

## Soil Microorganisms and Soil Chelation. The Pedogenic Action of Lichens and Lichen Acids

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The role of chelation within the soil itself is discussed. The usefulness of lichens for studying early stages of pedogenesis was investigated. Interactions between soil-, rock-, and bark-inhabiting lichens with powdered granite, muscovite, and greensand marl were determined by changes in light transmission of the aqueous supernatant solutions. Physodic and lobaric acids, two lichen constituents with powerful chelating capacities, were also tested for their ability to interact with rock materials. In some cases, reactions were found to occur within a few hours at room temperature. The pedogenic role of lichens is attributed to the weathering action of the lichen acids which they contain, and this weathering activity is believed to be due to chelation by the lichen acids.

**D**URING the past decade, much work has been done on the use of chelating agents to provide essential trace elements for plant growth. Less attention has been devoted to chelation as a naturally occurring reaction in the soil itself. Geologists have considered such studies to lie within the province of soil scientists. But the soil chemist and soil microbiologist have each left this area to the other. Consequently, there is only scant information on the subject. This state of affairs is surprising because of the importance of chelation in biochemical weathering of rocks and minerals, pedogenesis, microbiological assay for available soil nutrients, mycorrhizal associations, plant root secretions, and soil fertility. Problems involving solubilization, mobilization, and transport of insoluble mineral matter by microbial products have yet to receive the attention they merit in terms of chelation.

Even the limited studies so far carried out indicate the importance of chelation in agropedology. In 1954, chelation was first recognized as a major biochemical weathering factor in pedogenesis (28). Wright and Levick, in 1956, developed a podzolic profile in a soil column leached with ethylenediamine tetraacetic acid (38). That same year, Swindale and Jackson introduced soluviation and cheluviation as two new concepts of weathering and soil formation (37). The former depends on only water for solution of minerals and eluviation of decomposition products. In this process, iron and aluminum are less soluble than other common metals and tend to accumulate. With cheluviation, minerals are decomposed and eluviated in the presence of chelating agents. Here,

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strongly sequestered elements such as iron and aluminum are removed more rapidly than silicon and other weakly chelated elements.

Soluviation and cheluviation are believed to contribute to podzolic and latosolic soil formation. Several defined substances and some of unknown composition complex soil minerals. For example, 2-ketogluconic acid, a natural chelator produced by soil bacteria, liberates calcium from insoluble salts and minerals (7). The important chelating effects of microbial products and other forms of soil organic matter on soil minerals are discussed in Kononova's recent monograph (16).

Under favorable conditions, soil microbiota have a high rate of metabolism, produce a large amount and variety of complexing agents, and are in intimate contact with soil particles. They are therefore of considerable importance from the point of view of chelation in agropedology. This is true even though bacteria, actinomycetes, fungi, algae, and protozoa comprise only about 300 pounds, dry weight, of the total organic matter in the top 7 inches per acre of temperate zone soils (20). The important questions about soil chelation under natural conditions are: Which microorganisms produce what chelating agents at what rates and in what amounts? In what ways and with which minerals do these chelating agents react? Such studies are basic and important in agropedology. But they are difficult research problems and have no doubt for this reason been neglected.

Unfortunately, soil is an exceedingly complex system. Its microbiotic population consists of millions, or billions, of organisms per gram, and these are constantly changing in kinds, numbers, and

metabolic activity. The amount and nature of soil organic matter likewise varies, as do physico-chemical relationships between it and mineral constituents. For these and other reasons, it is extremely difficult to obtain definite information about reactions between specific chelating agents and mineral particles within the soil under natural conditions.

These difficulties, however, vanish if one works with crustose rock lichens. Here, the effect of one organism on a single rock or mineral can be easily studied. The antibiotic properties of lichen acids and unfavorable nutritional conditions on rock surfaces often limit growth and activity of other microbiota. For certain rock-lichen systems, this other flora need not be taken into account. These considerations motivated studies on pedogenic activity of lichens (19, 24, 26, 28-31, 36) and lichen acids (27). The experiments discussed in this paper were carried out to obtain information about weathering effects of mixtures of lichen constituents on different minerals. The interaction of two lichen acids with rock materials is also reported.

### Materials and Methods

Thirteen lichens representing 10 species and a variety of lichen acids were tested (Table I). Terricolous organisms were growing on soil. Saxicolous lichens were collected from rock surfaces. Arboreal specimens came from tree bark. Where more than one specimen of a species was included, the numbers I, II, and III identify them.

The rock materials used were granite (200-mesh), muscovite mica (325-mesh), and greensand marl (200-mesh). Some granite dust is presently sold as a fertilizer. Because of its high glauconite con-

**Table I. Species, Acid Content, and Source of Lichens**

Lichens	Lichen Acids <sup>a</sup>	Locale
TERRICOLOUS LICHENS		
<i>Baeomyces roseus</i>	Baeomycic	Mass.
<i>Cladonia furcata</i>	Fumarprotocetraric	Ark.
<i>C. sylvatica</i>	Ursolic, usnic, and fumarprotocetraric	N. J.
<i>Peltigera aphthosa</i>	Unknown	Mich.
SAXICOLOUS LICHENS		
<i>Caloplaca elegans</i>	Parietic	Arctic
<i>Parmelia conspersa</i> (I)	Salacinic	Pa.
<i>P. conspersa</i> (II)	Salacinic and usnic	Ark.
<i>P. stenophylla</i>	Salacinic and usnic	Kan.
<i>Umbilicaria arctica</i>	Gyrophoric	Greenland
ARBOREAL LICHENS		
<i>Evernia vulpina</i>	Vulpinic	Calif.
<i>P. furfuracea</i> (I)	Atranorine and lecanoric	Colo.
<i>P. furfuracea</i> (II)	Atranorine and physodic	Europe
<i>P. furfuracea</i> (III)	Atranorine and olivetoric	Europe

<sup>a</sup> *B. roseus*, *C. sylvatica*, *P. aphthosa*, *P. conspersa* (I), and *E. vulpina* were reported by others (1, 11) to contain the lichen acids shown above. The lichen acids listed for the other specimens were demonstrated by qualitative tests (1).

tent, greensand marl is marketed as a potash fertilizer. These minerals were leached with 0.002N HCl to remove exchangeable bases and then washed with distilled water. Five grams of rock powder plus 0.5 gram of ground, dry lichen and 50 ml. of distilled H<sub>2</sub>O were mixed in 250-ml., screw-cap Erlenmeyer flasks of borosilicate glass. Tests with physodic and lobaric acids were carried out with 5.0 grams of rock materials in 50 ml. of 0.067M phosphate buffer, pH 7.4, saturated with these compounds. The flasks were shaken 8 hours a day at room temperature and refrigerated overnight. After 1 week, the mixtures were centrifuged, and the clear supernatants were analyzed spectrophotometrically.

The results (Figures 4 through 7) are presented as changes in light transmission over the range of visible wave lengths. These changes were obtained by subtracting calculated from observed changes. A calculated change is the sum of the change produced by lichen alone, i.e., in the absence of rock, plus the change due to rock with no lichen present. Observed changes are for rock-lichen combinations. Curves are above zero when observed changes exceed calculated changes. This results from increases in solute and indicates rock weathering. Curves are below zero when calculated changes are greater than observed changes. This happens when soluble lichen constituents are removed by minerals.

Results (Figures 4 through 7) are presented for visible light over a wave length range of 420 to 640 m $\mu$ . Although many lichen acids absorb ultraviolet, they also form colored complexes with iron and other metals. These can be detected by spectrophotometry with visible light. The rock-lichen systems studied provided

possibilities for many kinds of chelating agents to react with various metals from several minerals and form complexes of different colors.

### Experimental Results

**pH Changes of Rock-Lichen Mixtures.** Table II presents pH data for lichens and rocks alone and in combination. Granite was somewhat alkaline. Mica was slightly acid. Marl was distinctly acid. For all thirteen granite-

**Table II. pH Data for Rock-Lichen Systems**

Lichen	Final pH of Lichen			
	Alone	+ Granite	+ Mica	+ Marl
<i>B. roseus</i>	5.2	6.4	6.2	...
<i>C. furcata</i>	4.9	6.7	7.2	...
<i>C. sylvatica</i>	5.2	6.9	5.7	5.1
<i>P. aphthosa</i>	6.2	6.5	5.6	6.2
<i>C. elegans</i>	6.4	6.8	7.8	...
<i>P. conspersa</i> (I)	4.5	7.5	5.3	4.8
<i>P. conspersa</i> (II)	4.4	7.0	7.4	...
<i>P. stenophylla</i>	4.7	6.7	5.7	...
<i>U. arctica</i>	4.7	6.3		
<i>E. vulpina</i>	4.8	6.9	5.7	4.8
<i>P. furfuracea</i> (I)	4.5	7.0	5.9	5.2
<i>P. furfuracea</i> (II)	4.7	6.7	5.7	4.9
<i>P. furfuracea</i> (III)	5.2	7.1	7.0	4.7
None		7.2	6.8	4.9

lichen mixtures, the pH was higher than for the plant alone. With *P. conspersa* (I), the pH of the mixture also exceeded that of granite. Eleven of the 12 mica-lichen combinations exhibited a rise in pH. In four of these, the final pH was greater than the pH of mica alone. In the seven marl-lichen systems, pH changes were not as great. Ordinarily, a drop in pH results from chelation since metals replace hydrogen ions. But in rock-lichen mixtures, the extraction of certain elements from silicates could also cause solubilization of alkaline and alkaline earth metals. The net result might be a rise in pH. A shift toward alkalinity was observed with granite and mica where, in some cases, the final pH exceeded the pH of the rock alone (Table II).

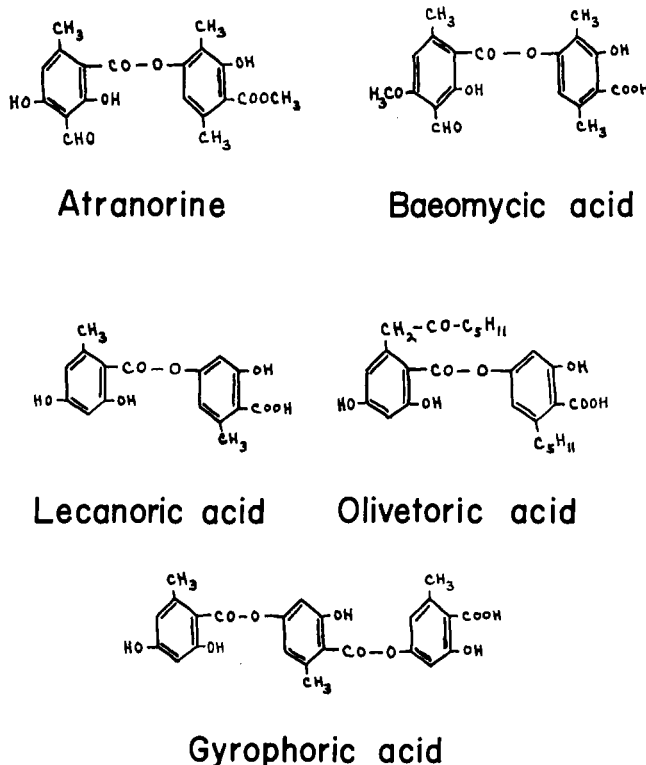


Figure 1. Structural formulas of depsides

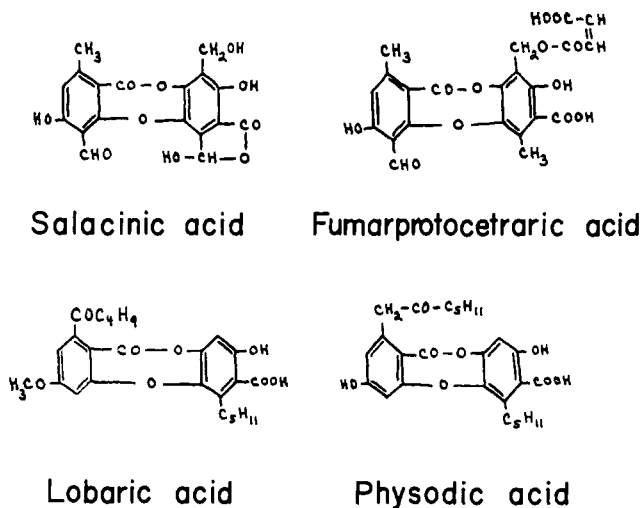


Figure 2. Structural formulas of depsidones

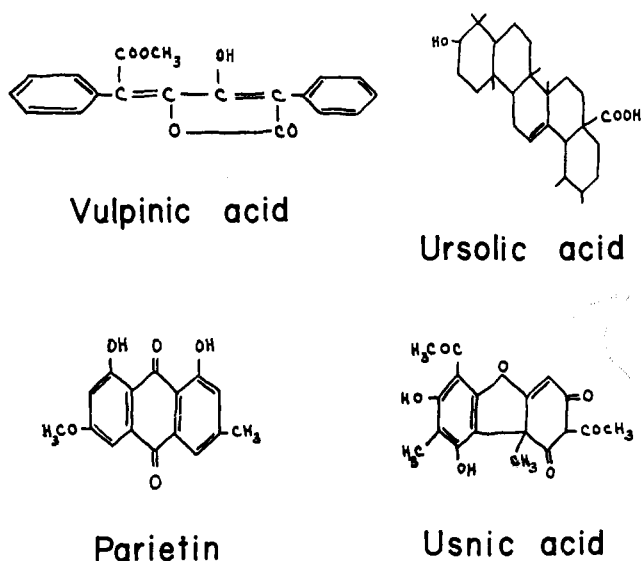


Figure 3. Structural formulas of compounds other than depsides and depsidones

**Chemical Nature of Lichen Acids.** The substances involved in rock weathering by lichens are lichen acids. Structural formulas of those of interest in the present studies (Table I) are shown in Figures 1, 2, and 3. Depsides (Figure 1) consist of two or three orcinol or  $\beta$ -orcinol-carboxylic acids in ester linkages. These include atranorine  $C_{19}H_{18}O_8$ , baeomyces acid  $C_{19}H_{18}O_8$ , gyrophoric acid  $C_{24}H_{20}O_{10}$ , lecanoric (glabratric) acid  $C_{16}H_{14}O_7$ , and olivetoric acid  $C_{26}H_{32}O_8$ . Depsidones (Figure 2) are characterized by a seven-membered ring consisting of a depside linkage and an oxygen bridge binding two aromatic rings. The four depsidones of interest in the present studies are fumarprotocetraric acid  $C_{22}H_{16}O_{12}$ , lobaric acid  $C_{24}H_{20}O_8$ , physodic (farinacic) acid  $C_{26}H_{30}O_8$ , and salacinic (saxatilisic) acid  $C_{18}H_{12}O_{10}$ . Parietin (Figure 3), also known as

physcion,  $C_{16}H_{12}O_5$ , is a quinone structurally related to anthraquinones produced by fungi. Vulpinic acid  $C_{19}H_{14}O_5$  (Figure 3) is a pulvic acid derivative. These compounds contain conjugated double bonds and are intimately related to phenylbenzoquinone pigments of higher fungi. Usnic acid,  $C_{18}H_{16}O_7$  (Figure 3), represents one of the dibenzofuran derivatives that have so far been found in nature only as lichen products. Ursolic acid,  $C_{30}H_{48}O_3$  (Figure 3), is a triterpenoid and the only aliphatic compound in this entire group. The term "lichen acids" has been used as a general designation for these substances. However, derivatives of pulvic acid and certain anthraquinones are known as lichen pigments. The polyphenolic nature of many lichen acids calls to mind the importance attributed by Davies *et al.* to polyphenols as complexing agents re-

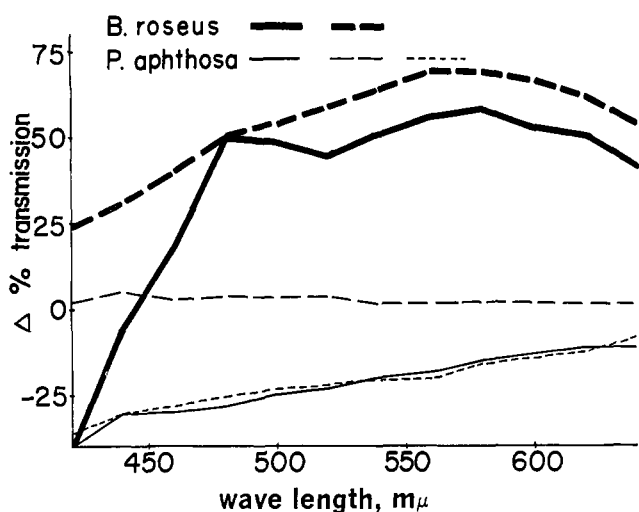
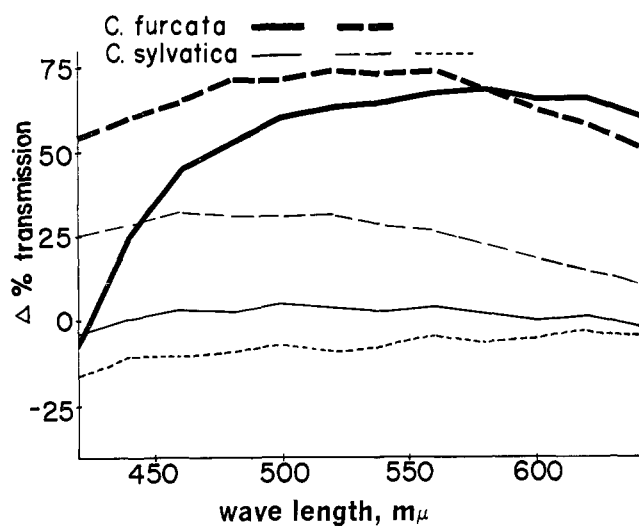


Figure 4. Interactions between terricolous lichens and rock materials

Mica—, Granite—, Marl—

sponsible for soil profile development (6). **Results Obtained with Terricolous Lichens.** Figure 4 represents tests with soil-inhabiting lichens. Of the two *Gladonia* species, *C. furcata* was the more reactive. Although these lichens are terricolous, they are not in as intimate contact with soil particles as *B. roseus* (Figure 1). Only the pink, aerial-fruited bodies of *B. roseus* were used because these were free of soil; the green terrestrial thalli could not be obtained that way. This lichen was fairly reactive with granite and mica. *P. aphthosa* showed no significant solubilizing effect with granite. Marl and mica seemed to remove lichen substances that had dissolved in the absence of the rock powders. Whether this was due to simple adsorption, formation of insoluble complexes, or other factors is not known. It was not due to change in pH.

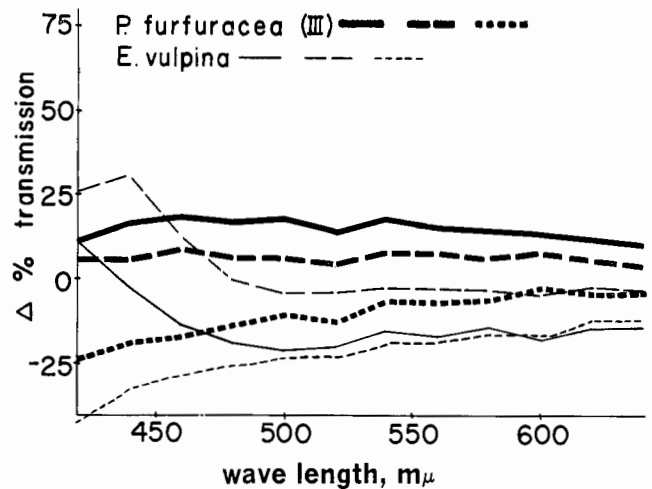
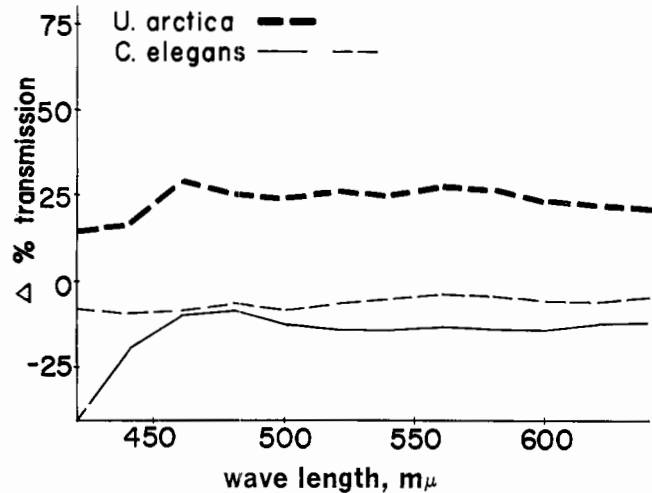
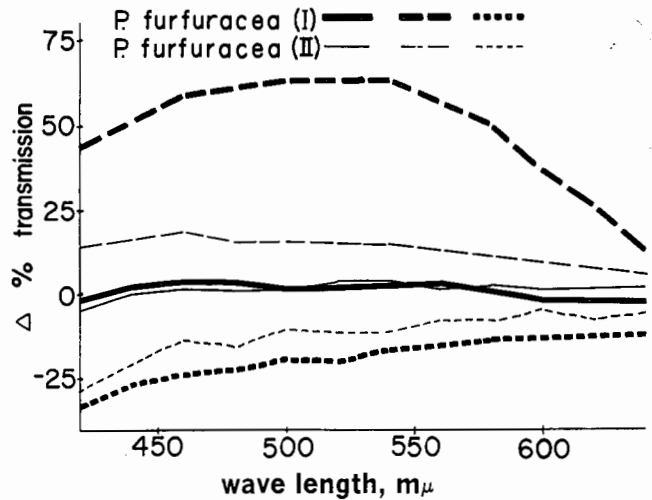
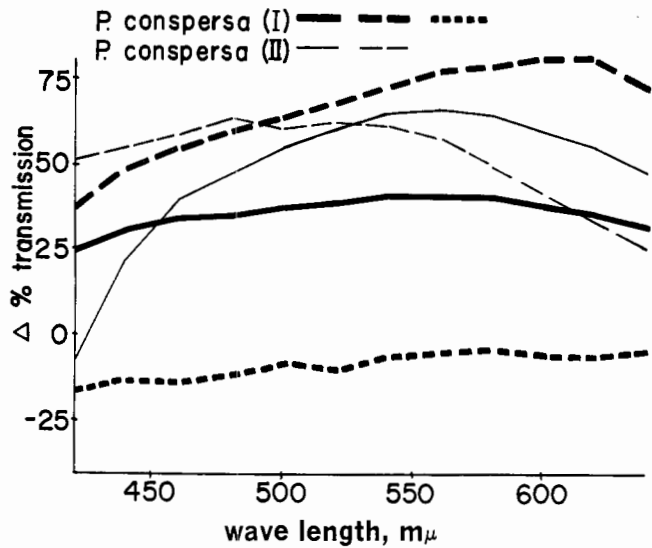


Figure 6. Interactions between arboreal lichens and rock materials

Mica——, Granite——, Marl-----

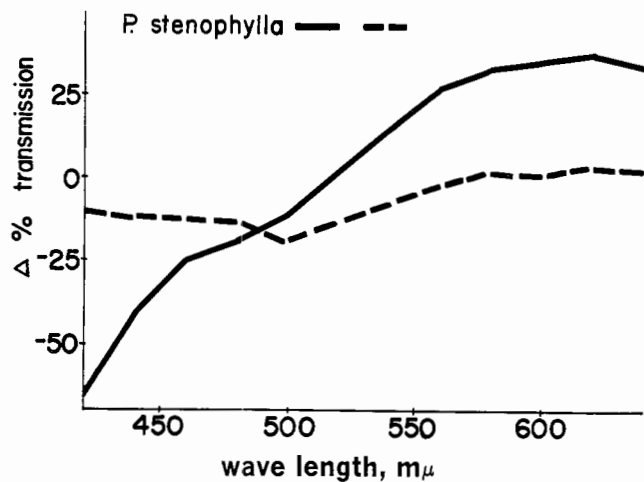


Figure 5. Interactions between saxicolous lichens and rock materials

Mica——, Granite——, Marl-----

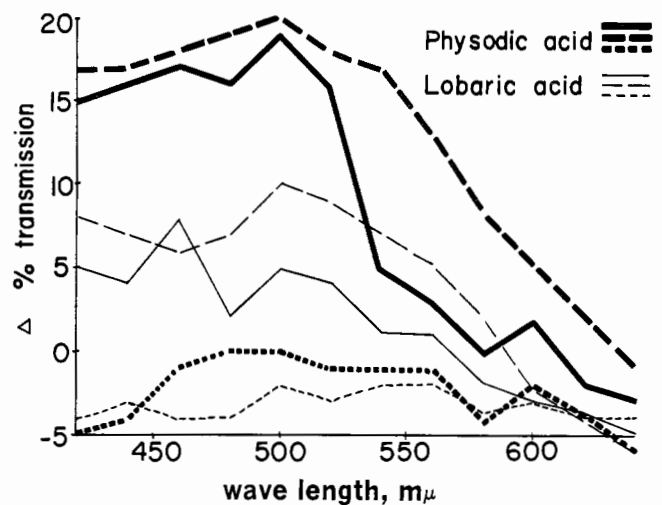


Figure 7. Interactions between lichen acids (physodic acid and lobaric acid) and rock materials

Mica——, Granite——, Marl-----

These experiments with dead, ground plant tissues reflect what may occur under natural conditions. Extracellular lichen acids are readily available from living as well as dead hyphae. The low solubility of these compounds does not rule out their importance in biochemical weathering. They are sufficiently soluble to be antibiotic. This means that they are soluble enough to react with rocks and minerals. Moreover, ammonia and other alkaline nitrogenous products from lichen phycosymbionts (12) would increase solubility and thereby enhance their pedogenic activity.

During the 7-day test interval, there was no apparent microbial growth for reasons, already discussed, which limit microorganisms associated with crustose rock lichens. Consequently, the results are due to lichen constituents. Of course, materials other than lichen acids were present and may have reacted with minerals. This too happens in nature. Lichens produce other substances while they are alive and liberate them after death.

Although lichen tissues could not be absolutely freed of all soil and bark, any effects of this contamination were eliminated by computing differences between observed and calculated changes in light transmission. Controls of lichens in buffers revealed that differences between observed and calculated values could not be attributed to variations in pH of rock-lichen mixtures compared to lichens alone. That lichen constituents reacted with insoluble rock rather than leachate, i.e., dissolved minerals, was shown by adding lichen tissues to clear supernatants from rock-water suspensions. Such tests showed no significant differences between calculated and observed changes in light transmission. Finally, when rock powders were shaken in buffers at the pH of the lichens, there was little or no effect on light transmission by these supernatants compared to supernatants from rocks in distilled water. This shows that solubilization of minerals was not mediated by hydrogen ions.

#### Results Obtained with Rock Lichens.

Figure 5 presents the results of tests with saxicolous lichens. The two specimens of *P. conspersa* reacted well with granite and mica. The effect of *P. conspersa* (I) was particularly rapid. With both minerals, the supernatant solutions developed a distinct reddish color within 3 to 4 hours. This rock-lichen system also showed the greatest rise in pH and the highest final pH (Table II) in the granite series. The rapid reaction between *P. conspersa* (I) and granite, together with other effects observed in these experiments, are at variance with Hale's belief that "lichens probably do take some part in soil formation, but their effects must be measured in terms of centuries not decades" (17). Beschel (2) went even further. "It is very

doubtful," he wrote, "if rock lichens contribute anything toward soil formation."

*P. conspersa* (I), as already stated, reacted with granite and mica in a matter of hours. Of course, the powdered rock used had a greater surface area than an equivalent weight of solid rock. On the other hand, hyphae of many crustose saxicolous lichens are in intimate contact with mineral crystals. Moreover, lichen acids are extracellular constituents which crystallize out on hyphae where they can act directly on rock substrates. In this respect, it is also important to realize that lichen acids "may average 2 to 5% of the dry weight of a lichen; in *Parmelia tinctorum* lecanoric acid may constitute up to 36% of the dry weight" (17).

In the present experiments, lichens and lichen acids were not in as close physical contact with minerals as they are in nature. On the other hand, the shaking and continuous presence of water would expedite substrate dissolution. The absence of water, however, need not necessarily mean cessation of weathering action, for this might still occur via contact exchange (14). Crustose rock lichens, by the way, seem to be ideal systems for studying contact exchange. Finally, the present studies were carried out at room and refrigeration temperatures. Under natural conditions, direct sunlight during hot summer days may raise temperatures and accelerate weathering. This comparison of conditions in nature and in the experiments reported here indicates that the fairly rapid reactions which were observed may be of the same order of magnitude as natural weathering. Some crustose rock lichens do develop fairly rapidly considering the nutritional inadequacies of their milieu. Perhaps growth of these organisms is limited more by water and nitrogen than by trace elements from rocks and minerals.

Figure 5 shows that *U. arctica* also reacted with granite. There was not enough of this lichen to test on mica and marl. Although *C. elegans* is a rock lichen, it did not seem to bring granite or mica into solution. With this plant (Figure 5), as with *P. aphthosa* on mica and marl (Figure 4), lichen constituents which were soluble in the absence of these minerals were removed from solution when the minerals were present. How *C. elegans* would react with other rocks, especially its own substrate, is not known. The curves for *P. stenophylla* (Figure 5) are different from those previously obtained. Here, mica seems to have been significantly more reactive than granite. Secondly, lichen constituents which absorb lower wave lengths were apparently withdrawn from solution by the mica. Changes in light transmission indicating reactions between lichen and mineral with formation of soluble products occurred only in the longer wave length region.

The ability of lichen acids to dissolve rocks as a factor influencing distribution and growth of saxicolous lichens is an important problem in agropedology and lichen ecology. In this connection, it is interesting that the most rapid reaction, evidenced by color changes, occurred with granite and *P. conspersa* (I) which was growing on granite when collected. A related problem concerns the relative significance of edaphic conditions, particularly the nature of rock substrates and microclimatic factors, which are responsible for the occurrence and geographical distribution of chemical strains of lichens. These are varieties of a species that differ only in lichen acid content (17).

#### Results Obtained with Lichens Growing on Tree Bark.

Figure 6 shows the effects of arboreal lichens which were included for comparison with those collected from soil and rock. The Colorado specimen of *P. furfuracea* was considerably more reactive with granite than the two European specimens. All three contained atranorine, but varied in their content of other lichen acids (Table I). Unfortunately, the concentration of each lichen acid in these chemical strains of *P. furfuracea* is not known. *E. vulpina*, from a California Sequoia tree, solubilized only granite to a slight extent.

Throughout these studies, differences between calculated and observed changes in light transmission for greensand marl-lichen mixtures showed that this mineral material generally removed constituents that were soluble in water in the absence of the marl. This does not seem to have been due to acidity since pH values for suspensions of lichens alone and lichens plus marl were not significantly different. This was somewhat surprising in view of the calcareous content of the greensand. Perhaps the adsorptive effect was due to ion exchange, for which this marl finds use as a water softener. There is no doubt, however, that lichens grow on greensand marl since the author has seen them there.

#### Results Obtained with Lichen Acids.

The pedogenic activity of saturated solutions of physodic and lobaric acids in 0.067M phosphate buffer at pH 7.4 is shown in Figure 7. Of these two depsidones (Figure 2), physodic acid was more reactive on both granite and mica. To what extent this acid, present in *P. furfuracea* (II) (Table I), may have been responsible for the effect of this lichen on granite (Figure 6) is not known. For lower wave lengths, the actions of *P. furfuracea* (II) and physodic acid on granite are of the same order of magnitude. But this did not apply to mica. These results show that low solubility of lichen acids does not prevent these substances from actively weathering rocks and minerals via chelation. However, as Hale (17) pointed out, their low solubility and weak acidity may rule them

out as effective weathering agents if they were to function exclusively as acids.

Reactions of physodic and lobaric acids with granite and mica became obvious within a few days. When mineral particles settled out during overnight refrigeration, the supernatant solutions from rock-acid suspensions were found to have developed a light violet coloration. Physodic and lobaric acids react with ferric chloride to produce soluble violet-colored iron complexes (7). Since maximum absorption of physodic and lobaric acids occurs in ultraviolet light, the activities of these two depsidones would probably have been more pronounced if spectrophotometry had been carried out at lower wave lengths. These effects of lichen acids and the marked reactivity of *P. conspersa* (I), readily detected by the appearance of soluble red substances within hours, attest to the rapidity with which lichens can weather rocks and minerals. The results also implicate lichen acids as specific weathering agents.

### Discussion

Geology, agriculture, and botany have yet to accord lichens the respect they merit. In addition to being important weathering and pedogenic agents, these cryptogams may carry specific oligotrophile microbiota (8) and may be important sources of soil nitrogen (33, 34). Despite antibiotic properties of lichen acids, microorganisms do decompose dead lichens (5) and liberate their nitrogenous constituents. Certain problems dealing with mycorrhizal associations may perhaps be fruitfully approached by studying lichens since these are actually the simplest and most primitive mycorrhiza. Decay of concrete structures, stone masonry, monuments, and the like is in part due to weathering by lichens. The importance of lichens in soil formation and the role of chelation in mediating their pedogenic activity (3, 28) pioneered development of the agricultural use of chelating agents to enhance higher plant growth.

The natural radioactivity of lichens is significant for pedogenesis as well as biogeochemical prospecting (23). Grodzinskii (10) found lichens to be intense accumulators of elements in the uranium-radium and actinouranium and thorium orders. Natural radioactivity of lichens greatly exceeded that of angiospermae, gymnospermae, pteridophyta, and bryophyta. This is not surprising in view of the intimate physical relationship between lichens and rocks, the high content of lichen acids with strong chelating capabilities, and the stability with which the above-mentioned radioactive elements form complexes. Grodzinskii's report (10) indicates the Russians may have prospected for uranium by scanning lichen herbaria with a Geiger counter.

Grodzinskii's publication (10) also

presents good evidence that lichens are more effective weathering agents than other plants. The reasons for this are understandable. Lichens excrete greater amounts and more kinds of chelating agents. The nutritional poverty of plain rock surfaces makes production of such extracellular substances in large quantities an anabolic luxury that saxicolous lichens can ill afford unless the acids are of some use to them. The most logical, indeed the only, function which can be attributed to lichen acids is that of supplying the symbionts with needed minerals. Since these have literally to be extracted from rocks, saxicolous lichens must be efficient weathering agents, and lichen acids must be the means by which they accomplish this action.

Chelation of strontium-90 by lichen acids may be in part responsible for the high content of this isotope in Alaskan Eskimos (32). These people feed on caribou which in turn consume some lichens. Subbotina and Timofeev-Resovskii (35) obtained high accumulation coefficient values in tests with a crustose lichen suspended in aqueous solutions of radioactive isotopes of different metals.

The pedogenic role of lichens has not been universally accepted. Cooper and Rudolf (4) "questioned . . . the classical role of lichens in soil formation" and "presented . . . evidence . . . to show that the importance of lichens is exaggerated." These authors, however, did not set up experiments to test their hypothesis. Lichens are not the only plants that can colonize unweathered rocks. The few instances cited by Cooper and Rudolf (4) where lichen contributions to higher plant growth seemed minimal or lacking may have been due to special edaphic conditions. In any event, these exceptional cases do not justify doubts about the general pedogenic importance of lichens.

Cooper and Rudolf (4) were also, unfortunately, unaware of earlier pertinent work by Soviet investigators such as Polynov, Bobritskaya, Aidinyan, Krasilnikov, Glazovska, Parfenova, Yarilova, Bolyshv, Aleksandrov, Zak, and others. Jacks (13) and Lovering (18) have summarized the findings of these workers who studied the pedogenic activities of lichens and other microbiota. Their reports antedate the publication of Cooper and Rudolf (4) who did not include any Russian references among 27 bibliographical citations in their paper. Pedology is that science dealing with the origin, formation, and distribution of soils. This was first recognized as an independent discipline and developed as such by Russian scientists (15). Consequently, the Russian literature on soil science contains many reports of research carried out to elucidate the pedogenic role of lichens.

Soviet studies in this area, however, were conducted prior to the recognition of chelation as a major form of chemical weathering that is coordinate with or perhaps even more important than oxidation, hydration, carbonation, solution, and deposition (15). Russian researchers, like others, were therefore unaware of the chelating capacity of lichen acids and so do not seem to have appreciated chelation as the mechanism, and lichen acids as the agents, whereby lichen weathering of rocks is effected.

So far, lichens have been considered only in chemical or biochemical weathering. They are also responsible for physical weathering, i.e., mechanical disintegration of rocks and minerals into smaller-size particles. This is accomplished through pushing and pulling forces exerted by swelling, gelatinous thalli and by pressure from growing hyphae (9). Polynov (27) maintains that chemical and mechanical weathering accompany one another.

"Though other branches of the botanical sciences have received considerable impetus from the activities of research in recent years, little of this force has carried over into the science of lichenology, which is not a popular study. It is reserved to a few specialists throughout the world whose studies are largely in the realm of lichen taxonomy, geography, and ecology." These words were written by Llano in 1950 (17). Since then, Asahina and Shibata's excellent monograph has appeared (1). More recently, Hale has compiled a much needed *Lichen Handbook* (11). Information about lichens, particularly lichen acids, is therefore now readily available.

Chelation has contributed much to agriculture by enhancing plant growth (3, 22) and has already entered the field of animal nutrition. Lichen pedogenesis and the weathering of rocks and minerals by lichen acids provide coordination chemists with an opportunity to apply chelation to agriculture literally "from the ground up." Lichen acids also merit attention because they represent rare kinds of complexing agents of biologic origin. Chemical structures have been elucidated, but little else is known about these compounds. One by-product of preliminary explorations in this neglected but fruitful area has been the development of new media for antibiotic production and other industrial fermentations (25). Others will no doubt follow. There are almost as many reasons for studying lichen acids as there are for studying chelation.

### Acknowledgment

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## CHELATION IN NUTRITION

### Chelates and the Trace Element Nutrition of Corn

THERE has been a growing recognition of the need for micronutrients for crop production. In a survey conducted by the Micronutrient Committee of the American Council on Fertilization Application (7), research investigators reported the existence of zinc deficiency of corn in 20 states in the U. S., while iron deficiency of corn was observed in three states. The need for supplying iron for crop production in Nebraska was recognized in the early 1930's. However, the existence of zinc deficiency of crops in Nebraska was diagnosed by the author as recent as 1954. Since that time, zinc deficiency of corn has been found in every area of Nebraska where the crop is grown (2). This problem is

associated mainly with the loss of soil organic matter by erosion, or by land grading for irrigation or terrace construction. Iron deficiency is generally found in soils with pH values above 7.0 under conditions of high moisture and poor aeration. This situation is generally associated with bottomland fields that have a high water table in the spring. Poor soil drainage tends to result in iron deficiency. In upland and bottomland fields, the presence of calcium carbonate reduces the availability of iron in the soil.

A number of materials have appeared on the market for use in correcting deficiencies of iron and zinc. These materials are both inorganic and organic in nature. Iron chelates have been

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used successfully to correct iron deficiency of fruit and ornamentals as well as soybeans (7). Viets (6) has indicated that any zinc compound that will dissolve in dilute hydrochloric acid is satisfactory as a fertilizer for soil application. There has been little information on the comparative effectiveness of iron and zinc chelates on the growth of corn. This report concerns information obtained at the University of Nebraska on the utilization of iron and zinc chelates by corn grown in a greenhouse environment. The results of these studies may be influenced by the fact that chelating agents may have stimulating effects upon the growth of plants (5, 7) and that interrelationships of micronutrients have been shown to