

THE PEDOGENIC ACTION OF *PARMELIA* *CONSPERSA*, *RHIZOCARPON GEOGRAPHICUM* AND *UMBILICARIA PUSTULATA*

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Introduction

The weathering of rock surfaces and soil formation are the result of two clearly distinguished processes, cheluviation and soluviation (Swindale & Jackson, 1956). In the presence of chelating agents, minerals are decomposed and then eluviated (Schatz *et al.*, 1954; Schatz, 1963). Lichens excrete various compounds the solubility of which has generally been discounted (Smith, 1921; Hale, 1961; Smith, 1962; Haynes, 1964). However, more recent studies have shown that at least certain lichen substances, namely depsides and depsidones, are in fact slightly soluble in water (Iskandar and Syers, 1971) and that the presence of electron donor groups in their respective molecules (Ginzburg *et al.*, 1963; Kononova *et al.*, 1964) might explain the formation of coloured complexes when either the thalli of certain lichens, or relevant lichen compounds, are allowed to react with water suspensions of minerals and rocks (Schatz, 1963; Syers, 1969). Moreover, it is known that certain lichen compounds can extract varying amounts of aluminium, calcium, iron and magnesium from silicates (Iskandar and Syers, 1972). More recent observations have shown that certain rock silicates are not only structurally modified in the presence of lichen compounds but that these substances, after promoting the release of cations, can give rise to new minerals under natural conditions (Ascaso and Galvan, in press).

That lichens can alter rock surfaces in nature producing new minerals has been discussed by several authors (Bachman, 1907; Polynov, 1945; Aidinyan, 1949; Yarilova, 1950; Schatz *et al.*, 1956) although in all these studies the possibility of extraneous contamination cannot be entirely ruled out. Laboratory studies under rigorously controlled conditions are therefore indispensable for a better understanding of the processes of chemical alteration of rocks and their consequent weathering and the promotion of soil formation. This paper observes and compares rock modifications by lichens in nature and in conjunction with carefully monitored studies in the laboratory.

Material and Methods

Material

The lichens used for this study were *Parmelia conspersa*, *Rhizocarpon geographicum* and *Umbilicaria pustulata*, species which can often form a succession or a single association on siliceous rocks given the appropriate substrate and environmental conditions (Ozenda and Clauzade, 1970). A mixture of four lichen

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compounds: atranorin, stictic acid and usnic acid, donated by the Koch Light Laboratory, plus norstictic acid, kindly provided by Dr Martinez (Universidad de Navarra, Pamplona, Spain), was used as a control for the laboratory studies. All these lichen substances normally occur in the thallus of *Parmelia conspersa* (Culbertson, 1969).

Granite (from Bustarviejo, Madrid) and gneiss (from Miraflores de la Sierra, Madrid) as well as albite, orthoclase, biotite, muscovite and quartz, all ground to a particle size ranging between 1.2 and 430 μm , were used in all experiments. The mineral samples were washed in 0.002 N hydrochloric acid for 2 h following the method of Schatz (1963) to remove exchangeable bases.

Methods

In order to carry out our investigation of the nature and composition of the mineral content of the substrate at the interface between acid rocks and the lichen thalli, we carefully scraped the rock surface of the colonized granite or gneiss to obtain an adequate lichen-mineral mixture. Organic material was eliminated by boiling this mixture several times in 80% hydrogen peroxide solution. The samples thus obtained were studied by both X-ray diffractometry and electron microscopy.

The relevant X-ray powder diffraction patterns, unless otherwise stated, were obtained by means of a PX 1050 equipped, Philips goniometer fitted with a copper target and a nickel filter. The samples were prepared according to the powder method, the minerals identified by means of the standard ASTM tables (now known as the PDF [Powder Data File]). In order to investigate the reaction between lichens and rocks under controlled conditions, the lichen thalli were cleaned, dried and crushed. 0.5 g of the treated material was then added to flasks containing 15 ml of demineralized, distilled and sterile (DDS) water, and shaken for 2 days at 25°C in a rotary shaker set at 250 rev/min. Supersaturated solutions of the mixture of four lichen compounds were obtained by shaking in the same way. Insoluble material was eliminated by filtration by means of Milipore filters of 0.45 μm pore size.

Following this, 500 g of silicate material, either granite, gneiss, quartz, albite, orthoclase, biotite or muscovite, was added to the prepared flasks and agitation continued for 96 h at the same temperature. Samples were then filtered through Milipore filters of 0.45 μm pore size and the filtrates analysed spectrophotometrically by means of a Beckman mod. DB-G spectrophotometer. Their pH was determined, aluminium, magnesium and iron contents of the extracts ascertained with an atomic absorption spectrophotometer, and the calcium concentration determined by a flame photometry method. Coloured metal complex formation was determined by subtracting the percentage transmittance values (between 700 and 320 μm) obtained after 2 h incubation (T_0) of minerals with lichen extracts or the artificially compounded mixture of lichen substances from the same values obtained at the end of the treatment, that is, after 96 h agitation (T_4). Curves were also plotted in the same way for control samples which contained only silicate material and DDS water. The blanks were made up from the same mixture but without the mineral being tested.

The insoluble material retained on the filter was examined with a EM 300 Philips electron microscope and by X-ray powder diffractometry following the

elimination of lichen fragments by boiling in 80% hydrogen peroxide solution. Sterility controls monitoring fungal and bacterial contamination showed values not exceeding 30 colonies/ml.

Results

Preliminary observations, using electron microscopy and X-ray powder diffractometry (Figs 1C, 2B), established that the granite and gneiss samples used in the present study were devoid of any detectable extraneous clay contaminants. Such information is essential in order to correlate and assess lichen activity and its role in the alteration of rock surfaces.

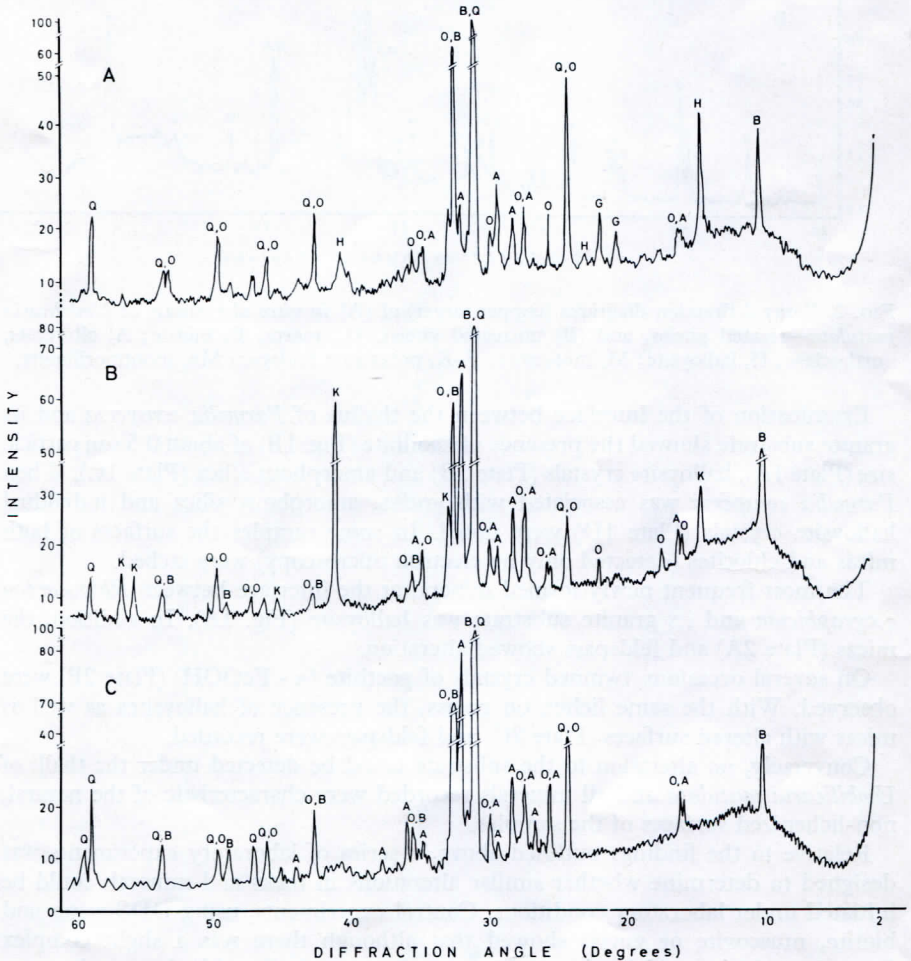


FIG. 1. X-ray diffraction diagrams (cobalt target) of rock scraping between (A) granite and *Rhizocarpon geographicum*, (B) granite and *Parmelia conspersa*. (C) Untreated granite. Q, quartz; B, biotite; A, albite; O, orthoclase; H, halloysite; K, kaolinite; G, geothite.

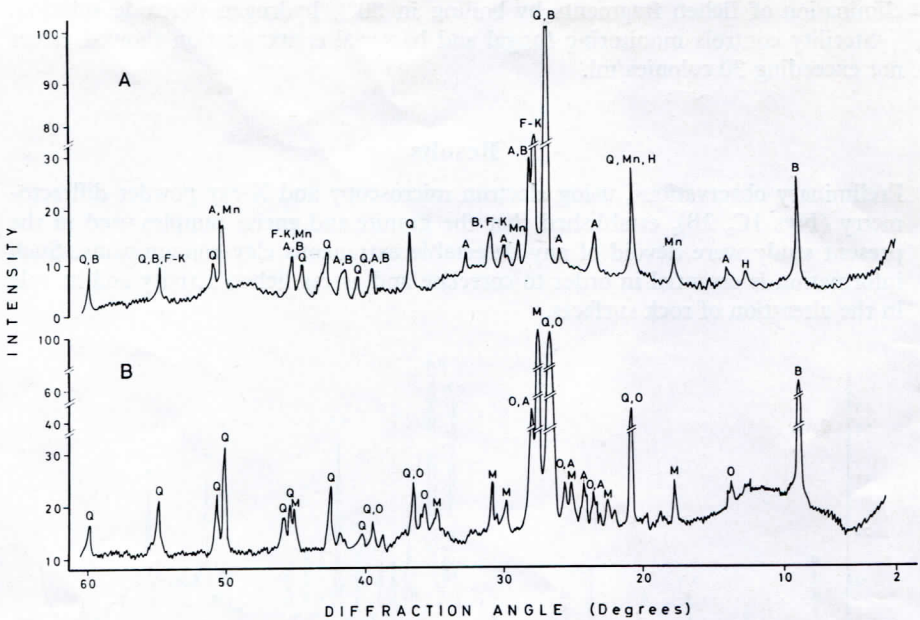


FIG. 2. X-ray diffraction diagrams (copper target) of (A) *in vitro* alterations of *Umbilicaria pustulata*—treated gneiss, and (B) untreated gneiss. Q, quartz; B, biotite; A, albite; O, orthoclase; H, halloysite; M, muscovite; F-K, potassium feldspar; Mn, montmorillonite.

Examination of the interface between the thallus of *Parmelia conspersa* and its granite substrate showed the presence of kaolinite (Fig. 1B) of about 0.5 μm particle size (Plate 1A), halloysite crystals (Plate 1B) and amorphous silica (Plate 1C). When *Parmelia conspersa* was associated with gneiss, amorphous silica and individual halloysite crystals (Plate 1D) were noted. In some samples the surfaces of both micas and chlorites (detected only by electron microscopy) were etched.

The most frequent newly formed mineral at the interface between *Rhizocarpon geographicum* and its granite substrate was halloysite (Fig. 1A). In addition, the micas (Plate 2A) and feldspars showed alteration.

On several occasions twinned crystals of goethite (α -FeOOH) (Plate 2B) were observed. With the same lichen on gneiss, the presence of halloysites as well as micas with altered surfaces (Plate 2C) and feldspars were recorded.

Conversely, no alteration to the substrate could be detected under the thalli of *Umbilicaria pustulata* and all minerals recorded were characteristic of the natural, non-lichenized surfaces of the samples.

Relative to the findings outlined above, a series of laboratory experiments was designed to determine whether similar alterations in rocks and minerals could be initiated under laboratory conditions. Control experiments, using DDS water and biotite, muscovite or gneiss showed that although there was a slight complex formation which could be detected spectrophotometrically with these rock types, no such phenomenon could be demonstrated in the case of granite, quartz, orthoclase or albite treated in the same way.

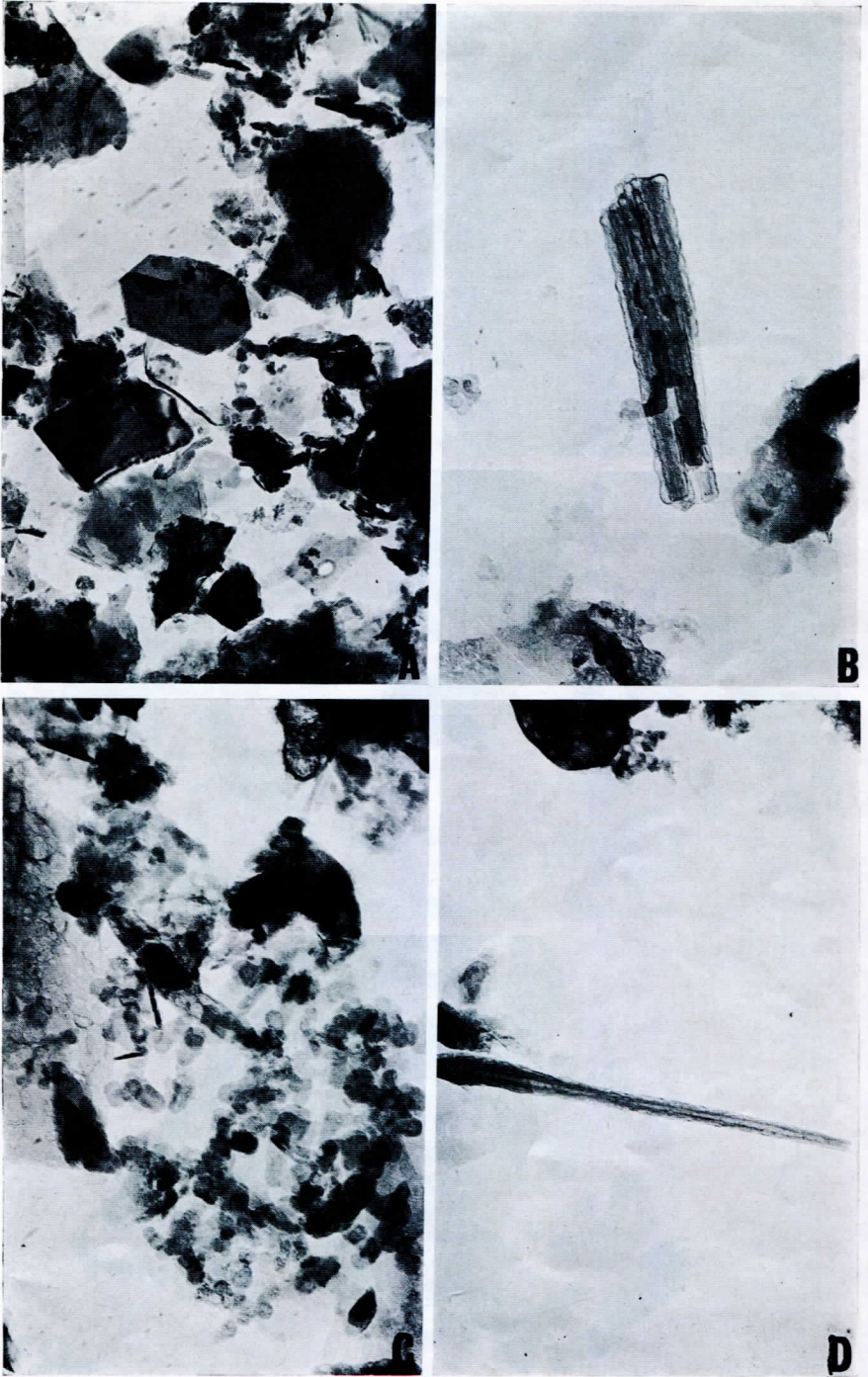


PLATE 1. Minerals at the interface between the thallus of *Parmelia conspersa* and granite substrate: A, Kaolinite (K) and micas ($\times 24\ 600$); B, halloysite crystals (parallel association) ($\times 61\ 500$); and C, amorphous silica ($\times 47\ 900$). D, Minerals at the interface between the thallus of *P. conspersa* and gneiss substrate: Single halloysite crystal ($\times 61\ 500$).

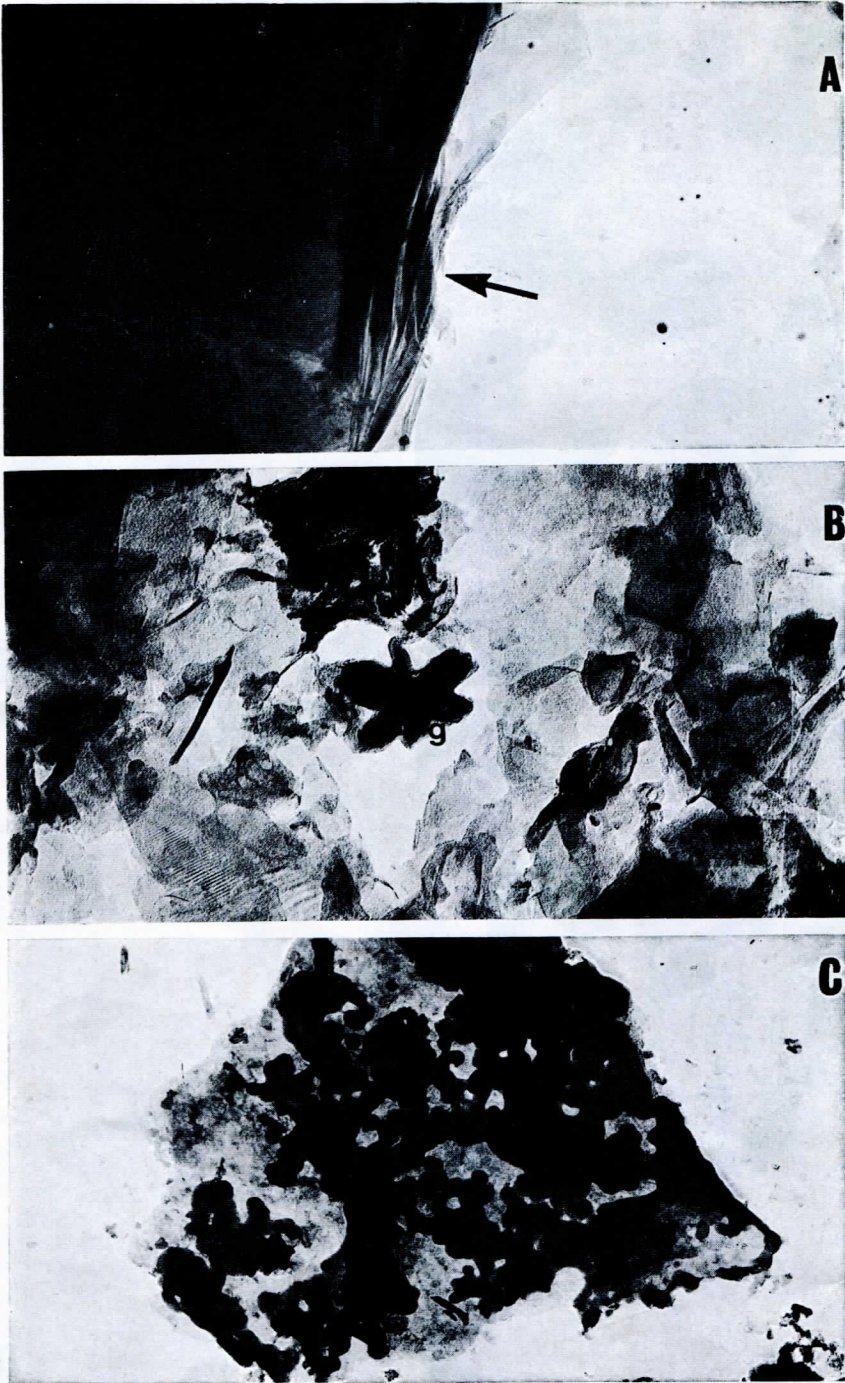


PLATE 2. A-B: Minerals at the interface between the thallus of *Rhizocarpon geographicum* and granite substrate: A, Micas with altered edges (arrow) ($\times 55\ 800$); and B, twinned goethite (g) ($\times 84\ 000$). C, Mineral alterations at the interface between the thallus of *R. geographicum* and gneiss substrate: Altered surface of mica ($\times 22\ 300$).

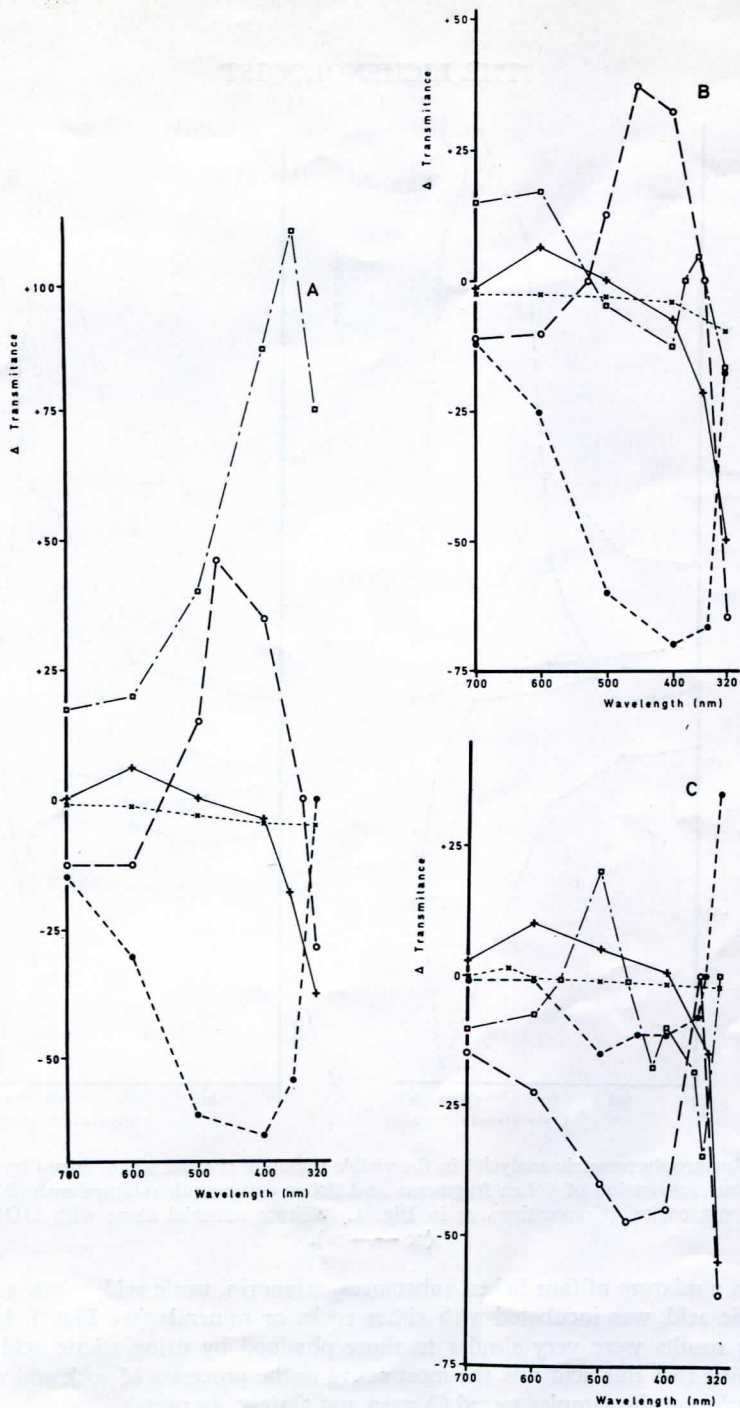


FIG. 3. Spectrophotometric analysis* in the visible region of the extracts obtained by shaking an aqueous suspension of *Parmelia conspersa* (○ — ○), *Umbilicaria pustulata* (● — ●) and *Rhizocarpon geographicum* (□ — □) fragments, and the mixture of the lichen compounds, atranorin, norstictic acid, stictic acid and usnic acid (+ — +) with (A) quartz, (B) albite and (C) orthoclase. Silicate material alone with DDS water (× — ×).

* Identical curves to that obtained with DDS water indicate that no formation of coloured soluble complexes occurred. When appearance of coloured complexes in the aqueous medium occurs the curves are below obtained with the same rock or mineral and DDS water. Sometimes coloured complexes are formed but they are absorbed by the silicate material and then the curves appear above the corresponding one with DDS water.

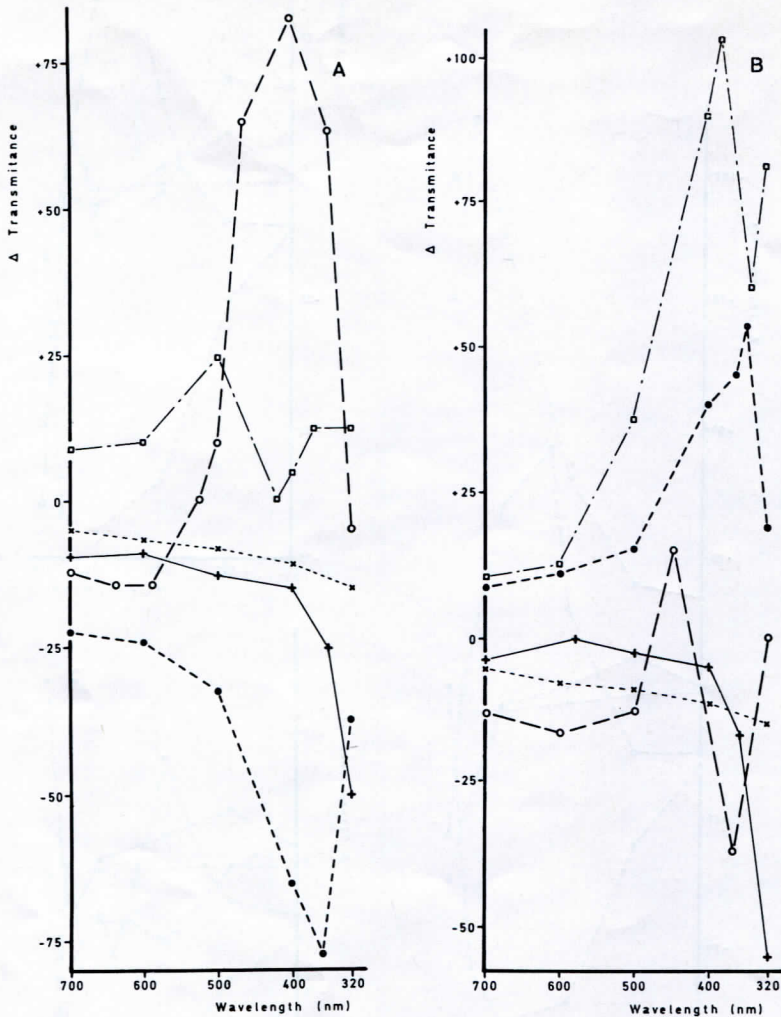


FIG. 4. Spectrophotometric analysis* in the visible region of the extracts obtained by shaking an aqueous suspension of lichen fragments and lichen compounds mixture with (A) biotite and (B) muscovite. (Conventions as in Fig. 1.) Silicate material alone with DDS water (\times — \times).

When a mixture of four lichen substances, atranorin, usnic acid, stictic acid and norstictic acid, was incubated with either rocks or minerals (see Figs 3, 4, 5) the ensuing results were very similar to those obtained by using stictic acid alone, confirming that this acid was the most active in the processes of rock and mineral degradation in the samples tested (Ascaso and Galvan, in press).

When fragments of the thallus of *Parmelia conspersa* are allowed to react with quartz (Fig. 3A), albite (Fig. 3B), biotite (Fig. 4A) granite (Fig. 5A) or gneiss (Fig.

* See footnote to Fig. 3.

5B), the results obtained for low wavelengths are similar to those given by stictic acid alone. This suggests that this lichen acid may be the one which is mainly responsible for coloured complex formation in the material studied. However, at higher wavelengths the correlation is less satisfactory suggesting the presence of one or more additional active compounds occurring in *Parmelia conspersa* which are not included in the lichen substance mixture utilized in the present studies.

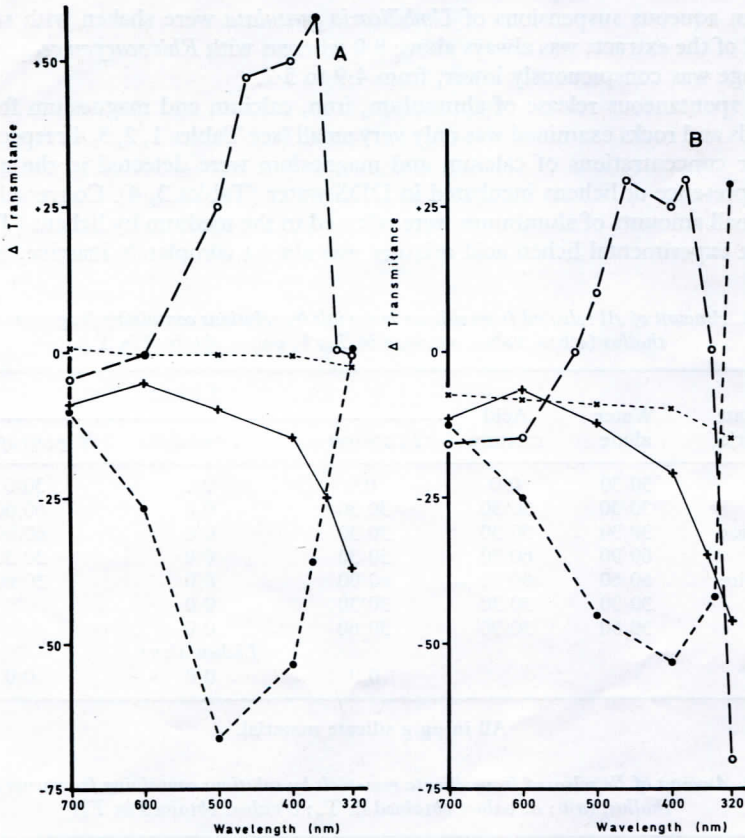


FIG. 5. Spectrophotometric analysis* in the visible region of the extracts obtained by shaking an aqueous suspension of lichen fragments and lichen compounds mixture with (A) granite and (B) gneiss. (Conventions as in Fig. 1.) Silicate material with DDS water (\times — \times).

The results obtained with *Umbilicaria pustulata* also showed coloured complex formation, the curves having a maximum absorbance between 350 nm and 500 nm (see Figs. 3, 4, 5); muscovite proved the only resistant mineral (Fig. 4B).

As the thallus of *Rhizocarpon geographicum* universally contains mineral fragments, the results obtained with this species should be treated with some caution. In any case it was not possible to obtain sufficient quantities of this lichen and for this

* See footnote to Fig. 3.

reason its reactions at the interface have not been studied. However, it should be noted that this species is able, under experimental conditions, to induce coloured complex formation with most of the minerals used.

The pH of the extracts obtained by shaking the lichens alone in water ranged from 5.1 for *Rhizocarpon geographicum* to 7.8 for *Umbilicaria pustulata*. For minerals and rock samples alone the values ranged from 6.7 for gneiss to 7.8 for orthoclase (Ascaso and Galvan, in press).

When aqueous suspensions of *Umbilicaria pustulata* were shaken with silicates, the pH of the extracts was always above 8.0 whereas with *Rhizocarpon geographicum* the range was conspicuously lower, from 4.9 to 5.2.

The spontaneous release of aluminium, iron, calcium and magnesium from the minerals and rocks examined was only very small (see Tables 1, 2, 3, 4 respectively). Greater concentrations of calcium and magnesium were detected in the medium in the presence of lichens incubated in DDS water (Tables 3, 4). Conversely, only very small amounts of aluminium were released to the medium by lichens (Table 1) and the experimental lichen acid mixture was almost completely inactive, more so

TABLE 1. Amount of Al released from silicate materials by solutions containing fragments of lichen thallus (a/b: a, values obtained in T₀; b, values obtained in T₄)

Silicate material	Water alone	Acid mixture	Lichen		
			<i>P. conspersa</i>	<i>U. pustulata</i>	<i>R. geographicum</i>
Quartz	30/30	0/0	0/0	0/0	30/0
Albite	30/30	30/30	30/30	0/0	60/60
Orthoclase	30/30	30/30	30/30	0/0	60/60
Biotite	60/90	60/90	30/30	0/0	30/30
Muscovite	60/60	60/90	60/90	0/0	30/60
Granite	30/30	30/30	30/30	0/0	
Gneiss	30/60	30/90	30/60	0/0	
			0/0	<i>Lichen alone</i> 0/0	0/0

All in µg/g silicate material.

TABLE 2. Amount of Fe released from silicate materials by solutions containing fragments of lichen thallus. (a/b: a, values obtained in T₀; b values obtained in T₄)

Silicate material	Water alone	Acid mixture	Lichen		
			<i>P. conspersa</i>	<i>U. pustulata</i>	<i>R. geographicum</i>
Quartz	0/0	0/0	6/9	27/12	6/48
Albite	0/0	6/12	6/0	6/6	24/30
Orthoclase	0/0	0/0	0/9	6/0	90/54
Biotite	96/234	99/222	66/147	30/18	93/90
Muscovite	9/15	12/18	15/39	6/9	12/33
Granite	15/24	18/48	15/12	0/12	
Gneiss	15/33	15/48	9/36	0/12	
			0/0	<i>Lichen alone</i> 0/0	0/0

All in µg/g silicate material.

TABLE 3. Amount of Ca released from silicate materials by solutions containing fragments of lichen thallus (a/b: a, values obtained in T₀; b, values obtained in T₄)

Silicate material	Water alone	Acid mixture	Lichen		
			<i>P. conspersa</i>	<i>U. pustulata</i>	<i>R. geographicum</i>
Quartz	0/60	30/30	120/300	90/120	120/300
Albite	0/30	30/60	90/420	60/120	180/240
Orthoclase	180/500	180/600	300/600	300/360	840/600
Biotite	60/120	30/90	120/360	150/240	240/120
Muscovite	30/60	30/120	60/300	120/300	90/360
Granite	30/30	0/30	60/660	60/120	
Gneiss	0/30	0/30	60/480	60/180	
			300/420	<i>Lichen alone</i> 170/240	120/180

All in µg/g silicate material.

than with *Parmelia conspersa*. The release of aluminium from the quartz samples can be explained on the basis of the feldspar-like contaminants which it contains.

The concentration of iron in the extracts (Table 2) was also very reduced. The release of iron from biotite was at the same level as the control (DDS). Orthoclase was the mineral which released the largest quantity of calcium (Table 3). This can be attributed to the fact that the sample of this mineral used in our experiments had a high calcium content (of 1.96% calcium oxide). All the selected lichens released calcium ions to the medium when samples of them were shaken in DDS water. The amounts of this cation in the medium were greater at T₀ than at T₄ time, suggesting that calcium ions may be absorbed to the silicate material.

Biotite lost magnesium (Table 4) when incubated with any of the three lichen species. The previously determined magnesium oxide content of biotite was 5.16%. In general the results obtained in our experiments showed a similarity of behaviour for calcium and magnesium.

Samples of both treated and untreated minerals and rocks were studied both with an electron microscope and by X-ray powder diffractometry. Untreated samples showed no traces of contamination with clay minerals. Amorphous silica

TABLE 4. Amount of Mg released from silicate material by solutions containing fragments of lichen thallus. (a/b: a, values obtained in T₀; b, values obtained in T₄)

Silicate material	Water alone	Acid mixture	Lichen		
			<i>P. conspersa</i>	<i>U. pustulata</i>	<i>R. geographicum</i>
Quartz	3/9	3/21	24/45	60/78	48/114
Albite	3/9	6/15	30/63	18/60	54/120
Orthoclase	12/39	12/51	48/102	51/141	27/420
Biotite	36/99	54/159	96/261	120/411	204/117
Muscovite	9/30	18/21	36/117	45/270	78/153
Granite	3/12	6/18	24/114	33/78	
Gneiss	6/6	6/12	27/96	21/120	
			80/96	<i>Lichen alone</i> 192/189	138/200

All in µg/g silicate material.

Albite (control)			<i>P. conspersa</i> -treated Albite					<i>R. geographicum</i> -treated Albite				
20	d	I	20	d	I	A	H. Hall.	20	d	I	A	Hall.
			30.44	2.934	15	×		30.30	2.947	18		×
30.55	2.924	36						31.20	2.864	12	×	
31.35	2.851	21	31.24	2.860	6	×		33.78	2.651	7	×	
34.00	2.634	15						35.00	2.561	13	×	×
35.25	2.544	18	35.12	2.553	5	×	×	36.50	2.459	16	×	
			36.56	2.455	10	×		37.30	2.408	6	×	
37.60	2.390	15						37.60	2.390	5	×	
								38.80	2.353	4	×	
								39.40	2.285	8	×	
			39.50	2.279	5	×						
39.60	2.274	15	40.22	2.240	3	×						
41.35	2.182	12	42.44	2.2128	8	×		40.30	2.236	5		×
								42.40	2.130	16	×	
42.50	2.125	26										
43.45	2.081	13						45.70	1.983	8	×	×
45.85	1.977	15										
48.35	1.881	16						50.00	1.822	19	×	
50.15	1.817	23										
50.75	1.797	17										
51.30	1.779	16										
53.40	1.714	13										
			54.90	1.670	5	×	×	54.80	1.673	5	×	×
								59.90	1.542	9	×	

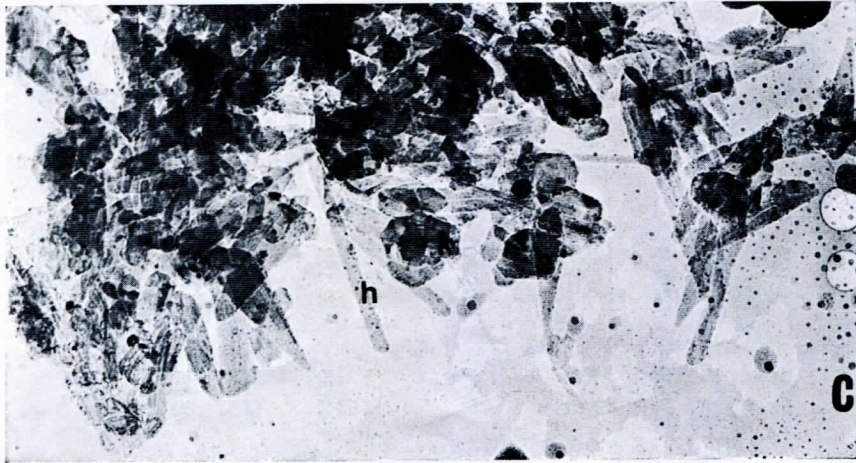
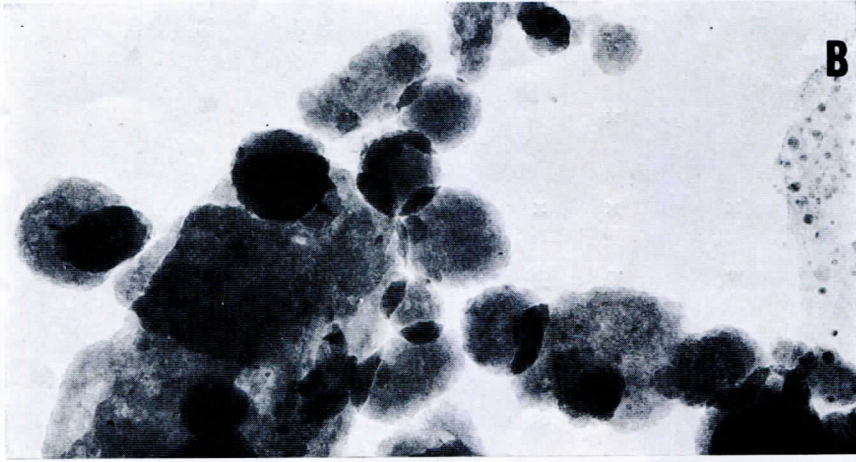
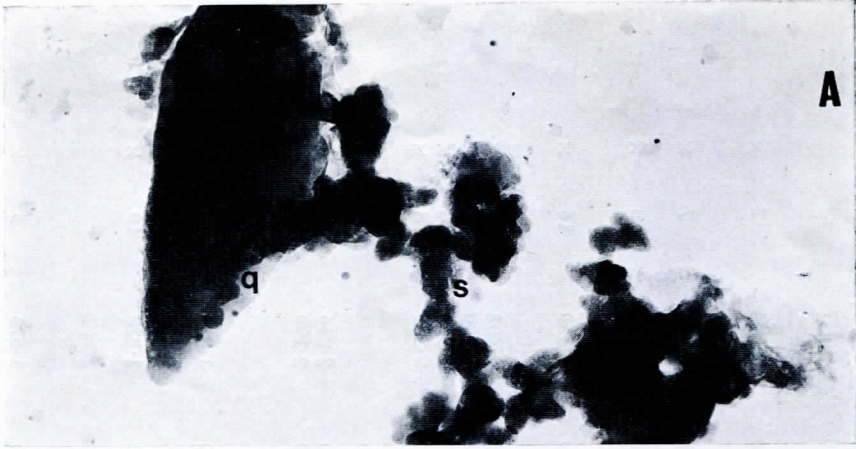


PLATE 3. A, Quartz samples treated with *P. conspersa*. Quartz (O₊) and amorphous silica (s) ($\times 71\ 800$). B, Albite altered by *P. conspersa* ($\times 111\ 700$). C, Kaolinite (k) and halloysite (h) produced in the treatment of albite with *P. conspersa* ($\times 111\ 700$).

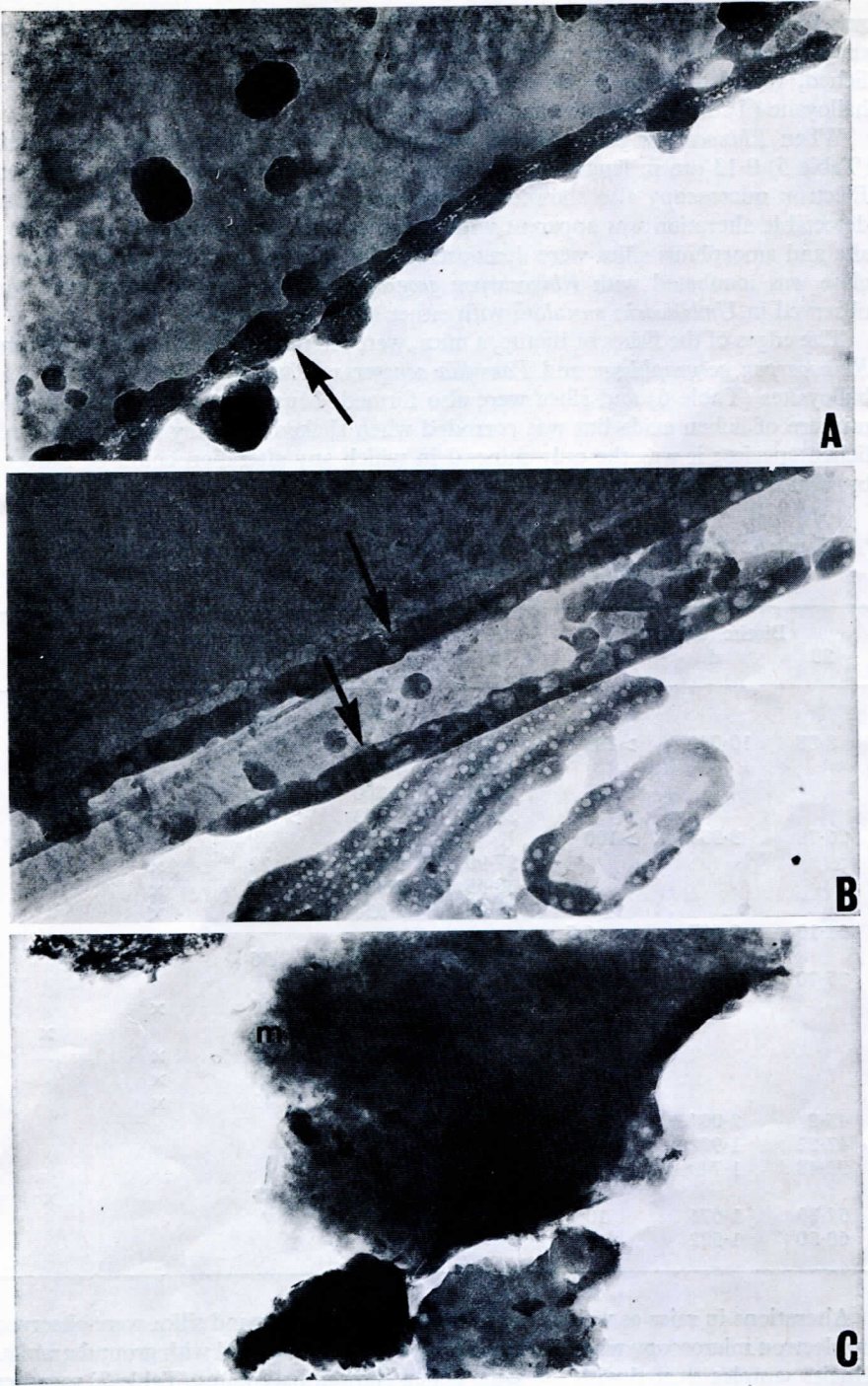


PLATE 4. A, Edge alterations of biotite (arrow); treatment with *R. geographicum*, *P. conspersa* or a mixture of lichen compounds ($\times 71\ 800$). B, Edge alteration (arrows) on muscovite, produced by treatment using *Umbilicaria pustulata* ($\times 71\ 800$). C, Gneiss treated with *U. pustulata*: montmorillonite (m) ($\times 28\ 700$).

was found in quartz samples treated with *Parmelia conspersa* (Plate 3A); this was the only case where quartz was altered. Albite was corroded by the same species of lichen, rounded forms being observed (Plate 3B) as well as the production of halloysite (Table 5), kaolinite and silica (Plate 3C).

When *Rhizocarpon geographicum* was incubated with albite, halloysite crystals (Table 5) 0.13 μm in length (as measured by electron microscopy) were detected. Electron microscopy also showed the presence of amorphous silica. Although no detectable alteration was apparent with X-ray powder diffractometry, both halloysite and amorphous silica were demonstrated by electron microscopy when orthoclase was incubated with *Rhizocarpon geographicum*. No visible alterations were observed in *Umbilicaria pustulata* with either albite or orthoclase.

The edges of the flakes of biotite, a mica, were altered by the lichen acid mixture, *Rhizocarpon geographicum* and *Parmelia conspersa* (Plate 4A). In the latter case, halloysites (Table 6) and silica were also formed. Muscovite was resistant to the mixture of lichen acids but was corroded when shaken with any one of the three lichen species; it was the only mineral in which any alteration could be induced by *Umbilicaria pustulata* (Plate 4B).

TABLE 6. X-ray powder data of untreated and *P. conspersa*-treated biotite. Symbols: Biot. biotite; Hall., halloysite. (For other symbols see Table 5)

Biotite (control)			<i>P. conspersa</i> -treated Biotite				
20	d	I	20	d	I	Biot.	Hall.
8.88	10.040	>100	8.75	10.109	>100	×	
			12.50	7.075	3.5		×
			20.81	4.266	6		×
			26.56	3.353	>100	×	×
26.70	3.335	>100	27.90	3.195	22	×	
			30.55	2.924	7	×	
			34.00	2.634	6	×	
			35.70	2.512	19.5		
34.10	2.627	6.5	35.65	2.516	56	×	
			36.75	2.444	5	×	
			38.30	2.348	5		×
			41.25	2.187	5	×	
			44.56	2.031	14	×	
45.2	2.004	12.5	45.00	2.012	42	×	
			47.22	1.922	10		
			52.48	1.740	8		
			54.80	1.674	10		
60.80	1.522	6					
			54.65	1.678	20		×

Alterations in mica as well as the formation of halloysite and silica were observed by electron microscopy when *Parmelia conspersa* was incubated with ground granite. Gneiss samples treated with the same lichen showed halloysites (Table 7) together

TABLE 7. X-ray powder data of untreated and *P. conspersa*-treated gneiss. Symbols: Q, quartz; O, orthoclase; A, albite; B, biotite; M, muscovite; F-K, potassium feldspar; Hall., halloysite. Other symbols are as in Table 5

Gneiss (control)								<i>P. conspersa</i> -treated Gneiss							
2θ	d	I	Q	O	A	B	M	2θ	d	I	Q	A	B	F-K	Hall.
8.80	10.040	60				×		8.74	10.109	42			×		
13.65	6.486	23		×				12.40	7.132	7					×
17.75	4.995	24					×	13.76	6.430	7		×			
19.80	4.480	17					×	14.86	5.956	7		×			
20.85	4.258	43	×	×				16.60	5.335	5		×			
22.05	4.029	18		×	×			19.70	4.502	4			×		×
22.55	3.941	21					×	20.80	4.266	66	×				
23.55	3.776	23		×	×			21.00	4.226	11				×	
24.25	3.668	23			×			22.50	3.948	5		×		×	
25.15	3.539	23					×	23.45	3.791	33		×			
25.60	3.477	23		×	×			24.34	3.653	9		×		×	
26.55	3.355	>100	×	×				25.60	3.476	13		×		×	
27.45	3.247	>100					×	26.60	3.348	>100	×		×		
27.95	3.190	44		×	×			27.50	3.240	>100				×	
								27.90	3.195	56		×	×		

TABLE 7 (cont.)

Gneiss (control)								<i>P. conspersa</i> -treated Gneiss							
20	d	I	Q	O	A	B	M	20	d	I	Q	A	B	F-K	Hall.
								29-04	3-072	4					×
								29-84	2-991	16		×			
29-90	2-986	19					×	30-40	2-937	7		×			
30-45	2-934	17		×				30-78	2-902	10			×	×	
30-85	2-896	23					×	31-26	2-858	6		×			
								32-30	2-769	7		×			×
34-80	2-576	18					×	34-84	2-572	17		×			
35-70	2-513	19		×				36-50	2-459	12	×				
36-55	2-457	24	×	×				39-40	2-285	8	×	×	×		
39-45	2-282	16	×	×											
40-20	2-241	14	×					40-26	2-238	7	×				
								41-70	2-164	11		×	×		
42-45	2-128	23	×					42-46	2-127	20	×	×			
								44-50	2-034	5		×			
45-10	2-008	18					×	45-36	1-997	10		×	×	×	
45-40	1-996	19	×					45-90	1-975	10	×				
								50-06	1-820	19		×			
50-10	1-819	30	×												
50-56	1-801	21	×					50-68	1-799	13	×				×
								52-85	1-731	5			×	×	
								54-80	1-673	11	×		×	×	
54-85	1-672	20	×												
59-90	1-543	15	×					60	1-54	16	×		×		

with surface alterations of mica. Montmorillonite (Plate 4C), halloysite and degraded mica were all formed in samples of gneiss treated with *Umbilicaria pustulata* (Fig. 2A).

Discussion

The present studies demonstrate that, in the case of the lichen species selected, fragments of thalli are more effective in inducing colour complex changes than are either combinations or single extracts of selected lichen substances (Ascaso and Galvan, in press; see also Figs 3, 4, 5). The exact reason for this has not yet been determined but it is probable that the species selected for this study contain other chelating agents. Such compounds might be allied to gluconic and galacturonic acids or perhaps some of the diverse substances that are often excreted by fungi, known to have a complex-formation ability (Stevenson, 1967; Williams and Rudolph, 1974). The ability of the lichens used in the present survey to form coloured complexes does not seem to be directly related with the concentration of cations found in the medium. Direct determination of the release of cations into the medium gave results which were very difficult to interpret. It is well established that lichens are able to take up metallic ions (see e.g. Puckett *et. al.*, 1973; James, 1973). However, in the case of *Umbilicaria pustulata*, the absence of aluminium in the samples can be explained by the fact that at pH values above 8 aluminium is precipitated as aluminium hydroxide ($Al(OH)_3$) and this could be retained on the filters. Experiments are in progress aimed at solving these problems.

The genesis of new minerals by lichens in nature and under laboratory conditions is summarized in Table 8. *Rhizocarpon geographicum* is able to generate halloysites from feldspars both in nature and in the laboratory; although goethite is also recorded for this species in nature it was not possible to confirm its formation in the laboratory.

TABLE 8. Summary of the generation of new minerals by the action of lichens

Silicated material*	Lichen		
	<i>R. geographicum</i>	<i>P. conspersa</i>	<i>U. pustulata</i>
Quartz		SiO ₂	
Micas		Halloysite	
		Amorphous SiO ₂	
Feldspars	Halloysite	Halloysite	
	Amorphous SiO ₂	Kaolinite	
		Amorphous SiO ₂	
Rocks	not determined	Halloysite	Montmorillonite
		Amorphous SiO ₂	
Granite	Halloysite	Halloysite	
(field observation)	Goethite	Kaolinite	
		Amorphous SiO ₂	
Gneiss	Halloysite	Halloysite	
(field observation)		Amorphous SiO ₂	

*All laboratory experiments unless otherwise indicated.

Rhizocarpon geographicum attacks the edges of biotite. Iron must be removed into aqueous state as indicated by our results and the experiments of Williams and Rudolph (1974). It is not, however, detectable in solution by atomic absorption techniques nor is it deposited as goethite as in nature. It may be absorbed on either mineral or lichen surfaces.

In nature, *Parmelia conspersa* was found to be associated with halloysites, kaolinite and amorphous silica. In the laboratory this species is also able to generate the same new minerals. It seems likely, in our view, that the minerals halloysite and kaolinite are formed in nature by the action of this lichen on feldspars. Amorphous silica probably originates from the three primary rock minerals, quartz, micas and feldspars. However, as the identification of amorphous oxides presents considerable difficulties further work is needed to elucidate their chemical composition.

It is not clear why *Umbilicaria pustulata* does not generate new minerals in nature; under laboratory conditions montmorillonite is produced. Except at the attachment umbilicus the species is not in close contact with its substrate and therefore it is likely that if new minerals are formed in nature they are quickly removed by rain-water.

The results demonstrated here show that the lichens characteristic of a particular rock type are able to modify them 'in vitro' as well as 'in vivo'.

Summary

The nature of the minerals occurring at the interface between two types of acidic rocks, granite and gneiss, and the thalli of three characteristic lichens, *Parmelia conspersa*, *Rhizocarpon geographicum* and *Umbilicaria pustulata*, have been studied. In addition to alteration of the edges and surfaces of mica and feldspars in the rocks, amorphous silica, twinned goethite crystals (α -FeOOH), halloysites and kaolinite were noted. Cross-contamination, microbial contamination and lixiviation were eliminated in a series of rigorously controlled *in vitro* experiments. It is concluded that lichens are able to induce both chemical and morphological changes in rocks as well as in their mineral content.

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