THE ROLE OF LITHOPHILOUS LICHENS IN THE WEATHERING OF MASSIVE CRYSTALLINE ROCKS

Ye. A. Yarilova

(Laboratory of Soil Mineralogy, Soil Institute imeni V. V. Dokuchayev)

Pochvovedeniye, No 3, pp 533-548, 1947.

Translated for:

JET PROPULSION LABORATORY
4800 Oak Grove Drive
Pasadena, California 91103

NAS 7-100

THE ROLE OF LITHOPHILOUS LICHENS IN THE WEATHERING OF MASSIVE CRYSTALLINE ROCKS

Ye. A. Yarilova
(Laboratory of Soil Mineralogy, Soil Institute imeni V. V. Dokuchayev)

"The process of rock weathering," has written Academician V. I. Vernadskiy, /533* "is a sluggish biological process which is ordinarily not taken into consideration. This apparently explains the backwardness of this field of chemical geology (the weathered crust) in comparison to the modern level of knowledge. It is approached only as though it were a physicochemical process. Much is to be gained from a biogeochemical approach to the solution of this problem."

This approach was taken by B. B. Polynov, who in 1940 began together with his coworkers to study the first stages in soil formation caused by the action of lithophilous lichens on the gneissose granite of Mt. Kosaya in the southwestern part of the Il'men' State Park. Interrupted by the war, these investigations were resumed in 1944 in the Laboratory of Soil Mineralogy organized anew by B. B. Polynov in the Soil Institute of the Academy of Sciences USSR. The present work is among those carried out by the laboratory in 1946.

Lichens are known to be one of the first settlers on outcrops of massive crystalline rocks. In this unique symbiosis of a terrestrial (or green or blue-green) alga with an ascomycetous fungus, Genkel' and Yuzhakova discovered a third component -- the nitrogen-fixing bacterium Azotobacter (Ref. 2; see also Refs. 3, 4, 9). The presence of the azotobacter also explains why lichens can grow on anitrogenous media.

Because of a series of ecological characteristics -- resistance to mechanical effects and drought, tolerance of substantial temperature fluctuations by many of them -- the lichens are widely distributed under the most varied natural conditions. They are encountered both on mountain summits above the permanent snow line and in deserts where the temperature in the hot season rises to 60° C. Their morphological, anatomical, and biological characteristics, as well as their distribution in nature, have been the subject of extensive research in the literature (domestically, the works of Yelenkin and Danilov; abroad, a long line of authors). It is not part of our immediate task to scrutinize this literature.

Most investigators have proceeded from the wide dissemination of lichens in nature on the most varied substrata from bare rock and glass to living leaves and have seen in them genuine epiphytes deriving their food from atmospheric dust and precipitation, but have regarded the organs connecting the thallus to the substratum (the stalk in fruticose lichens, the rhizinae in foliose lichens) only as organs of attachment into which no substances from the substratum penetrate. The great hygroscopicity of the lichen body helps them gain nourishment from atmospheric moisture. As early as 1861 Fries (Ref. 27) and Uloth (Ref. 52) opposed this assumption. On the basis of a microscopic study of sections through lichens and the tree bark on which they grew, Uloth stated that the stalk and rhizinae consisting of fungus hyphae were unquestionably adapted to absorbing

*Numbers in margin indicate pagination in the original foreign text.

solutions from the substratum. This pertains in even greater measure to crustose lichens growing together with their substratum on the whole lower surface which is devoid of a cortical layer. The validity of the views of these two authors in regard to foliose lichens was confirmed in the experimental investigations /534 of Berdau (Ref. 1), Zukal (Ref. 60), Salomon (Ref. 46), and Yelekin (Ref. 8) at the end of the last and the beginning of this century. It was found that both sides of the lichen thallus were capable of absorbing water and the substances dissolved in it, but many species absorb it faster and more easily from the under side. This leads to the result that it rises upwards along the capillaries formed by the hyphae lying parallel to each other and loosely touching, bundles of which form the rhizinae.

As for the ability of the stalk to perform absorption functions, Zukal's experiments (Ref. 60) demonstrated that this organ is a very poor conductor of water and the water moves to the stalk from the younger, upper parts of the thallus.

"The question of whether lichens derive nutrient substances from the substratum," writes our eminent lichenologist Danilov (Ref. 5), "is settled differently, depending on the nature of the substratum and the characteristics of the lichens themselves. It is quite obvious that substrates like glass can have no nutrient value under any conditions." The present author cannot agree with the last statement, since many high-ash elements (SiO_2, TiO_2, Al, Fe, Ca, Mg, Mn, Na, K, S, etc.) are included in the composition of glass. While some lichen species are universal and can vegetate on both wood and stone, others are confined to a certain substratum.

Attention was drawn long ago to the division of lithophilous lichens into two large groups: (1) limestone or "calciphilous" and (2) silicate or "calciphobic" lichens.*

The most recent investigators have managed to observe an even stricter confinement of certain species of lichens to a definite rock, e.g., Motyka indicates (Ref. 44) that among the calciphilic species we find on marls only a few which are less sensitive to the chemical composition of the substrate, but some species may be found on marls which are not found either on limestone or, even less, on granite. In reporting on an expedition into Karelia in 1920-1921, V. V. Savich writes that "a definite substratum is matched by a definite lichen (and moss) formation ... (a formation on diabase rocks, a formation on dolomites, etc.). The formation are arranged into a number of associations conditioned by the effect of the environment, i.e., illumination, moisture, direction in which they lie, prevailing winds, and human interference" (Ref. 13).

The research of Fünfstück (Ref. 30), Bachmann (Ref. 17), Lang (Ref. 40), Friederich (Ref. 26), and others disclosed the effect of the petrographical composition of the substratum on the anatomical structure and chemism of the lichens' thallus. Let us recall that the thalli of most lichens consists cross-sectionally

*The terms "calciphilicity" and "calciphobicity" in regard to plants are conventional, since almost all plants need calcium for normal growth; an exception is only some lower fungi and algae. In regard to lichens, this question is not yet clear. Stahlecker (see below) believes that hyphae need calcium to grow.

of the following layers or zones: (a) superior and inferior cortex (the latter is lacking in crustose lichens) dark in color and consisting of a narrow strip of dense hyphal tissue (the hyphae are either intimately intertwined or, more rarely, are arranged in parallel rows); (b) a gonidial layer in the form of an interrupted or continuous strip composed of an agglomeration of round green algae intertwined with fungus hyphae; and (c) pithy tissue consisting of a loose mass of colorless ramifying hyphae (fungous filaments). In foliose lichens, dark growths in the form of thick filaments, the rhizinae, drop down from the inferior cortex, while in fruticose lichens it is a dense element -- the stalk -- by which these lichens attach themselves to the substratum. The most typical limestone lichens belong to the so-called endolithic group which grows its thallus inside /535 the stone. Silicate lichens are epilithic forms in which the thallus is almost entirely located above the rock. Fat formation in limestone lichens is in direct dependence on the $CaCO_3$ content of the rock. The thickness of the individual sections of the thallus also depends on this (the higher the lime content in the rock, the more strongly developed is the hyphal layer and the more weakly the gonidial; in endolithic lichens, the gonidial layer takes up an insignificant portion of the tahllus. In epilithic lichens, it reaches a great thickness -- exceeding even that of the hyphal layer). Zopf (Ref. 50) revealed the effect of the substratum on formation of lichen acids and links this to the chemical features of the substratum. The acids are generally stored in greater amount in lichens growing on stone or dead plant matter than in those living on live vegetation.

Several investigators have carried out observations of the nonuniform settlement of different minerals of magmatic rocks by lichens. In discussing this question, in a special study Stahlecker (Ref. 48) comes to the conclusion that this phenomenon is associated, not with the physical features of the substratum -- as Brisson (Ref. 21), Weddel (Ref. 53), and others assumed -- but with its chemical composition. Noting that fresh rock is preferred to weathered rock for settlement, Stahlecker points out that minerals having greater basicity are favored. This author observed that, as the calcium and magnesium content in the rock grows larger, the thickness of the thalli of the crustose lichens Rhizocarpon coniopsoideum and Rh. subconcentricum also becomes greater. He concludes that these elements are very important in hypha growth.

Similar observations were made by Senft (Ref. 47): "In granite composed of potash feldspar (orthoclase), soda-lime feldspar (oligoclase), alkali-poor mica (ferruginous mica), and quartz the lichens first and in greatest quantity appear on the oligoclase, to a considerably less degree on the orthoclase, to a still lesser degree on the mica, and are entirely absent on the quartz."

Lemmleyn's article (Ref. 12) also contains indications of the differential relationship of lichens to different rock components. In the rock crystal deposits of the circumpolar Urals, the quartz crystals are often covered with small crystals of prochlorite; lichens settle principally on these sites and far less often may they be encountered on the smooth crystal faces. The author associates this phenomenon not only with the physical, but also with the chemical properties of the prochlorite.

Gümbel (Ref. 32) as early as 1852 pointed out a number of so-called siderolichens (also formerly called formae oxydatae) which, because of the depositing of brown iron compounds on the exterior of the cell envelopes forming the ends of the hyphae on the surface of the thallus, become entirely or partially rust-colored. Some of these lichens have been thoroughly studied by Molisch (Ref. 43). They belong to six related families of crustose lichens on igneous rocks (Acarospora, Aspicilia, Lecidiea, Jonaspis, Rhizocarpon, Urceolaria) and prefer those which are rich in iron. Molisch even deals with the relationship between the iron content of the rock and the divergence of these lichens from normal ones in form and color. He regards the ferruginous deposits in the lichens as excretion of the surplus absorbed iron.

Zahlbruckner (Ref. 57) notes that in their nutriment lichens are more closely bound to the substratum than are more highly organized green plants since in lichens -- especially in their most widespread crustose forms -- more CO_2 is excreted /536 than assimilated, which favors the passage into solution and entry into the lichen of the elements comprising the various minerals of the rock.

Salomon (Ref. 46) indicates that the substratum composition does not play the latter role in lichen absorption of phosphorus. Thus, Umbilicaria from argillaceous shale contained less P than did the same genus from granite.

Let us now turn to the data in the literature on the action of lithophilic lichens on rock.

The most thorough studies were carried out by Bachmann who presented their results in a series of articles (Refs. 16-20).

This author successfully settled the disputed question of the relationship of the limestone lichens to their substratum. Contrary to the view widely held at that time that these lichens deposit around themselves, in the form of a carbonate of lime, the calcium which they extract from the substratum and are therefore creators of new rocks, Bachmann showed that endolithic lichens penetrate the limestone substratum in different directions, dissolving it with some of their secretions, probably acid in nature.

More complex and more difficult to investigate is the question of the relationship of the epilithic lichens to their substratum. Lang (Ref. 40), Friederich (Ref. 26), and Stahlecker (Ref. 48), who specifically engaged in research on the problem of the relationship of lithophilic, particularly silicate, lichens to their substratum were only in isolated cases able to observe that their hyphae penetrated the rock along cracks in it to a depth of from 0.5 to several millimeters.* They did not succeed in detecting any action by lichen hyphae on the rock consitituents. Only quartz crystals offer a surprising exception. According to these authors, these crystals are corroded by special so-called precurrent hyphae of the crustose lichen Rhizocarpon coniopsoideum which spread in all directions from the maternal thallus and form a new thallus when they encounter algae cells. Stahlecker attributes a special chemical nature to these hyphae which gives them the ability to take over rock that is entirely new.

At the same time, references to the intensive decomposition of rock by the

*Frey (Ref. 25) indicates a considerably greater depth -- up to 30 mm.

lichens, particularly crustose, which grow on it appear repeatedly in the literature.

An especially large number of such observations were made by Göppert (Ref. 31). He points out that on a very hard gneiss the tender lobes of the lichen Biatropa polytropa dendritica lay in small depressions whose shape completely matched that of the lichen lobes. On the identical rock, the areas uncovered by vegetation were perfectly hard, but under the lichens the substratum was friable and decomposed for several millimeters.

The application of a new investigatory method -- microscopy of thin sections of rock and crustose lichens -- enabled Bachmann to go farther than other investigators in clarifying the effect of epilithic lichens on their substratum. He discovered that these lichens behave differently toward the diverse minerals in granite. Mica suffers the most from their action. The cleavage planes of its crystals often prove to be covered with interlaced lichen hyphae, including on the edges of the crystal the gonidia also, which leave traces of etching on them. Hyphae are also seen to grow through the mica sheets in different directions. Such crystals lose their characteristic appearance and become white as chalk; the hyphae grown over them split them into separate sheets, making them look like a slightly flexed book. It should be noted that Stahlecker also observed the /537
permeation of mica crystals by fungal hyphae, but arrived at the conclusion that they did not belong to the lichen, but to a fungus parasitic on it. Bachmann resolutely opposes this view.

Bachmann observed particularly large numbers of completely decomposed crystals in an argillaceous layer beneath the thallus of Pertusaria corallina, but in the interstices of the reticular or filamentous plectenchyma small particles of mica were preserved. The depth to which the hyphae penetrate the mica crystals depends on the lichen species and the nature of the rock. Bachmann indicates a depth of 0.2 mm for Lithoica chlorotica, and 3 mm for Rhizocarpon atroalbum.

It is of interest to remark that in his lectures on mineral weathering given in 1887-1888 Dokuchayev (Ref. 6) refers to Puzyrevskiy and Struve's observation of the almost complete absence of mica in the Finnish rapakivi, while the sites where it had previously been were occupied by lichens.

A similarly distince chemical effect by lichen hyphae on the other constituents of the granite -- feldspars,quartz, augite, and hornblende -- Bachmann was unable to detect*; they merely penetrate these minerals along cracks and expand in them during their further growth, i.e., disintegrate them by mechanical action.

Of extraordinary interest are Bachmann's observation on the decomposition of garnet (almandine) in micaceous schist by lichens of Rhizocarpon geographicum D. C. (Ref. 20). At the sites of contact between the hyphae and the garnet crystals (whose settlement usually begins from the edges and gradually spreads in

*In one of his papers he remarks that the "kaolinization of orthoclase is apparently accelerated by certain lichens, but this cannot be noticed under the microscope."

depth) a yellow fine-grained mineral substance is formed. A $K_4Fe(CN)_6$ test in this substance disclosed substantial amounts of it, but the powder of fresh garnet failed to give this reaction at all.

The chemical action of silicate lichens on their substratum was attributed by Bachmann to the elevated carbon dioxide (carbonic acid) and oxygen in the lichen medium. An important factor in mineral destruction is also enzymes and organic acids, chiefly oxalic, excreted by fungal hyphae (Kunze [Ref. 39], Lind [Ref. 41]).* The reagent with which lichens corrode garnet and quartz, which under laboratory conditions yield only to hydrofluoric acid, still remains unclear.

The mechanical effect of lithophilic lichens on their substratum has also been more thoroughly studied recently. Lichens also break down the substratum in other ways than by hyphal penetration of the rock along capillary cracks, mentioned by a number of investigators, which leads to their gradual expansion and loosening of the bond between its constituents, or by their splitting of mica crystals which Bachmann studied.

Buchet (Ref. 22), and Mellor (Ref. 42) considerably later, had discovered that, under the lichens settling on the glass in church windows, little pits /538
were formed which ran together at places. Bachmann compared this phenomenon with the solvent action of limestone lichens on their substratum, but the interesting experiments and investigations by Fry (Refs. 28, 29) gave it an entirely new interpretation. The action of the muculent body of lichens on their substratum is found to be similar to the effect of a layer of gelatin applied to glass. This gelatin layer contracts on drying, separates from the substratum, and in so doing tears out and takes with it scale-like pieces of the glass which have become firmly attached to it. On the under side of crustose lichens removed from their substratum can always be seen bits of rock which are solidly fastened to it. Under the microscope, the same sort of rock particles are also seen inside the lichen tissue. Fry investigated different rocks and the lichens growing on them. Lichen tissues on clay shale are found to be raised above the substratum like an arc covered on the under side with platelets of rock. The same sort of platelets form several layers inside the lichen tissue and follow its bend exactly. Hyphae spreading to the substrate penetrate the cavity thus-formed through the cracks in the floor. Overgrowing the substratum, they are able subsequently to cause new disintegration in the rock. A similar phenomenon also occurs on hard rocks -- crystalline schist, gneiss, etc., but here it is considerable less marked since the lichens cannot, as in the first case, tear away whole layers of rock, but they can only remove small bits of it and individual minerals which during further growth of the lichen are scattered through the tissue without any regular arrangement.

---

*Some authors attribute this role to lichen acids, but this seems improbable. These complex high-molecular compounds which are insoluble in water and which belong primarily to the aromatic series (natural depsides) and partially to the fatty series (Zopf [Ref. 58], Hesse [Ref. 33]) can take only an indirect part in the weathering process by binding the bases entering the lichen in the form of slightly soluble salts. Keegan's observation (Ref. 35) is interesting that the lichens which produce a comparatively large amount of Ca oxalate have few lichen acids.

In connection with research on the problem of the relationship of lichens to their substratum, interest was aroused in determining the high-ash elements in them.

Thomson (Ref. 50) in 1845 had already made a number of determinations of the ash content of lichens. He analyzed only the upper parts of these plants without the substratum particles adhering to them. A lichen (the sort is not indicated) from micaceous schist contained 5-6.7% of ash, of which 63.64% was silica, 0.75% was soluble salts, 8.75% was clacium carbonate, and 29.04% was alumina, iron oxide, and their phosphates and calcium phosphate. The author inferred that the lichen drew ashy materials from the substratum.

In 1847 Knop and Schuedermann (Ref. 37) analyzed the lichen Cetraria islandica from peat on a granite placer deposit. In 100 parts of ash comprising 1.9-10% of the weight of the young lichen and excepting CO_2 they found:

Silica	41.6%	An Iron Oxide	6.9
Potassium Oxide	20.3	Alumina	1.0
Sodium Monoxide	2.3	A Manganese Oxide	7.2
Calcium Oxide	5.8	Phosphorus Pentoxide	6.5
Magnesia	8.3		

Somewhat later, Uloth (Ref. 52) made a comparative identification of the ashy elements in the lichen Evernia prunastri gathered from sandstone and birchbark.

In the analyses of different lichens quoted in Wolff's famous report (Ref. 56), the ash content fluctuates from 0.75% to 17.55%, with the crustose lichens richest in high-ash elements and the fruticose lichens poorest. The ash content is found to depend on the substratum composition, e.g., Cladonia rangiferina from a peaty soil contained 0.83% pure ash, while that from syenite contained 1.28%. /539

	On Birchbark	On Stone
K_2O	4,17	5,29
Na_2O	14,93	8,33
CaO	8,38	11,03
MgO	10,41	5,23
Al_2O_3	1,57	3,49
Fe_2O_3	5,51	6,62
Cl	9,12	6,21
SO_4	3,25	1,58
P_2O_5	1,60	2,50
SiO_2	41,05	49,76

For the foliose rock lichen Parmelia saxatilis Keegan (Ref. 36) found 5.4% of ash containing 13.3% of dissolved salts, 5.5% SiO_2 and earthy matter, 2.8% CaO, 18% MgO, about 20% Fe and Mn, 4.1% P_2O_5, and 1.1% SO_4.

Stoklasa (Ref. 49) gives the following figures for the same species of lichen: Al_2O_3 comprises 0.38% of the ash and Fe_2O_3, 10.64%. The crustose lichen Rhizocarpon geographicum which is widely distributed on diverse rocks has ash containing 0.33% of Al_2O_3 and 1.57% of Fe_2O_3, according to Stoklasa.

Stahlecker (Ref. 48) subjected crustose and fruticose lichens (names not given) from a quartz vein in Bavaria to analysis and derived the following data: ash content 19% of dry weight with 13.18% CaO, 13.7% MgO, 6.3% Na_2O, 5.6% K_2O, 15.3% Fe_2O_3 and traces of Al_2O_3, traces of Mn_2O_4, 34.2% SiO_2, 5.8% SO_3, 4.3% P_2O_5, and traces of Cl. Qualitative tests revealed a very high concentration of SO_3 and P_2O_5, a higher content of K_2O than in the preceding case, and a lower Fe_2O_3 content in the ash of lichens gathered from the same vein from sites adjacent to cracks. Unfortunately, the author did not analyze the substratum, and his conclusion that the main supplier of ashy elements to the lichen investigated was atmospheric dust and water is not adequately based. This is particularly true because the data available in the literature -- few, to be sure -- on the mineralogical composition of atmospheric dust indicate that it contains very few phosphorus minerals and only traces of mineral sulfur (Ref. 45).

Salomon (Ref. 46) carried out qualitative microchemical tests for the presence of several ashy elements in a number of lichens. He points out that their Ca content undergoes great fluctuations and that as a rule crustose lichens are richer in this element than are foliose and fruticose ones. The quantity of Mg also varies within considerable limits; thefruits prove to be richest of all in this element. The same thing is also true of P; lichens usually contain both organic and inorganic P compounds in different ratios. The K content varies in different lichens, even when the substratum is the same.

Braconnot (Ref. 24) called attention in 1825 to the high content of calcium oxalate in certain lichens (in Pertusaria communis 47% CaC_2O_4 of dry substance, in Chlorangium Jusuffii, more than 55%). Other authors have obtained similar figures (Geobel, Errera, Sulte, Ref. 24). Crustose lichens are particularly rich in calcium oxalate. However, some of them, as well as foliose and fruticose lichens, do not contain it at all. Stater (Ref. 24) asserts that soluble oxalates may be present in lichens.

A cautious stand must be taken in regard to the data on the ashy element concentration in lithophilic lichens, since they were derived at a time when the methods of ash analysis were still less advanced than they are at present. These figures moreover are incomplete, refer to diverse lichen species, and are not accompanied by analysis of the substratum. As we shall subsequently see, however, for the most part they match our findings.

The first conjoint analysis of the ash of the lichen Parmelia and its rock was obtained in B. B. Polynov's laboratory (Ref. 15). It is given in Table I.

TABLE I

Object Analyzed	Firing Loss, %	Ash, %	SiO_2%	Al_2O_2%	Fe_2O_2%	MgO,%	CaO%	MgO%	K_2O%	Na_2O%	P_2O_2%	SO_2%
Lichen, Parmelia	-	3.71	15.70	2.50	5.50	0.16	22.10	4.80	18.00	6.80	9.30	12.10
Gneissose Granite	0.42	-	70.90	14.67	3.61	0.06	1.55	0.36	4.35	4.23	0.14	-

/540

We will subsequently return to these findings when discussing our own results.

We made a conjoint chemical analysis of the rock and ash analysis of the following lichens:

(1) Haematomma ventosum -- a typical silicate crustose lichen with a pale green cortical layer and thick white mealy medullary tissue tightly adherent to the rock and including many rock fragments in itself.

(2) Squamaria rubina -- a lichen with bright pink apothecia on a greyish-greenish thallus; the marginal exciples of this lichen grow out into squamae, and the lichen -- according to Yelenkin (Ref. 7)-- occupies an intermediate position between the crustose and foliose lichens.

(3) Gyrophora cylindrica sp. -- a dark gray foliose lichen with black apothecia; Motyka (Ref. 44) avers that this lichen settles only on an inorganic substratum and therefore along with the preceding species belongs to the first generation of lichens taking over this substratum and entering into direct contact with the minerals of the rock.

All the lichens were collected from micaceous schist on the summit of one of the mountains in the depression of the River Damkhurts in Bol'shoy Dabu (height, 3000 meters above sealevel in the Northern Caucasus). The indicated Gyrophora species were moreover also taken from amphiobolite cropping out amidst the massif of micaceous schist.

The lichens were cleaned of physical impurities by means of a small brush while being checked under a binocular loupe. In this way, of course, it is impossible to remove substratum particles which have gotten into the lichen thallus, and at the same time there may be a considerable number of them. In the crustose lichen Haematomma ventosum, the residue after treatment of the ash with HCl and KOH was 37% of the ash weight. Ashing took place in a muffle whose temperature was kept at 350-400°C. We borrowed the process of ash analysis and the methods of determining the individual elements from a manuscript work by L. N. Aleksandrova, "Methods of Lichen Ash Analysis." After we completed the ash analysis, however, it was found necessary to modify this method further, especially in application to the crustose lichens. Complete dissolution of all the constituents of the ash by treating the ash with 5% HCl, while boiling for the purpose of ascertaining the CO_2, is not always achieved. Inspection of the finely ground tissue of Haematomma ventosum under the microscope disclosed that it is thickly incrusted with rosettes of calcium oxalate, which we ascertained both on the basis of optical findings -- strong pseudoabsorption (Ng-Np=$\approx$0.16) refractive indices Ng = 1.690, Np = 1.490 completely congruent with those adduced /541 by Winchell (Ref. 55) for the mineral whewellite ($CaC_2O_4 \cdot H_2O$) -- and of microchemical testing (Ref. 51). Ashing did not convert them entirely into $CaCO_3$* . When the ash was treated with HCl in the amount and concentration used for determining carbonates, the calcium oxalate did not completely dissolve, and therefore a reduced figure was obtained for the calcium.

An unsolved problem is the determination of the silicic acid in the ash. By letting 5% KOH act for 20 min. on the residue undissolved in HCl while boiling, we achieved only partial solution of the vegetal silicon formations -- frustules of diatoms and phytolitharia (Tyurin [Ref. 15]), and in our case the tiny silicon envelopes (found in the ash) of the hyphal tissue of the lichen (see below). Results which are known in advance to be too low are obtained for the silicic acid. It seems to us necessary to accompany the ash analysis with quantitative consideration of the separate constituents of the ash under the microscope,possibly after previously separating them by means of heavy liquids.

We will now turn to a consideration of our findings in Table II. Above all, we see that the different species of silicate lichens growing on the same igneous rock vary substantially in their ash content. This is highest in the typical crustose lichen Haematomma ventosum and lowest in the foliose lichen Gyrophora cylindrica. The very same lichen, Gyrophora cylindrica,from different rocks has ash percentages which are very close. The concentration of the individual ash elements in the different species of silicate lichens fluctuates in wide limits. The ash of the crustose lichen Haematomma ventosum is characterized by its large calcium content (the higher ash content is also connected with their richness in calcium oxalate) and a correspondingly lower content of the other elements in comparison to foliose lichens. It is interesting to note that in the ash analysis data on the foliose lichen Parmelia given in Table I the substantial amount of calcium is also noteworthy. It is very probable that in some cases Mg takes the place of Ca (see Keegan's data above). Foliose lichens contain more potassium than anything else (this element makes up the greatest percentage, after calcium, in the ash of crustose lichens); then come silica, sulfur, and phosphorus. Aluminum is in the last place.** In most cases the iron concentration is also small. Calcium and magnesium concentrations which are close to each other are noted in Gyrophora cylindrica. The species characteristics of this lichen are displayed in the fact that the elements have the same distribution with respect to their percentage content in the ash. Since we know neither the quantity nor the composition of the atmospheric

---

*Research by Willard and Boldyreff (Ref. 54) indicates that calcium oxalate is precipitated from pure reactants and is practically all converted into $CaCO_3$ in 3 hr of heating at 400°C; spherulites of oxalates of plant origin prove to be more resistant to the influence of the temperature.

**Hutchinson in his survey of the biochemistry of aluminum (Ref. 34) also points out the low amount of Al in lichens.

TABLE II

Chemical Composition of Two Rocks of the Region of Bol'shyye Laby (Northern Caucasus) and of the Ash of Three Lichens from Them

Object Analyzed	Hygroscopic Water	Loss From Firing	Ash %	SiO_2	M_2O_2	Fe_2O_2	MnO	CaO	MgO	K_2O	Na_2O	P_2O_2	SO_2
Micaceous Schist	0,38	2,35	—	70,14	15,06	3,91	0,10	1,58	0,91	2,64	2,93	0,21	traces
Lichen Haematomma Ventosum	14,6	—	7,88	1,13	0,68	0,27	traces	17,01	1,38	13,10	1,50	1,02	2,12
Lichen Squamaria Rubina	14,6	—	2,40	7,95	0,15	2,24	0,21	46,38	1,17	18,67	4,42	8,12	8,02
Lichen Gyrophora Cylindrica	15,7	—	1,29	12,83	2,17	2,81	0,34	5,12	5,93	24,00	10,70	15,55	18,00
Amphibolite	0,20	0,60	—	48,19	15,91	12,96	0,42	10,47	5,65	2,32	2,41	0,20	traces
Lichen Gyrophora Cylindrica	15,5	--	1,60	18,77	0,29	4,55	0,30	5,44	4,16	27,23	13,67	9,00	16,21

dust deposited in the sites where the subjects of our investigation were collected, we cannot take this factor into consideration, although it possibly plays a certain role in supplying the lichens with ashy elements. From the data in the literature which we scrutinized, however, we have every reason for believing the substratum to be the main source of these elements for the lichen. Below we give a series of ashy elements arranged in decades in decreasing ratio of their occurrence in lichen ash to their occurrence in the rock -- the so-called biological absorption series after B. B. Polynov. For comparison, we present the same series for Parmelia based on the data in Table I. The elements for which this ratio is close are separated from the others by two vertical lines. /542

Haematomma ventosum	On Micaceous Schist	S — Ca — ‖ K — P ‖ — Mg — Na — Fe — Al — SiO_2
Squamaria rubina		S — ‖ P Ca ‖ — K — Mg — Mn — Na — Fe — SiO_2 — Al
Gyrophora cylindrica		S — P — K — Mg — ‖ Mn — Na — Ca ‖ — Fe — SiO_2 — Al
Gyrophora cylindrica	On Amphibolite	S — P — K — Na — ‖ Mg — Mn — Ca ‖ — SiO_2 — Fe — Al
Parmelia	On Gneissose Granite	S — P — Ca — Mg — K — Mn ‖ Na — Fe ‖ SiO_2 — Al

In all cases, the first place is occupied by sulfur, for which all the lichens are concentrators; then follows phosphorus, for which the lichen Parmelia is a concentrator. Potassium is in the third place in almost all cases. Aluminum and silica occupy the last places. In most cases, iron adjoins silica.

Characteristic of crustose lichens is the high relative absorption of calcium, which in Squamaria rubina competes with phosphorus and in Haematomma ventosum even precedes this element.

The biological absorption series for Gyrophora cylindrica from various rocks are very close and are characterized by the phosphorus being followed by potassium, while calcium is shifted considerably to the right, assuming a position behind magnesium, sodium, and manganese.

The explanation for the great intensity of sulfur, phosphorus, and potassium absorption, it seems to us, is to be sought in the phenomenon of chemotropism. It was described by Pfeffer at the end of the last century for the lower organisms and consists in their motion toward chemical stimuli. This same phenomenon is also observed in fungi, which are apparently able to extract from rock the nutrient elements located therein in dispersed state (which also takes place in our case), dissolving the obstacles encountered en route by means of the enzymes and organic acids which they secrete.

The entry of other mineral elements into the lichens is determined by the amounts of these elements which pass into solution under given conditions of rock weathering. Correns' studies have demonstrated (Ref. 23) that water dissolves, in the form of ions, all elements comprising silicates (the rate at which the individual elements are dissolved is, of course, not identical). This process is substantially intensified in the presence of acids and alkalies; the products of the vital activity of lithophilic organisms unquestionably also exert an effect on it.

In order to obtain some idea of the distribution of the ash elements in the /543 lichen, we cinerated thin sections of it between two cover glasses at 400°C and then examined them under the microscope in a drop of immersion fluid.

Haematomma ventosum and Squamaria rubina have ash which is identical in nature. The bulk of it is comprised of fine crystals of calcium oxalate and calcium carbonate gathered together in the form of rosettes, and the thickly incrusted mat of colorless hyphae of the medullary tissue which has kept its shape. The average size of these rosettes is 10 microns. They are perceptibly larger in the ash of Haematomma ventosum. The ash of the cortical layer has the appearance of a dense tissue of isotropic hyphal envelopes which have kept their shape and are brownish in color, with rarer inclusions of carbonate and oxalate rosettes and agglomerations of iron oxides. In this layer of Haematomma ventosum are found phytolaria of diverse shapes and diatoms which have apparently entered this layer from the outside (Fig. 1).* A rather large number of rock mineral was detected in the ash of both lichens.

The ash of the foliose lichen Gyrophora cylindrica has another form. It is a brown-stained film of intertwined hyphae with a mass of, for the most part, very fine inclusions of diverse, chiefly brown granules with a high index of refraction showing various interference colors under crossed Nichols. Under the microscope, only the nature of the largest of these granules can be distinguished; these are fragments of the primary minerals of the rock -- micas, chlorite, epidote, hornblende, zircon, quartz, etc. Aggregates and films of Fe oxides (hematite) and a few carbonate rosettes are additionally seen. Dentate phytolarians, as well as rounded or elongate, weakly polarized particles with rounded edges and a refractive index less than that of quartz, are encountered.

In order to clarify the nature of the action of silicate lichens on massive crystalline rocks and individually on their component minerals, we employed Bachmann's method -- microscopy of plane-parallel preparations representing a cross-section perpendicular to the contact surface between lichen and rock.

We studied five different rocks and crustose lichens of the Rhizocarpon species. We shall give a description of these preparations.

Slide No. 1. Rhizocarpon geographicum on quarzite.

The lichen in a thin layer of 150-300 microns covers the rock. Its dark cortical layer has a thickness of about 20 microns; its gonidial layer in the form of a continuous ribbon made of round green algae is 60-100 microns thick;

---

*A. Krylov (Ref. 10), who made a microscopic examination of amorphous silicic acid sediments obtained under various conditions found bodies in them which quite resembled the phytolarians described by Ehrenberg; on this basis he infers that they may be generated in a purely chemical fashion. We repeated several of Krylov's experiments, but in the preparations consisting of irregularly-shaped (costate) spongy particles we were unable to find such well-formed corpuscles of characteristic appearance as are present in the ash of the lichens that we studied and which are entirely congruent with the siliconized cells of grasses and sedges described by Kohl (Ref. 39) and other authors.

under the gonidial layer is located a thin dark-colored layer 20-40 microns thick reminiscent of the cortical layer. A distinct flexuous boundary between rock and lichen is noted, but nevertheless the lichen is solidly united to the rock. In agreement with Frey's observations, quartz fragments of 20 microns or less are visible adhering tightly to the under side of the lichen pulled from the rock in preparing the slide. The same sort of fragments are also found inside the lichen thallus. At one spot on the slide a small bundle of hyphae extends to the quartz under the apothecia (which, according to Frey and Bachmann's observations, exert the strongest destructive effect on the rock).

/544

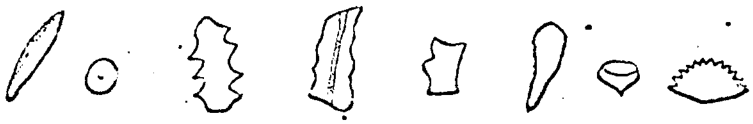


Figure 1. Shape of Diatoms and Phytolarians in Lichen Zone

Slide No. 2. Rhizocarpon on micaceous schist. The lichen thallus is 0.5-1 mm thick. Its 20-micron dark-yellow cortical layer consists of hyphal coils interwoven with fungal filaments into a thick tissue. Under crossed Nichols almost this whole layer is seen to be incrusted with fine granules of yellowish interference hues (oxalate rosettes and possibly lichen acids) (Photograph 1). They are not found in the 50-60-micron thick gonidial layer. The medullary tissue consists of colorless hyphae; in its upper part are observed almost continuous accumulations of a multitude of spherical oxalate aggregations from 20 microns on down in size, with bright yellowish-white interference coloration. Many fine 10-40 micron fragments of rock minerals are included in the medullary tissue. These fragments are chiefly mica (Photograph 2) and are surrounded by webs of thick brown hyphae. The hyphae penetrate the large fragments along the cleavage planes and split them apart (Photograph 2). Isolated phytolarians are found in this layer (Photograph 4).

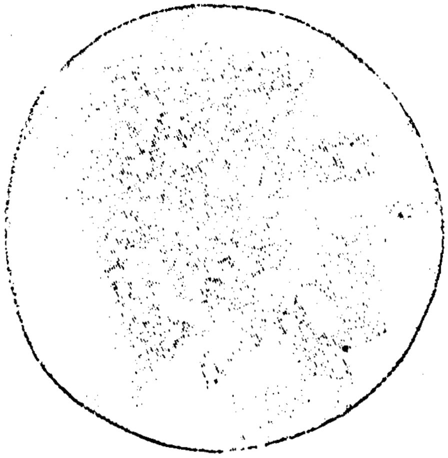
Along cracks in the rock, the lichen hyphae penetrate its interior to a depth of 1-2 mm, destroying the mica crystals which it meets on the way. On the rock surface are seen enlarged gulf-like depressions with ragged edges, obviously owing their origin to the decomposing action of the lichen on mica crystals (Photograph 5).

Where the lichen comes into contact with mica crystals arranged at an acute angle to the rock surface, it penetrates them along the cleavage planes and splits them into separate lamellae which become dull. It was impossible to trace the relationship of the lichen to the quartz in the slide sufficiently clearly. In some places on the slide where it was too thick, a mica crystal covered with a hyphal network was seen to be imposed on quartz which was completely free of hyphae (Photographs 6 and 7). At the same time, colorless fine hyphae spread into the rock for 10-20 microns along the edges of cracks.

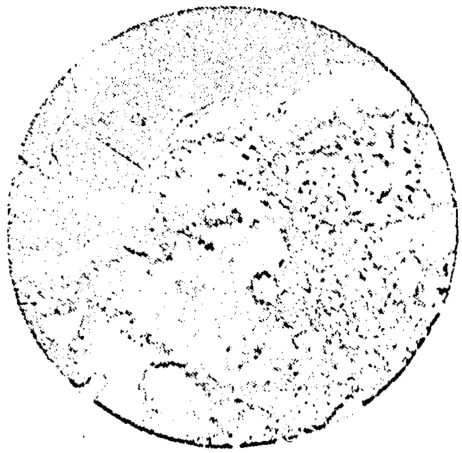
Hyphae penetrate feldspar crystals along cracks, and only in isolated places under the apothecia do small bundles cover this mineral to a distance of 20-30 microns from the point where the lichen contacts the rock.

Slide No. 3. Rhizocarpon on amphibolite.

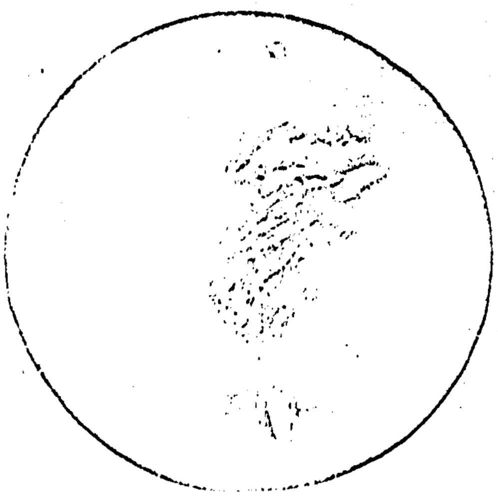
The thickness of the lichen thallus is 200-300 microns. Under a dark cortical layer of 20-30 microns is situated a continuous gonidial layer of 40 microns. Below is situated the medullary layer composed of lighter and more delicate hyphae, which are colored dark brown at points of contact with the minerals. The hyphae penetrate deep into the rock along its cracks, as well as into the hornblende crystals along cleavage cracks and separate from them fragments of different sizes which are surrounded by hyphal tissue and enter the lichen body (Photograph 8). On some hornblende crystals, the hyphal network extends for a slight distance from the contact boundary with the lichen. /545



Photograph 1. Oxalate Rosettes Inside Thallus of Crustose Rhizocarpon Lichen (dark-colored region). Magnification 300 X.

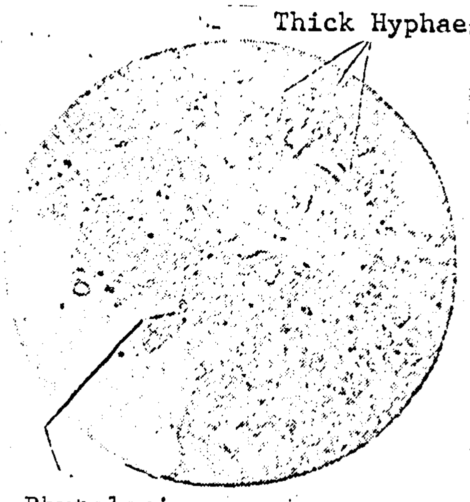


Photograph 2. Cross-Section Through Thallus of Crustose Lichen on Micaceous Schist Under Crossed Nichols. After the Fine Black Cortical Layer Follows a Dark Gray Band, and After that the Medullary Tissue Thickly Incrusted with Oxalate Rosettes (white-colored). In the Lower Part of the Medullary Tissue are Scattered Fragments of Rock Mineral. Magnification 50X.



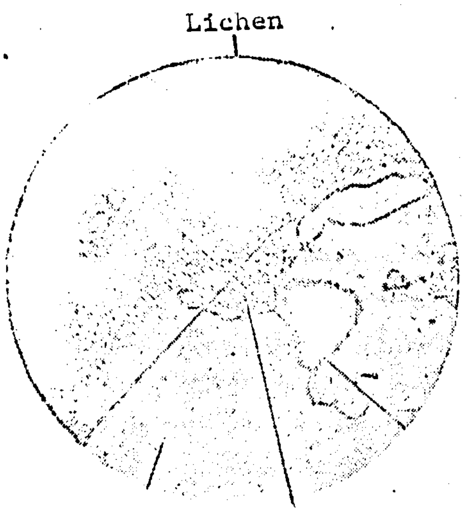
Photograph 3. Muscovite Fragment Inside Body of Rhizocarpon Lichen (dark-colored region) and Split by Lichen Hyphae Along Cleavage Plane Magnification 300 X.

Slide No. 4. White Crustose lichen on syenite. The lichen thickness varies in different regions of the rock from 150 to 1000 microns or more. The cortical layer of 20-30 microns is colored dark brown; the gonidial layer of 50-80 microns consists of accumulations of rounded green algae interwoven with light brown hyphae with many nodes. The medullary tissue displays webs of brownish hyphae with many nodes. Under crossed Nichols, it is discovered that

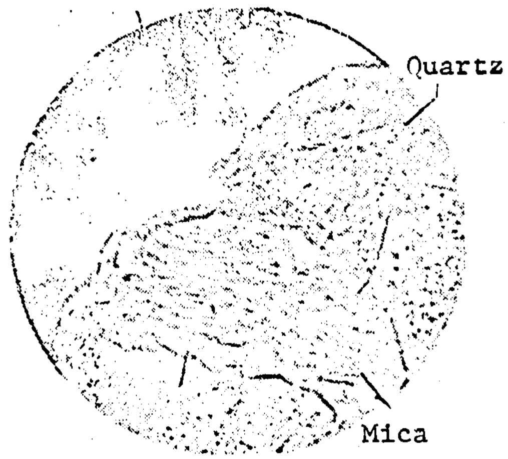


Photograph 4. Thallus of Crustose <u>Rhizocarpon</u> Lichen on Micaceous Schist. Thick, Dark Hyphae, Phytolarians, and Oval Bodies Can be Seen. Magnification 300 X.

Photograph 5. Gulf-like Depression in Micaceous Schist Due to Destructive Effect of Lichen on Mica. Magnification 50 X.



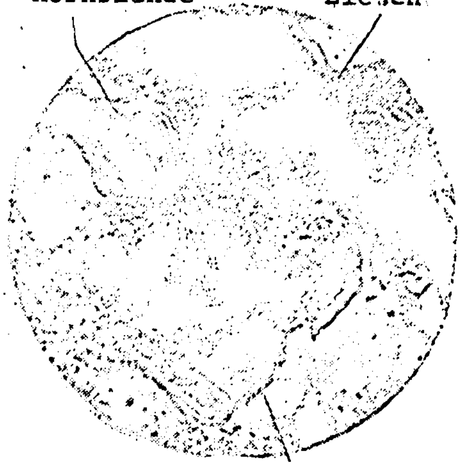
Photograph 6. Hyphae of <u>Rhizocarpon</u> Lichen Penetrate Mica Crystal Threading It in All Directions, but not Spreading into Quartz Surrounding It. Magnification about 300 X.



Photograph 7. Penetration of <u>Rhizocarpon</u> Hyphae into Micaceous Schist Along Interface Between Quartz and Mica and Their Spread to the Mica. Magnification 300 X.

the layer is incrusted with very tiny spherical aggregations extending like tongues also into the gonidial layer.

The hornblende crystals located at the interface with the lichen are divided along cleavage cracks by the brown lichen hyphae which extend to a depth of up to 4 mm (Photograph 9). Some hornblende crystals are covered at a slight distance



Photograph 8. Penetration of Hyphae of Rhizocarpon Lichen on Amphibolite into Hornblende Crystal Along Cleavage Plane. Magnification about 300 X.

Photograph 9. Hyphae of White Crustose Lichen on Syenite Which Penetrate Hornblende Crystal Along Cleavage Cracks and Break It Down. Magnification about 300 X.

from the rock surface by a network of fine hyphae. Under the lichen action, the hornblende turns brown and in some cases loses color; its coloration under crossed Nichols gets duller and takes on a greyish-yellowish shade. In some spots the hornblende crystals are completely disarticulated into parts thickly woven about by the lichen hyphae. Feldspar crystals (acid plagioclases) contiguous to the hornblende are substantially less subject to lichen action. In some places the hyphae were observed to spread to the surface portion of these crystals.

We were particularly interested in the relationship of lichens to apatite because of their high phosphorus content, on the one hand, (which, to be sure, is less in Haematomma than in foliose species) and, on the other, because of the significant corrosion (observed by Kunze [Ref. 39]*) of apatite by the hyphae of fungi found in the humus of coniferous forests. We were unsuccessful, however, in detecting lichen hyphal concentration on apatite crystals located along the contact line (nor could Novorossova [Ref. 11] note this for the lichen Parmelia on miaskites of the Il'men' State Park). This matter requires careful study in a large number of preparations.

Slide No. 5. Rhizocarpon geographicum on diorite.

The 20-40-micron-thick cortical layer of the lichen is made up of thickly interwoven brown hyphae. The gonidial layer consists of rounded green algae in

*Kunze set up his experiments by covering polished plates of different minerals with fresh humus from a coniferous forest. In 8-10 days the fungal hyphae had spread over the whole plate. On removing the humus, three weeks later it was found that the apatite was perceptible corroded.

a web of light brown hyphae with their numerous coils. Thickness of this layer is 40-80 microns. The medullary tissue, yellow-brown in color, is 500-1700 microns thick. Under crossed Nichols, very fine whitish-yellow granules (less than 0.5 micron) are visible in many places. This layer contains many fragments of rock minerals (hornblende, feldspars, epidote, etc.) from 0.01 to 0.15 mm in size. They are surrounded by hyphae which penetrate them along cleavage cracks and split them apart. The surface of fragments like these of quartz and epidote remains clean; the feldspar granules (a middle plagioclase) are more pelitized, and carbonated than in the rock. The contact boundary between the rock and lichens is very flexuous; the hyphae are chiefly concentrated on the interfaces between the grains of different minerals, and also penetrate between their cleavage planes. In these places the hyphae have a stronger brown color. The lichen hyphae spread only to a slight degree onto the quartz and epidote crystals. The brown coils of lichen hyphae which end in bundles of fine colorless twisting hyphae are observed to spread to the feldspar crystals, which are here more strongly pelitized. /546

The lichen action on a chlorite crystal situated perpendicular to the rock surface is particularly great; black hyphal coils penetrate it to a depth of 0.5-0.7 mm along its cleavage cracks and split the crystal into separate lamellae, which subsequently are pulverized by them into tiny parts. From brownish-green, the chlorite becomes brown, almost black in spots. The portion of the hornblende crystal directly contiguous to the lichen is split by the lichen hyphae along the cleavage cracks into a large number of tiny fragments which, when dispersed through the hyphal tissue, are all oriented upwards and give the impression that they are literally being drawn into the lichen body. A magnetite crystal situated on the rock surface is broken up by a thick web of hyphae into a mass of fine fragments which are being converted or have been converted into iron oxides (brown in reflected light).

The results of our investigations of plane-parallel preparations of lichens with rock may be generalized in the following manner.

Crustose silicate lichens of the genus <u>Rhizocarpon</u> penetrate their substratum with the hyphae of their medullary tissue along capillary cracks in the substratum and the cleavage cracks of the individual minerals to a depth of up to several millimeters. In agreement with Frey's observations, the thallus of these lichens displayed numerous fragments of the rock's minerals torn from the rock by the lichen as it grew.

The lichen hyphae coming into contact with the different minerals in the rock act on them in different ways. Different types of mica (muscovite, chlorite, and, according to Novorossova's findings [Ref. 11], also biotite), are, as Bachmann also noted, subjected to the greatest breakdown, both mechanical and biochemical. These micas are split into separate sheets, lose their transparency, and change color. Hornblende crystals are split into tinier pieces principally by the hyphae penetrating them along cleavage cracks. The finer pieces are then gradually drawn into the lichen body and now also undergo a certain chemical decomposition, which manifests itself as a change in color and interference hue. To a considerably less degree and only in the uppermost surface zone (20-30 microns) are feldspars (acid and middle plagioclases) subject to the action of lichen hyphae. However, fragments of these minerals in the lichen body undergo substantial biochemical treatment -- they are more strongly pelitized than in the rock. We were unable to trace the relationship of lichen hyphae to quartz with adequate clarity. The hyphae exert no perceptible effect on epidote. Magnetite, on the contrary, is greatly decomposed by them, breaking up into fine pieces covered with iron oxides or entirely converted into them. No corrosion of apatite by lichen hyphae was discovered in the preparations investigated.

In the future, we propose to extend our studies to a number of other rocks.

In summarizing a survey of the material in the literature and of our own investigations, we arrive at the following general conclusions:

1. Lichens play a great role in the first stages of the weathering of the /547 outcrops of massive crystalline rocks. Since they are one of the first settlers on them, the crustose forms of lichens, intimately associated with their substratum, intensively break it down both by mechanical disaggregation and biochemical decomposition of the separate minerals in the rock.

2. The destructive effect of lichens on rock, despite the fact that it extends to a negligible depth (several millimeters at the most), is of enormous importance, in that it leads to the formation of a first thin layer (1-2 mm) of a small-grained organomineral mass which is the rudimentary stage of a new natural structure -- soil. This new substratum is suitable for the development of more highly organized plant organisms which come to replace the lichens and which further intensify the process of weathering and soil formation.

3. The biogeochemical significance of lichens lies in the fact that they extract atoms of different elements from the inert mineral compounds first coming to the earth's surface and form the first link in the complicated chain of the further transformations of these elements in the biosphere. Lichens are concentrators of several elements -- sulfur,phosphorus in part, calcium, iron (more questionable), and probably a number of microelements.

REFERENCES

1. Berdau, F. Lichens Studied to the Present in the Region of Warsaw School District (Lishayniki, Issledovannyye do Kikh por v Oblasti Varshavskogo Uchebnogo Okruga). Warsaw, 1876.
2. Genkel', P. A., and Yuzhakova, L. A. "Nitrogen-Fixing Bacteria in Lichens," Izvestiya Permskogo Biologicheskogo Nauchno-Issledovatel'skogo Instituta, Vol. 10, No. 9-10, 1936.
3. Genkel', P. A. "Lichen Symbiosis," Byulleten' Moskovskogo Obshchestav Ispytateley Prirody, Vol. 17, 1938.
4. Genkel', P. A. "New Observation on the Triple Nature of Lichen Symbiosis," ibid., Vol. 51, No. 6, 1946.
5. Danilov, A. N. "Lichen Symbiosis," Priroda, No. 11, 1933.
6. Dokuchayev, V. V. "Mineral Weathering," a course given in 1887-1888. Compiled by K. Glinka. Manuscript in the Library of the Soil Institute of the Academy of Sciences USSR.

7. Yelenkin,A. A. "Lichens and Soil, "Pochvovedeniye, No. 4, 1901.
8. Yelenkin, A. A. "Lichens as a Subject for Teaching and Scientific Investigation," Ekskursionnoye Delo, No. 2-2 for 1921.
9. Iskina, R. Ye. "The Question of Nitrogen-Fixing Bacteria and Lichens," Izvestiya Permskogo Biologicheskogo Nauchno-issledovatel'skogo Instituta, Vol. 11, No. 5-6, 1938.
10. Krylov, A. "The Podzol in the Mogilev District," Zapiski Imperatorskogo St-Peterburgskogo Mineralogicheskogo Obshchestva, Series 2, No. 8, 1873.
11. Lazarev, A. A. "Accumulation and Transformation of Phosphorus on Miaskites and Gneissose Granites in the First Stages of Soil Formation," Pochvovedeniye, No. 7, 1945.
12. Lemmleyn, G. G. "Lichens and Mosses on Crystals of Quartz Containing Chlorite," Priroda, No. 4, 1936.
13. Polynov, B. B. "First Stages in Soil Formation on Massive Crystaline Rocks," Pochvovedeniye, No. 7, 1945.
14. Savich, V. P. "Report on an Expedition to the Olenetz District in 1920 and 1921," Izvestiya Glavnogo Botanicheskogo Sada za 1921, Vol. 20, No. 2, 1921.
15. Tyurin, I. V. "Biological Accumulation of Silica in Soils," in the collection: Problems in Modern Pedology (Problemy Sovremennogo Pochvovedeniya), No. 4, 1937.
16. Bachmann, E. Die Beziehungen der Kalkflechten zu ihrem Substrat. Ber. d. Deutsch. Botan. Ges., Vol. 8, (The Relationships of Calcium Lichens to Their Substratum), 1890.
17. Bachmann, E. Der Thallus der Kalkflechten. Ber. D. D. Bot. Ges. Vol. 10, (The Thallus of Calcium Lichens), 1892.
18. Bachmann, E. Die Beziehungen der Kieselflechten zu Ihrem Substrat. Ber. d. Deutsch. Botan. Ges. Vol. 22, (The Relationships of Silica Lichens to Their Substratum) 1904.
19. Bachmann, E. Die Rhizoidenzone Granitbewohnender Flechten. Pringsh. Jahrb. f. wiss. Botanik, Vol. 44, 1, (The Rhizoid Zone of Granite-Dwelling Lichens), 1907.
20. Bachmann, E. Die Beziehungen der Kieselflechten zu Ihrer Unterlage. III Granit und Quartz. Ber. d. Deutsch. Botan. Ges. Vol. 29, (The Relationship of Silica Lichens to Their Substrate), 1911.
21. Brisson Lichens des Environs de Château Thierry. Mem. de la Soc. d'agrienit Sciences et Arts de la Marne (Lichens of the Environs of Château Thierry), 1880.
22. Buchet, G. Comptes Rendus de la Société de Biologie, V. XI, No. 1.
23. Correns, C. Die Chemische Verwitterung der Silikate, Naturw. 28 Jrg., H. 24, (The Chemical Weathering of Silicates) 1940.
24. Czapek. Biochemie der Pflanzen. Vol. II. Mineralstoffe der Flechten (Biochemistry of Plants. Vol. II. Mineral Substances in Lichens).
25. Frey, E. Die Bedeutung der Flechten und Moose bei der Besiedelung von Silikaifels und Silikatschüttboden. Ber. d. Schweizerisch. Botan Ges. (The Significance of Lichens and Mosses in the Settling of Silicate Rock and Silicate Detrius Soils.), 1922.
26. Friederich, A. Beiträge zur Anatomie der Silikatflechten. Fünfstück's Beitr. f. wiss. Botanik, Vol. V, (Contributions to the Anatomy of Silicate Lichens) 1906.
27. Fries. Genera Heterolichenum Europaea Recognita. Ref. v Flora, No. 8, (Recognized European Genera of Heterolichena. Abstract in Flora, No. 8,) 1861.

28. Fry, J. A. Suggested Explanation of the Mechanical Action of Lichens (Litophytic Lichens on Rocks). Annals of Botany, V. 38, 1921.
29. Fry, J. The Mechanical Action of Crustaceous Lichens on Substrata of Shale, Schist, Gneiss, Limestone and Obsidian. Annals of Botany, V. 41, 1927.
30. Fünfstück, M. Der Gegenwärtige Stand der Flechtenforschung Nebst Ausblicken auf Deren Voraussichtliche Weiterentwicklung. Ber. d. Deutsch. Botan. Ges. Vol. 20, Generalversammlungs-Heft I, (Present State of Lichenology with Prospects of Presumable Development) 1902.
31. Göppert, H. R. Über den Einfluss der Pflanzen auf Felsige Unterlage. Flora 11, (The Effect of Plants on Rocky Substrata) 1860.
32. Gümbel, G. W. Mitteilungen über die Neue Färbenflechte Lecanora Ventosa Ach. Denkschriften d. Kais. Akad. d. Wiss. in Wien, Math-Nat. Cl., XI, 2 Abt., (Reports on the New Pigmented Lichen Lecanora ventosa.) 1856.
33. Hesse, O. Beitrag zur Kenntis der Flechten und Ihrer Charakteristischen Bestandteile. Mitteilungen 1-8. J. f. Prakt. Chemie, (A Contribution to the Knowledge of Lichens and Their Characteristic Constituents.) 1898-1903.
34. Hutchinson, E. The Biochemistry of Aluminium. Quart. Rev. of Biol., V. 18, 2, 1943.
35. Keegan, F. Q. Notes on Plant Chemistry. The Origin of the Lichen Acids. Chemical News, V. CV, No. 2720, 1912.
36. Keegan, F. Q. Notes on Plant Chemistry. Rock Lichen (Parmelia Saxatilis). Chemical News, Aug. 18, 1916.
37. Knop, W. u. Schuedermann, G. Über die Flechten, J. f. pr. Chemie, Vol. 40, (Lichens) 1847.
38. Kohl, F. G. Kalksalze und Kieselsäure in der Pflanze. (Calcium Salts and Silicon Salts in Plants.) Marburg, 1889.
39. Kunze, F. Über die Säureausscheidungen der Wurzeln und Pilzhyphen und ihre Bedeutung. Pringsh. Jahrb. f. wiss. Botanik, Vol. 42, (The Acid Excreta of Roots and Fungal Hyphae and Their Significance) 1906.
40. Lang, E. Beiträge zur Anatomie der Krustenflechten. Fünfstück's Beitrage f. wiss. Botanik, Vol. 5, (Contributions to the Anatomy of Crustose Lichens) 1906.
41. Lind, K. Uber das Eindringen von Pilzen in Kalksteine und Knochen. Pringsh. Jahrb. f. wiss. Botanik, Vol. 32, (The Penetration of Limestone and Bone by Fungi) 1898.
42. Mellor, E. Les Lichens Vitricoles et la Déterioration des Vitreaux d'églises. Rev. Gén. Bot. Mai et Juin, (Vitricolous Lichens and the Deterioration of Church Windows.) 1922.
43. Molisch, H. Die Pflanze und ihre Beziehung zum Eisen. Jena, (Plants and Their Relationship to Iron.) 1892.
44. Motyka, J. Studien über Epilithische Flechtengesellschaften. Bull. Acad. Pol. Sci. et Lettres. Cl. Sci. Math. et Nat., No. 1-20, (Studies on Epilithic Lichen Communities.) 1926.
45. Russell, R. Composition of Atmospheric Dust. Am. J. of Sci., V. 31, No. 184, 1936.
46. Salomon, H. Über das Vorkommen und die Aufnahme Einiger Wichtiger Nährsalze bei den Flechten. Pringsh. Jahr. f. wiss. Botanik, Vol. 54, (Occurrence and Ingestion of Some Important Nutirent Salts in Lichens.) 1914.
47. Senft, F. Z. Deutsch. geolog. Ges., Vol. 23, 1871 (See Blanck's Handbuch der Bodenlehre [Handbook of Earth Science], Vol. II, 1929).

48. Stahlecker, E. Untersuchung über Thallusbildung und Thallusbau in ihren Beziehungen zum Substrat bei Silizischen Krustenflechten. Fünfstück's Beiträge f. wiss. Botanik, Vol. 5, (Study of Thallus Formation and Structure in Their Relationships to the Substratum in Silicate Crustose Lichens.) 1906.
49. Stoklasa, J. Über die Verbreitung des Aluminiums in der Natur und Seine Bedeutung Beim Bau- und Betriebsstoffwechsel der Pflanzen. Jena, (The Distribution of Aluminum in Nature and Its Significance in Constructive and Basal Metabolism in Plants.) 1922.
50. Thomson, R. D. Über Parietin, Einen Gelben Farbstoff und über die anorganischen Bestandteile der Pflanze. Lieb. Ann. Vol. 53, (The Yellow Pigment Parietin and the Inorganic Constituents of Plants.) 1845.
51. Tunman-Rosenthaler Pflanzenmikrochemie, (Microchemistry of Plants) Berlin, 1931.
52. Uloth, W. Beiträge zur Flora der Laubmoose und Flechten von Kurhessen, Flora, (Contributions to the Moss and Lichen Flora of Hesse-Cassel) 1861.
53. Weddel, H. Sur le rôle du substratum dans la Distrubution des Lichens Saxicoles, C. R., T. 76 (The Role of the substratum in the Distribution of Saxicolous Lichens) 1873.
54. Willard, H. and Boldyreff, A. The Determination of Calcium by Ignition of Calcium Oxalate to Carbonate in Air. J. Am. Chem. Soc., V. 52, No. 5, 1930.
55. Winchell, A. Elements of Optical Mineralogy. New York, 1933.
56. Wolff, E. Aschenanalysen, etc., Vol. I, Vol. II, (Ash Analyses, etc.) Berlin, 1871, 1889.
57. Zahlbruckner, A. Flechten. Spezieller Teil in " Die Natürlichen Pflanzenfamilien" Herausgegeben von A. Engler und K. Prantl, I. Part 1. (Lichens. A Special Section in The Natural Plant Famlies edited by A. Engler and K. Prantl) 1907.
58. Zopf, W. Untersuchungen der Flechten in Beziehung aui ihre Stoffwechselprodukte. Beihefte zum Botan. Zentralblatt, Vol. XIV, H. 1, (Studies of Lichens in Relation to Their Metabolic Products) 1903.
59. Zopf, W. Die Flechtenstoffe. Jena, (Lichen Materials) 1907.
60. Zukal, H. Morphologische und Biologische Untersuchungen über die Flechten. II Abhandlung. Sitzungsbericht d. Kais. Akad. d. Wiss. in Wein, Vol. CIV (1), (Morphological and Biological Studies of Lichens) 1906.