica-rich layer (L). Numbers 1 and 2 refer to analysis points. (d) Energy-dispersive X-ray spectra from spot analyses of two parts of the biotite grain in (c). Spectrum 2 is from the unaltered interior of the grain whereas spectrum 1 is from an area of the grain that has been biomechanically weathered.


(a)
50 μm
C
M
AF
(b)
10 μm
(c)
10 μm
L
1
2
(d)
1
2
O Kα
Mg Kα
Al Kα
Si Kα
K Kα
Ti Kα
Fe Kα
KeV
1
2
3
4
5
6

therefore be used as a tool to track the progress of chemical weathering in any environment within which they occur (Lee and Parsons, 1995, 1998; Lee et al., 1998). Lastly, surfaces of the granite are available that have been exposed and presumably encrusted by lichens for very different lengths of time, allowing an assessment of the temporal development of biomechanical and biochemical weathering processes.

2. Materials and methods

Granite surfaces encrusted by a single species of lichen, *Rhizocarpon geographicum* (L.) DC, were collected for study. This is a bright yellowish-green coloured crustose species that is common on acid rocks in upland locations in Britain (taxonomic identification by B. Coppins, pers. comm., 1997). Samples were collected from two localities: (i) vertical south-facing disused faces of a working quarry in the granite (National Grid Reference NY 556 083) (hereafter termed 'quarry faces') and (ii) glacially scoured south-facing rock surfaces at an outcrop of the granite on Shap Fells (NGR NY 545 101) ('outcrop surfaces'). Because the granite quarry opened in 1875 (Holland, 1959), the quarry faces examined (in 1997) must have been exposed for ≤ 122 years; the outcrop surfaces have been exposed for ≤ 10 kyr (since the end of the last glaciation). These exposure ages give only the maximum duration of time that the granite surfaces can have been encrusted by *R. geographicum*. Both localities lie at an altitude of 400 m above O.D. and the climate is cool (summer maxima rarely $> 20°C$ and winter minima rarely $< -5°C$) and wet (rainfall ~ 250 cm year^{-1}).

The main method used for imaging the lichen–granite interface was a technique developed by Wierzchos and Ascaso (1994). Transverse sections of the interface, a few cm^2 in size, were cut with a rock saw using an oil–water emulsion lubricant. These surfaces were then fixed with glutaraldehyde, post-fixed with OsO_4 and dehydrated through a graded acetone series prior to being impregnated with Araldite under a vacuum. After the Araldite had cured, the granite surfaces were dry-polished using carborundum papers of progressively finer grade and finally polished using 6 μm then 1 μm Kemet diamond compound. Polished surfaces were coated with carbon then imaged using backscattered elec-

Table 1
Chemical compositions of the silica-rich layer, of unweathered biotite from the interior of the granite and biomechanically weathered biotite in the lichen's thallus

	Quarry face samples			Outcrop surface samples	
	Si-rich layer (wt.%)[a]	Unweathered biotite (wt.%)	Biotite in thallus (wt.%)	Unweathered biotite (wt.%)	Biotite in thallus (wt.%)
SiO_2	75.10 (5.46)	36.66 (0.32)	36.01 (1.52)	36.69 (0.33)	37.75 (1.02)
TiO_2	n.a.	3.93 (0.14)	4.29 (0.78)	4.09 (0.22)	4.38 (0.61)
Al_2O_3	3.59 (1.85)	12.98 (0.17)	12.23 (0.86)	12.99 (0.16)	12.88 (0.42)
FeO	n.d.	16.17 (0.19)	14.91 (0.99)	16.24 (0.25)	14.80 (0.67)
MnO	n.d.	0.56 (0.02)	0.49 (0.07)	0.51 (0.04)	0.40 (0.11)
MgO	0.70 (0.22)	13.62 (0.31)	12.81 (0.70)	13.17 (0.19)	12.70 (0.64)
CaO	0.53 (0.19)	n.d.	0.18 (0.17)	n.d.	0.17 (0.15)
Na_2O	0.78 (0.21)	0.13 (0.03)	0.25 (0.17)	0.15 (0.03)	0.23 (0.07)
K_2O	0.88 (1.05)[b]	9.54 (0.06)	7.78 (1.25)	9.17 (0.32)	7.52 (0.89)
F	n.a.	1.25 (0.16)	1.48 (0.27)	1.72 (0.10)	1.78 (0.21)
Total	81.58 (5.98)	94.84 (0.38)	90.43 (2.83)	94.73 (0.31)	92.61 (1.73)
n	11	16	20	8	27

[a] Pb occured in all spectra, but concentrations were not quantified.
[b] In most analyses, $K_2O = \sim 0.3$ wt.%, but in two $K_2O = 3.61$ and 2.10 wt.%, producing the large standard deviation. Figures in parenthesis are standard deviations of mean compositions.
n.a. denotes not analyzed for and n.d. denotes not detected.

trons (BSE) in a Cambridge Instruments S250 SEM, operated at 20 kV, and a Philips XL30 CP SEM, again operated at 20 kV. The lichen–granite interface was also studied at higher resolutions by imaging surfaces that had been fractured in the laboratory using secondary electrons (SE) in a Cambridge In-

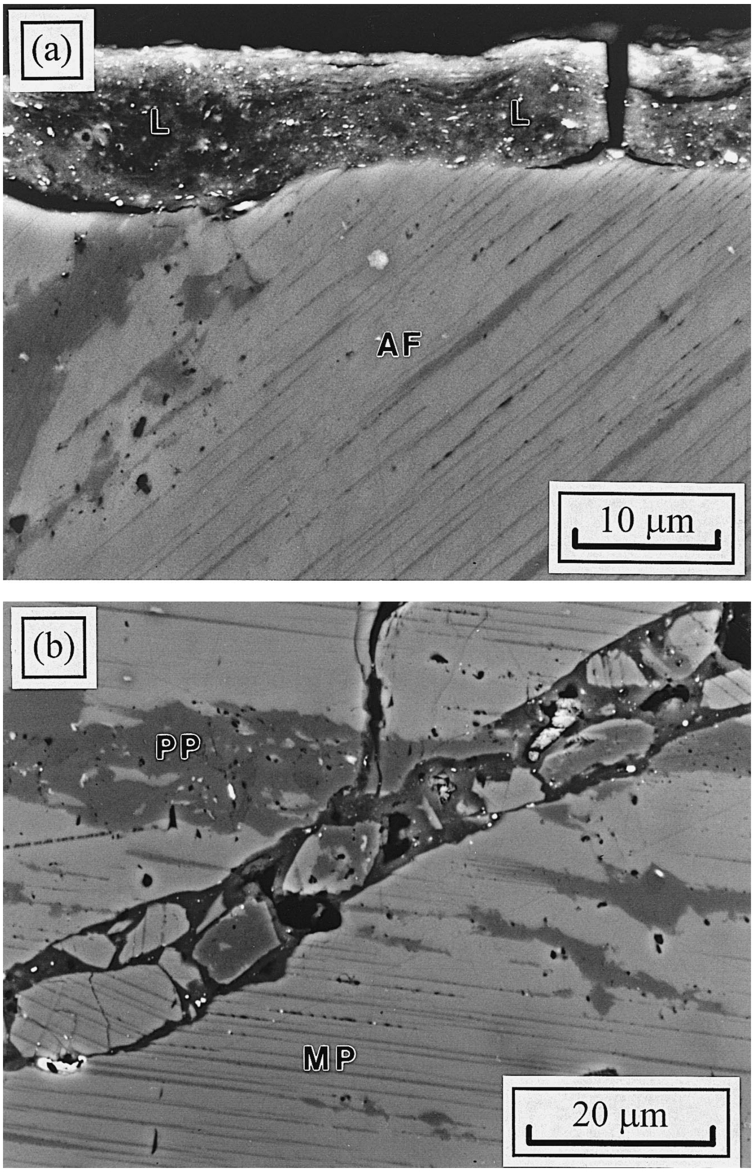


Fig. 2. BSE images of polished transverse sections of a sample from the quarry face. (a) The silica-rich layer (L) on alkali feldspar (AF). The base of the lichen's thallus is just above the top of the image. Particles within the layer with a bright BSE signal are rich in Pb and S. Most of the alkali feldspar substrate is a microperthite with albite films (dark grey) in orthoclase (light grey). The irregular microtexture on the left hand side is a vein of patch perthite. (b) A lichen-encrusted alkali feldspar grain that is cut by a fracture, which runs from upper right to lower left. The fracture contains displaced pieces of alkali feldspar that are cemented by the silica-rich substance (dark grey). This fracture may have been created during quarrying. The surrounding alkali feldspar grain contains areas of microperthite (MP) and patch perthite (PP).

struments S250 SEM operated at 7.5 kV. In order to minimise shrinkage of the lichen in the high vacuum of the SEM, some of the fracture surfaces were freeze-dried. Others were frozen in liquid nitrogen following fracturing and prior to gold coating and imaging using the S250 SEM. For those samples where preservation of biological materials was not so important, the fracture surfaces received no pre-treatment prior to gold coating and imaging at 20 kV.

The chemical composition of biotite in the polished samples was determined using a Cameca Camebax wavelength-dispersive electron probe operated at 15 kV with a 10 nA beam current in spot mode. Data were quantified using an on-line PAP correction procedure. The chemical composition of a silica-rich layer was determined using the Philips XL30 CP SEM equipped with an Oxford Instruments energy-dispersive X-ray detector and ISIS analytical system. X-ray spectra were collected at 15 kV and quantified using mineral standards.

3. The Shap Granite

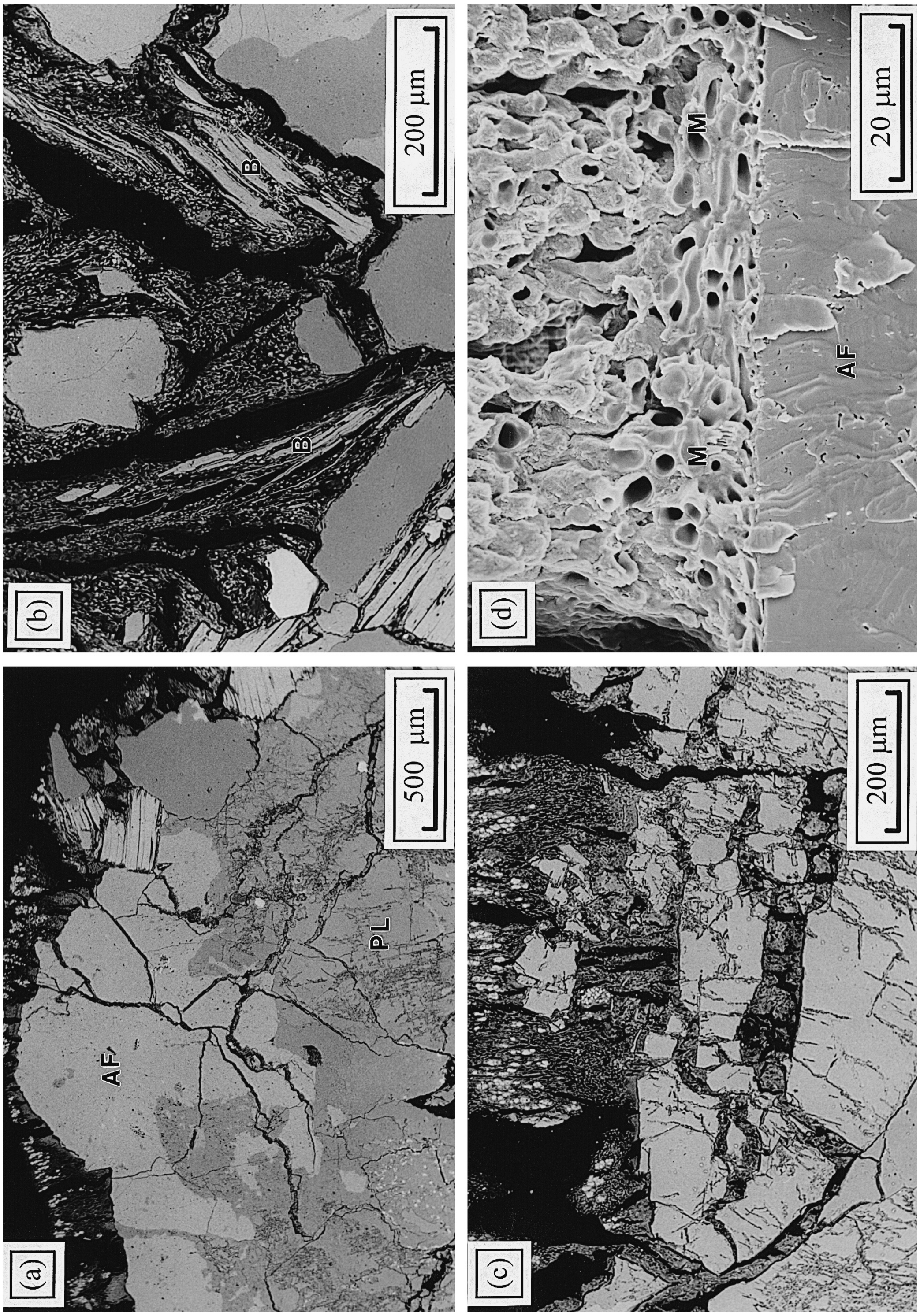
3.1. Mineralogy of unweathered granite

In order to assess the impact of lichen encrustation, it is firstly necessary to understand the character of unweathered Shap Granite. The mineralogy of the unweathered granite has been described by Grantham (1928), Caunt (1986) and Lee et al. (1995). It is an adamellite composed of coarse ($< \sim 50$ mm) alkali feldspar phenocrysts in a groundmass of smaller ($< \sim 2$ mm) alkali feldspar grains, partially sericitized plagioclase feldspar (oligoclase, $Or_{1.7}Ab_{71.8}An_{26.5}$), quartz and partially chloritized biotite. Some grains of biotite examined also contained selvages of galena along cleavages. Alkali feldspar phenocrysts often contain inclusions of oligoclase ($Or_{2.3}Ab_{72.9}An_{24.8}$), quartz and biotite. The phenocrysts have a mean bulk composition of $\sim Or_{71}Ab_{28}An_1$ and are perthites composed of albite-rich (hereafter termed Ab-rich) feldspar (albite) in orthoclase-rich (Or-rich) feldspar (predominantly tweed orthoclase). Differences in the morphology and coarseness of areas of Ab-rich feldspar and their relationship to Or-rich feldspar define three different perthite microtextures that occur in all grains. These microtextures, called cryptoperthite, microperthite and patch perthite, have been described in detail elsewhere (Lee and Parsons, 1995, 1997a,b, 1998; Lee et al., 1995, 1998), but characteristics of microperthites will be briefly reiterated because they are important for understanding weathering mechanisms. The microperthites have a bulk chemical composition of $Or_{71.8}Ab_{27.6}An_{0.7}$ and are composed of coarse (> 0.075 μm wide by many μm long) albite exsolution lamellae, called films, in orthoclase. Owing to the size of these films, the Al,Si–O framework cannot be continuous between albite and orthoclase along the entire length of the interface and edge dislocations, in the plane $\sim (\bar{6}01)$, have developed in order to reduce strain between the two phases.

3.2. Natural weathering of alkali feldspars

Lee and Parsons (1995) and Lee et al. (1998) examined naturally weathered alkali feldspars from glacially-scoured surfaces of the granite at outcrop. Lee et al. (1998) defined five weathering stages

Fig. 3. Images of transverse sections of the lichen–granite interface from outcrop surfaces. (a) Low magnification BSE image illustrating the depth to which fungal hyphae have penetrated beneath the lichen–granite interface (top of image). Most of the image is occupied by alkali feldspar (light grey, AF) and plagioclase (darker grey, PL). Fungal hyphae occur throughout the interior of plagioclase grains as irregular veins. (b) Details of the lichen–granite interface showing how sheets of biomechanically-weathered biotite (B) are incorporated into the medulla. The orientation of the sheets suggests that they are moving upwards through the thallus relative to the original lichen–granite interface BSE image. (c) Biomechanically weathered plagioclase at the lichen–granite interface. Penetration of fungal hyphae into the interiors of grains has facilitated their subsequent fragmentation, creating a mineral-rich layer within the medulla BSE image. (d) Transverse fracture surface of the interface between the medulla of *R. geographicum* (M) and alkali feldspar (AF). Tubular structures at the base of the medulla are fungal hyphae. Micrometre-sized pores within the alkali feldspar have been formed by deuteric alteration during igneous cooling of the Shap Granite and are not products of chemical or biochemical weathering. SE image of sample prepared using liquid nitrogen.


(a)
500 µm
AF
PL
(b)
200 µm
B
B
(c)
200 µm
(d)
20 µm
M
M
AF

(termed [a] to [e]) on the basis of the growth and coalescence of etch pits at edge dislocation outcrops on microperthitic areas of grain surfaces. Unweathered microperthite is termed stage [a], initial etch pits are stage [b] and complete disintegration of the surface following coalescence of the pits is seen at stage [e]. As all weathered grains overlie glacially scoured granite, the five stage sequence must take ≤ 10 kyr to complete. This model provides a frame of reference to judge the degree of weathering of alkali feldspars within lichen-encrusted granite.

4. Description

4.1. Quarry faces

The thallus of *R. geographicum* is divided into three: (1) a thin outer cortex, which comprises a

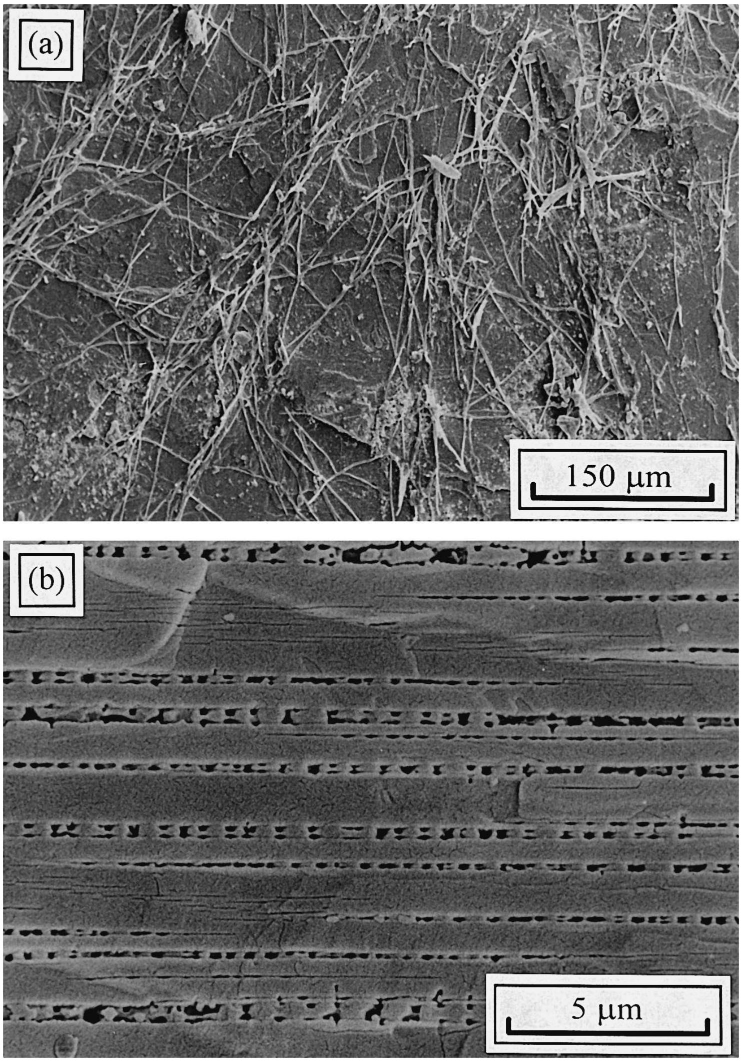


Fig. 4. SE images of the interior of lichen-encrusted alkali feldspars from outcrop surfaces. These feldspar surfaces have been freshly created by mechanical fracturing in the laboratory. (a) Cleavage surface of alkali feldspar which is oriented normal to the lichen–feldspar interface that is covered by fungal hyphae. Feldspar exposed between the hyphae is free of etch pits. (b) A heavily etched area of microperthite displaying mainly stage [b] etch pits along albite films (oriented E–W in the image).

mass of fungal hyphae, (2) an intermediate algal layer, and (3) a lower medullary region of interwoven fungal hyphae that is in direct contact with the former granite surface (Fig. 1a). Fungal hyphae have penetrated a maximum of 0.3 mm into the interior of these samples, predominantly along ≤ 15 μm wide fractures within alkali feldspar. There is no evidence for dislocation etch pits in the alkali feldspar. Fungal hyphae have also exploited cleavages in biotite, separating out individual sheets as small as 0.5 μm in thickness (Fig. 1b). Quantitative chemical analyses of fragmented biotite grains show that they are depleted in K and Fe relative to unaltered biotite from the interior of the granite (Table 1). Energy-dispersive X-ray spectra of one biotite grain that was covered in a silica-rich layer (described below) showed that areas of the grain closest to the biotite–lichen interface had been heavily leached, leaving a silica-rich relic (Fig. 1c,d).

In addition to biotite, surfaces of alkali and plagioclase feldspar and quartz are encrusted by a silica-rich layer (Fig. 2a). In cross-section, this layer is < 10–15 μm in thickness and structureless but contains numerous sub-μm sized S- and Pb-rich particles. The silica-rich substance that comprises the layer also occludes pores and fractures within quartz and feldspar beneath the interface (Fig. 2b). Chemically, the silica-rich substance is dominated by SiO_2 and gives low analytical totals (Table 1). Calcium and magnesium compounds other than silicates were sought for in the thallus by electron probe and X-ray diffraction analyses, but none were found.

4.2. Outcrop surfaces

Fungal hyphae have penetrated up to 3 mm into granite surfaces at outcrop, mainly by exploiting intergranular boundaries (Fig. 3a). Spaces between grains that contain hyphae are ~ 10–50 μm in width whereas those free of hyphae are $< \sim 1$–2 μm wide. Fungal hyphae and, in areas close to the lichen–granite interface, algal cells, have extended from the intergranular boundaries into the interiors of some grains. Biotite has been the most heavily disrupted, by penetration of hyphae along cleavages. Some grains have completely disintegrated and 2–25 μm thick sheets of biotite lie enclosed within the medulla (Fig. 3b). Wavelength-dispersive X-ray analyses again show that the biomechanically weathered biotite is depleted in K and Fe relative to unweathered biotite (Table 1).

The mycobiont and photobiont have penetrated along cleavages and fractures in plagioclase feldspar and, in addition, hyphae are widely dispersed throughout plagioclase grain interiors as irregular veins and patches. Some grains have been broken into 30–300 μm sized angular fragments which form a ~ 0.5 mm thick mineral-rich zone within the medulla (Fig. 3c). In cross-section, the lichen–alkali feldspar interface is sharp, with no evidence for dissolution (Fig. 3d). Mats of fungal hyphae cover some of the alkali feldspar cleavage surfaces that have been freshly exposed by fracturing lichen-encrusted grains in the laboratory (Fig. 4a). Dislocation etch pits occur on these fungally encrusted surfaces but also on freshly exposed cleavage and fracture surfaces where hyphae are absent (Fig. 4b). In size and shape, these pits are comparable to stage [b] and [c] etch pits characteristic of natural weathering (Lee et al., 1998). The silica-rich layer again occurs on mineral surfaces but is less well developed than on the samples from quarry faces.

5. Discussion

5.1. Biomechanical weathering

Penetration of fungal hyphae into the interior of the Shap Granite is the main mechanism by which *R. geographicum* biomechanically weathers its substrate. The hyphae exploit pores between mineral grains and also intragranular pores along cleavages and fractures. Biotite is especially susceptible to biomechanical weathering owing to its closely-spaced and perfect cleavages. It is for this reason that biotite inclusions in alkali feldspar and sericite (white mica) inclusions within plagioclase also act as a focus for biomechanical weathering. Despite the fact that alkali and plagioclase feldspar both possess one perfect and one good cleavage, plagioclase grains biomechanically weather much more readily than alkali feldspar owing to the greater abundance of mica inclusions in the former. It should be noted that some of the exfoliation of biotite may have taken place during a previous period of inorganic weathering. Quartz has no cleavages or inclusions and has accordingly escaped biomechanical weathering.

The rate at which fungal hyphae biomechanically weather the granite is difficult to accurately quantify. As lichens on the quarry faces must be ≤ 122 years in age and have penetrated to ~ 0.3 mm, rates of hyphal penetration at this locality were ≥ 0.002 mm year^{-1}. Rates of biomechanical weathering of outcrop surfaces are harder to estimate as the ages of the lichens are unknown. In principle, it would be possible to estimate lichen ages because *R. geographicum* is a species used in lichenometry. If we assume that the lichens we studied are ≤ 1000 years old (possible for arctic/alpine lichens, Nash, 1996), this yields penetration rates of > 0.003 mm year^{-1}.

Other studies have provided data on rates of penetration of the mycobiont into rock surfaces. For example, Barker and Banfield (1996) showed that hyphae of the lichens *R. grande* and *Porpidea albocaerulescens* had penetrated up to 10 mm into an amphibole syenite within 90 years (i.e., > 0.11 mm year^{-1}). McCarroll and Viles (1995) calculated that the endolithic lichen *Lecidea auriculata* can lower the surface of gabbro within which it occurs at a rate of ≥ 0.0012 mm year^{-1}; this is 25–50 times greater than weathering due to other processes in the same geographic area. In contrast to igneous rocks, sedimentary rocks, which are typically less tightly consolidated and have a higher intergranular porosity, may be much more susceptible to biomechanical weathering. For example, Wessels and Schoeman (1988) demonstrated that the endolithic lichen *L. sarcogynoides* could remove the outermost 9.6 mm of a sandstone surface in 100 years (0.1 mm year^{-1}). Interestingly, Cooks and Otto (1990) noted that *L. sarcogynoides* could penetrate to a depth of 3.21 mm into a sandstone but only 1.12 mm into quartzites, which typically have a more tightly interlocking texture and lower intergranular porosity.

The question of the mechanism by which fungal hyphae create space in the interior of tightly consolidated igneous rocks was raised by Wierzchos and Ascaso (1994), although no explanations were proposed. With regard to the Shap Granite, grains at the lichen–granite interface can be readily wedged apart by hyphae because fragments produced by biomechanical action are able to move upwards into the medulla (Fig. 3b,c). Creation of space below the lichen–granite interface is considerably more difficult because little or no room is available for expansion. Measurements from samples frozen in liquid nitrogen prior to imaging show that hyphae are ~ 2.5–3 μm in diameter (Fig. 3d). As we describe below, intercrystalline and intracrystalline pores of such size could have been created by mechanical and chemical weathering prior to establishment of the present generation of lichen.

5.2. Biochemical weathering of primary minerals

5.2.1. Leaching of biomechanically weathered biotite

Compositional differences between biotite fragments within the medulla and unaltered biotite from the interior of the Shap Granite provide the clearest evidence for biochemical weathering. The most consistent trend is a depletion in K and Fe, although evidence from energy-dispersive X-ray spectra show that parts of some biotite grains closest to the thallus can be reduced to a silica-dominated relic (Fig. 1c, d). Analyses of lichen-encrusted biotite by Wilson and Jones (1983) showed that biochemical weathering had leached Mg, Al, K and Fe, leaving a Si- and Ti-enriched relic phase. Wierzchos and Ascaso (1996) found that biochemical alteration of biotite in lichen-encrusted granite had produced a significant decrease in K/Si and Fe/Si, but an increase in Al/Si (Wierzchos and Ascaso, 1996, Table 1). The mineralogy of this biochemically weathered biotite is unknown to us because preparation of samples for transmission electron microscopy (TEM) was unsuccessful. However, replacement of biotite by vermiculite has been commonly observed in other studies of biologically-mediated weathering (e.g., Barker et al., 1997). In addition to being a good indicator of biochemical weathering, biotite may also play a central role in the formation of silica-rich layers (see below).

5.2.2. Etching of alkali feldspar

The occurrence of etch pits on cleavage and fracture surfaces within lichen-encrusted alkali feldspar grains from outcrop provides unambiguous evidence for chemical weathering. Etching of alkali and plagioclase feldspars beneath crustose lichens has been previously described by Jones et al. (1981) and Wilson and Jones (1983). These authors concluded that the etching, which was again selective to exsolution lamellae and dislocations at grain surfaces, was biochemically mediated. Recently, Jongmans et al. (1997) illustrated free-living fungal hyphae apparently in the process of etching ~ 5 μm wide tubes in alkali feldspars from European soils. They concluded that the etching was mediated by organic acids exuded from hyphal tips and that the pores could form at a rate of 0.3–30 μm $year^{-1}$.

Despite this evidence, the role of the fungal partner of *R. geographicum* in etching Shap Granite alkali feldspars is ambiguous. Although hyphae encrust some of the etched cleavage and fracture surfaces, they are absent from others. In addition, etch pits were not seen at the interface between alkali feldspar and the base of the thallus (Fig. 3d), a site where they may be expected if the current thallus had been actively involved in biochemical weathering. Etching of intragranular surfaces in alkali feldspars is therefore unlikely to have been exclusively biochemically mediated. As these outcrop surfaces have potentially been exposed for 10 kyr, the observed etching is more likely to be the product of a number of different episodes of biochemical and chemical weathering. These earlier periods of weathering will have played an important role in enlarging intergranular and intragranular pores, facilitating later access of fungal hyphae.

5.3. Biochemical reaction products

5.3.1. Formation of the silica-rich substance

The silica-rich substance, which occurs at the lichen–granite interface from both quarry and outcrop localities, is interpreted to be a by-product of biochemical weathering. The exact nature of the substance is unclear to us because preparation of samples for TEM was unsuccessful. From previous work, which is described below, we suspect that the substance is non-crystalline and probably a hydrous gel.

Amorphous silica has been previously reported in association with lichen-encrusted rocks, but its origin is controversial. Ascaso et al. (1976) produced amorphous silica by incubation of *R. geographicum* with albite and orthoclase. Wilson et al. (1981) described X-ray amorphous silica gels that had formed by oxalic acid-mediated weathering of chrysotile by *Lecanora atra*. Magnesium that was leached from the chrysotile to leave a silica-rich pseudomorph was subsequently reprecipitated to form the oxalate glushinskite. Wilson and Jones (1983) also described the formation of siliceous pseudomorphs of anorthite by lichen-mediated weathering. The work by Wilson et al. was performed on residues produced by the chemical oxidation of lichens. Barker and Banfield (1996) and Barker et al. (1997) have argued that treatment of lichen–mineral mixtures with hydrogen peroxide may in fact create silica-rich gels, implying that the materials previously described are artefacts of sample preparation. Our observations of in situ silica-rich layers fully support the earlier observations of Wilson et al.

From comparisons with the work described above, we suggest that the silica-rich substance in samples from Shap has formed by the leaching of silicates by oxalic acid derived from *R. geographicum*. A number of laboratory experiments have shown that oxalic acid selectively removes aluminium from aluminosilicate substrates, a consequence of its acidity and complexing ability (Barker et al., 1997). The precise mechanisms by which the silica-rich layers form is unclear to us. They could be true residual layers and directly analogous to the ‘leached layers’ which are inferred to form during laboratory dissolution experiments using a variety of acids (Petrovic et al., 1976). Because the silica-rich substance also cements fractures in alkali feldspar, it is more likely that it was deposited from an aqueous solution. Any formational mechanism also needs to take into account the abundance of Pb- and S-rich particles. The occurrence of these particles suggests that much of the silica-rich substance may be derived from the biochemical weathering of galena-mineralised biotite.

Deposition of the silica-rich substance may affect rates of biochemical in a number of ways. First, occlusion of fractures by the substance will considerably reduce the porosity and permeability of the substrate, limiting the advection of aqueous solutions and also preventing fungal hyphae from gaining access to grain interiors. As suggested by Wilson et al. (1981), biochemical reactions may also be slowed by the necessity for ions to diffuse through the layer. We suggest that silica-rich layers are a common feature of lichen-encrusted rock surfaces and so may have a significant affect on mechanisms and rates of biomechanical and biochemical weathering.

5.3.2. Other biochemical reaction products

None of the common oxalate minerals were found within the thallus by electron probe or X-ray diffraction. As there is no reason to believe that the mycobiont of *R. geographicum* does not produce oxalic acid (for example, *R. calcareum* excretes oxalic acid, Mitchell et al., 1966), the absence of oxalates probably reflects the scarcity of appropriate cations in the granite (bulk chemical composition = 1.2% MgO, 1.8% CaO; O'Brien et al., 1985).

6. Conclusions

The inferred sequence of weathering processes within lichen-encrusted Shap Granite is as follows: (i) chemical and/or mechanical weathering of bare rock surfaces, widening intergranular and intragranular pores, (ii) establishment of the lichen and penetration of fungal hyphae into the interior of the rock, (iii) biomechanical weathering of minerals by penetration of fungal hyphae, increasing the surface area/volume ratio of the grains, and (iv) biochemical weathering of fragmented mineral grains leading to leaching of biotite, possibly some etching of feldspar and deposition of the silica-rich substance.

In answer to our original question about the effect of *R. geographicum* on the weathering rate of granite, our results are equivocal. Biomechanical weathering is clearly important, especially for minerals with well developed cleavages and abundant inclusions. However, the thallus binds mineral fragments, preventing them from entering soils or other environments within which rates of chemical weathering are likely to be greater. Encrustation of a rock surface by lichen may also have a thermal insulating effect, inhibiting mechanical disaggregation by freeze–thaw. The role of *R. geographicum* in biochemical weathering is probably limited to the leaching of biotite, and possibly etching of feldspar, and deposition of the silica-rich substance. This substance may well play a protective role by covering mineral surfaces and cementing intragranular pores, thus inhibiting access of hyphae and acids into grain interiors. We therefore conclude that encrustation of the Shap granite by *R. geographicum* most probably slows its weathering rate relative to bare rock surfaces.

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