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A COMPARATIVE STUDY OF THE ROLE OF LICHENS AND "INORGANIC" PROCESSES IN THE CHEMICAL WEATHERING OF RECENT HAWAIIAN LAVA FLOWS

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ABSTRACT. The lichen *Stereocaulon vulcani*, which grows abundantly on recent lava flows on the Island of Hawaii, greatly accelerates the chemical weathering of its substrate. The importance of the lichen (or its associated microflora, or both) in chemical weathering is indicated by the following evidence: (1) The weathering crust of lichen-covered rock is thicker by some orders of magnitude than the weathering crust of bare rock; (2) the lichen-covered weathering crust is considerably enriched in Fe and impoverished in Si, Ti, and Ca with respect to the lichen-free weathering crust, whose chemical composition is much closer to that of the unaltered rock; (3) the lichen-covered weathering crust is an assemblage of residual oxides apparently devoid of clay minerals, but halloysite and mica-like material were detected in samples of lichen-free weathering crust; and (4) the iron oxide in the lichen-covered weathering crust is mineralogically different from the iron oxide in the lichen-free weathering crust.

Biological acceleration of chemical weathering can be explained by the action of respiratory CO_2 and the H^+ ions of organic acids, but the data also suggest the action of organic complexing agents. It is shown, however, that the biogenic "primary laterite" could not have been formed by differential accumulation of rock-forming elements by the lichen. Thus, a considerable proportion of the Si and Al solubilized by the organisms must be leached into the subsurface by rain water.

INTRODUCTION

Lichens are among the first organisms to colonize a freshly exposed rock surface. There is evidence that lichens, or the micro-organisms associated with them, or both, participate in the chemical and physical weathering of the rocks on which they grow, but opinion differs as to the importance of their role in soil development and concomitant plant succession (Fry, 1922 and 1927; Jacks, 1953 and 1965; Schatz, 1963; Smith, 1962; Cooper and Rudolph, 1953; Krumbein, 1969; Cooper, 1913 and 1928; Keever, Oosting, and Anderson, 1951; Oosting and Anderson, 1939; Webley, Anderson, and Taylor, 1963; Duff, Webley, and Scott, 1963; Henderson and Duff, 1963).

The purpose of the present research was to investigate the role of pioneer lichens and its importance relative to "inorganic" processes in the chemical weathering of recent lava flows on the Island of Hawaii.

MATERIALS AND METHODS, AND THE NATURE OF THE FIELD AREA

The alteration of lichen-covered rock samples was compared with the alteration of bare rock samples, which served as controls. This involved analysis of secondary minerals, measurements of depth of weathering, and investigation of the accumulation of major rock-forming elements by lichens.

On the Island of Hawaii, in the summer of 1967, samples were collected from the following lava flows, designated by year of eruption:

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The Mauna Loa flows of 1950 (east branch), 1926, 1919, 1907 (west branch), and 1859 (aa phase), and the Kilauea flow of 1955 (aa phase) (fig. 1). The lavas of 1950, 1926, 1919, and 1907 were sampled near Route 11; the 1907 lava was also sampled near the intersection of Tiki Lane and Hukilau Drive. The 1859 lava was sampled near Route 19, and the 1955 lava near Route 13. Each sampling station was located more than 30 m away from the road. The lava flows are similar in chemical composition, mineralogy, and texture; they are tholeiitic basalts, and at the sampling stations they all possess the aa texture (Macdonald, 1949a, b, 1953; Macdonald and Katsura, 1962 and 1964; Muir and Tilley, 1963; Nockolds and Allen, 1956; Powers, 1954a, b, 1955).

According to the rainfall maps of Blumenstock (1961) and Taliaferro (1959), the annual rainfall is between 51 and 76 cm at the sampling station on the 1859 lava and slightly more than 254 cm at the station on the 1955 lava; at all other stations, taken as a group, the values range from approximately 127 to 191 cm. Rainfall fluctuates greatly from year to year and from month to month, but in general, showers occur very frequently (Blumenstock, 1961; Stidd and Leopold, 1951). At the altitudes at which the samples were collected (256-914 m above

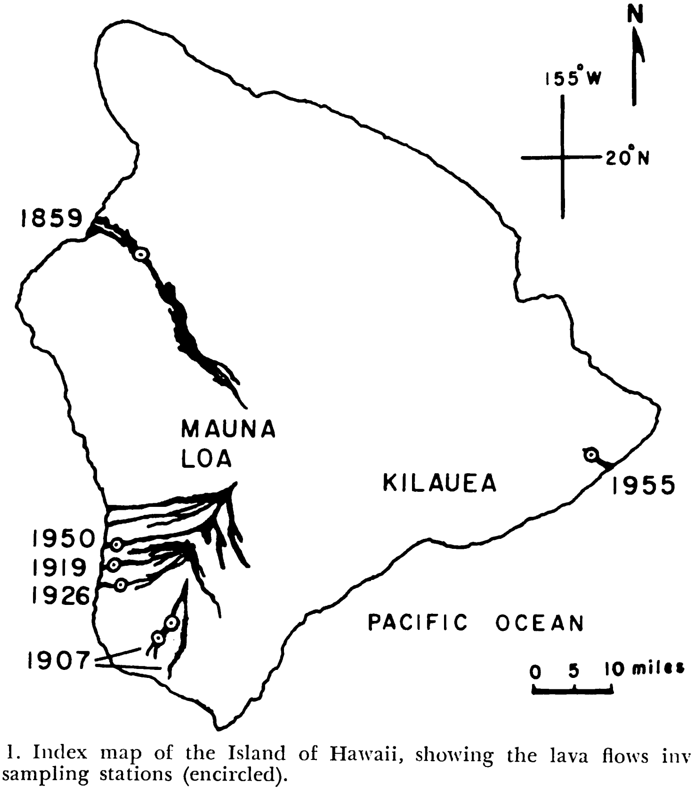

Fig. 1. Index map of the Island of Hawaii, showing the lava flows investigated and the sampling stations (encircled).

sea level) the temperatures are moderately warm and equable throughout the year (Blumenstock, 1961).

The most abundant cryptogamic pioneer plant on the lava flows is the pale gray fruticose lichen, *Stereocaulon vulcani* (Jackson, 1968 and ms; Doty, 1967; Skottsberg, 1941). Investigation of biochemical weathering was confined to this species.

The weathering crusts of both lichen-covered and lichen-free rock samples were analyzed quantitatively for Fe, Al, Si, Ti, and Ca by electron microprobe using a 10μ beam for the lichen-covered crusts and a 1μ beam for the thinner lichen-free crusts. Weathered material beneath the lichen was scraped from the rock surfaces, purified by handpicking under a microscope, and analyzed by X-ray diffraction (before and after calcination to 1000°C), and by electron diffraction, differential thermal analysis (DTA) in an atmosphere of N_2, Moessbauer spectroscopy, and measurement of magnetic susceptibility by the Gouy method (Selwood, 1964); in the X-ray and DTA work, samples of lichen tissue and fresh rock were used as blanks. A dehydration curve was constructed by heating samples at different temperatures, estimating their H_2O/OH ratios by infrared spectrophotometry employing thallous bromide pellets, and plotting the values against temperature. Material in the weathering rind of lichen-free "control" rock was separated from the underlying fresh rock by ultrasonic vibration, collected on silver millipore filters ($0.45\ \mu$), and X-rayed (before and after calcination at 400° and 500°C). The weathering crust of lichen-covered and lichen-free rock was examined petrographically, and its thickness was measured at randomly selected points, using polished sections. Detailed analysis of secondary minerals was restricted to samples from the 1907 lava (the Tiki Lane-Hukilau Drive locality) and the 1926 lava, because the weathering crust under the lichen was thickest on these lavas.

Replicate samples of *Stereocaulon vulcani* from each lava flow were analyzed quantitatively for Si, Al, and Fe. Si was determined by the colorimetric ammonium molybdate method (Shapiro and Brannock, 1952), Fe by the colorimetric o-phenanthroline method (Sandell, 1959), and Al by emission flame photometry. Since the net accumulation of elements by plants depends not only on absorption but also on retention of the elements against the leaching action of rain water (Stenlid, 1958), a lichen-leaching experiment was performed; replicate samples of *S. vulcani* from the 1907 lava were soaked in water for 24 hours in polycarbonate bottles, after which the supernates were analyzed.

Chemical analyses of the lavas were furnished by the U.S. Geological Survey.

RESULTS

Depth of the weathering front.—On all the lavas except the 1859 lava, the reddish weathering crust is consistently thicker by one or more orders of magnitude on rock surfaces colonized by *Stereocaulon vulcani* than on areas of bare rock (table 1). Even in the field the contrast is

TABLE 1

Thickness of the weathering crust on lichen-covered and lichen-free rock surfaces

Lava flow	Sample	Mean thickness (mm)	Range of thickness measurements (mm)
1955 (aa)	Lichen-covered	0.0298	0.0059-0.094
	Lichen-free	<0.002	——
1950	Lichen-covered	0.143	0.0059-0.81
	Lichen-free	<0.002	——
1926	Lichen-covered	0.111	0.0118-0.565
	Lichen-free	$\leqslant 0.004$	——
1919	Lichen-covered	0.0246	0.0059-0.135
	Lichen-free	<0.002	——
1907*	Lichen-covered	0.142	0.0118-0.43
	Lichen-free	<0.002	——

* Near intersection of Tiki Lane and Hukilau Drive

strikingly apparent. However, the data show no perceptible dependence on the age of the lava.

The chemistry and mineralogy of the weathering crust.—The weathering crust under the lichen is a soft, brittle, reddish-brown mineral "gel" (10-R-3/4 to 10-R-4/6 on the "Rock Color Chart" of the Geol. Soc. America). In thin section the gel is translucent and massive, and electron microscopy reveals a variety of colloidal-sized acicular crystallites. An ignition test showed that the substance is inorganic, and the following petrographic features proved that the gel was formed by direct alteration of the rock: (1) gradational contacts between gel and fresh rock (despite a generally sharp boundary); (2) unsupported plagioclase crystals and "xenoliths" of partially decomposed rock with hazy boundaries "floating" in the gel; and (3) plagioclase crystals cutting across the gel-rock boundary.

Chemical composition.—The electron microprobe analyses of the lichen-covered and lichen-free weathering crusts on the lavas of 1907 and 1926 are shown in table 2, together with the average composition of the parent rocks, all data being expressed as millimoles/100 gm. The data for Fe, Al, and Si are shown graphically in figure 2. The weathering crusts (especially the lichen-covered ones) vary considerably in composition from point to point, and so the mean values for the microprobe data should be regarded as rough approximations. The most abundant element in the lichen-covered crusts is Fe, but the most abundant element in the lichen-free crusts, as in the fresh parent rocks, is Si. Thus, the lichen-covered crusts are greatly enriched in Fe and depleted in Si, Ti, and Ca with respect to the lichen-free crusts, though

TABLE 2

Analyses by electron microprobe of lichen-covered and lichen-free bulk analyses of unaltered parent rock. The arithmetic means are given. Ratios indicating enrichment or impoverishment

	Lava flow	Sample	Type of data	Element				
				Fe	Al	Si	Ti	Ca
Analyses (millimoles/100 gm)	1907	Lichen-covered crust	raw data	942	320	290	1	0.5
				1120	20	130	2.0	1
				1350	110	220	16	0.7
				509	150	170	15	2
				895	210	75	<0.2	<0.2
			$\bar{X}$	964 ± 382	160 ± 140	180 ± 88	(6.8)*	(0.8)*
		Lichen-free crust	raw data	202	180	1140		
				190	140	1420		
				188	100	1230		
				195	130	879		
				160	10	801		
				160	160	872		
				193	200	844		
			$\bar{X}$	184 ± 16.8	130 ± 66	1030 ± 217	(24.6)**	(230)**
		Fresh rock	$\bar{X}$	151.5	277.9	861.4	25.5	186.2
	1926	Lichen-covered crust	raw data	940	160	82	5.0	2
				594	210	120	7.3	20
		Lichen-free crust	raw data	222	240	947	24.2	150
				220	170	862	22.1	180
				231	210	922	21.5	170
				190	170	922	29.9	170
			$\bar{X}$	216 ± 29.0	200 ± 65	913 ± 112	24.4 ± 5.81	170 ± 20.5
		Fresh rock	$\bar{X}$	152.5	284.8	844.8	24.5	180.1

both sets of samples are roughly similar in Al content. Computing the ratio of the concentration of each element in the lichen-covered crust to its concentration in the lichen-free crust (table 2) and arranging the values in order of decreasing magnitude gives the series Fe > Al > Ti > Si > Ca. The order of resistance of the elements to leaching (removal from the zone of weathering) in the presence and absence of the lichen was determined by computing the ratio of the concentration of each element in the weathering crust to its concentration in the parent rock (table 2) and arranging the values in descending order[1]; the results are as follows:

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[1] Normalization of the analytical data for the weathering crusts and fresh rocks prior to computation of these ratios does not change the proportions of the ratios to each other and is therefore unnecessary.

TABLE 2

weathering crusts on the lavas of 1907 and 1926, together with ($\overline{X}$) and 95 percent confidence intervals on the means ($t_{0.95}s/\sqrt{n}$) of one sample relative to another are shown for each element.

Lava flow	Sample	Type of data	Fe	Al	Si	Ti	Ca
1907	Lichen-covered crust / Lichen-free crust	Concentration ratios	5.24	1.2	0.17	0.28	0.003
	Lichen-covered crust / fresh rock		6.36	0.58	0.21	0.27	0.004
	Lichen-free crust / fresh rock		1.21	0.47	1.20	0.965	1.24
1926	Lichen-covered crust† / Lichen-free crust		4.35 2.75	0.80 1.1	0.090 0.13	0.20 0.30	0.01 0.12
	Lichen-covered crust† / fresh rock		6.16 3.90	0.56 0.74	0.097 0.14	0.20 0.30	0.01 0.11
	Lichen-free crust / fresh rock		1.42	0.70	1.08	0.996	0.944

* Means for Ti and Ca are of questionable significance; confidence intervals are ±9.8 and ±0.9 respectively.

** Based on a single point-analysis.

† Individual raw values for the lichen-covered crust but mean values for the lichen-free crust and fresh rock were used to compute the ratios.

1907, lichen-covered crust:	Fe > Al > Ti > Si >> Ca
1907, lichen-free crust:	Ca ⩾ Fe ⩾ Si > Ti > Al
1926, lichen-covered crust:	Fe > Al > Ti > Si > Ca
1926, lichen-free crust:	Fe > Si > Ti > Ca > Al.

The results for the lichen-covered crusts make sense from the standpoint of known weathering processes, but the results for the lichen-free crusts do not. Clearly, the composition of the lichen-free crusts is much closer

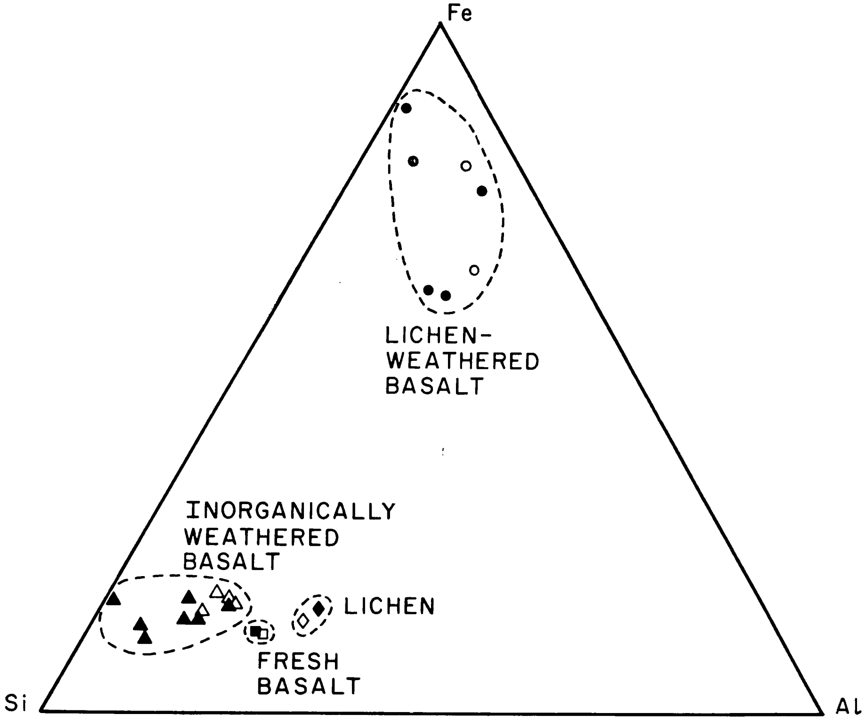

Fig. 2. The composition, in terms of Fe, Al, and Si, of lichen-covered and lichen-free weathering crusts from the lavas of 1907 and 1926. Each point represents a single point analysis by electron microprobe. The mean composition of the unaltered parent rock and the lichen are shown.

Solid symbols: material from lava of 1907. Open symbols: material from lava of 1926.

to that of the primary minerals from which they were formed (see discussion).

Mineralogical composition.—X-ray diffraction indicated that the lichen-covered and lichen-free weathering crusts differ mineralogically. Since this finding has biogeochemical implications, a detailed mineralogical study was undertaken. Of particular interest are (1) differences in iron oxide mineralogy, and (2) the presence or absence of clay minerals.

The X-ray diffraction pattern of the lichen-free weathering crust shows a small peak at about 2.70 A, corresponding closely to the most intense line of hematite. No lines indicating the presence of other ferric oxide polymorphs were seen, and calcination at 500°C for 1 hour did not increase the size or sharpness of the hematite peak, thereby ruling out the presence of an iron oxide phase metastable with respect to hematite. Thus, hematite is probably the only form of iron oxide present in this material. The 1907 (but not the 1926) lichen-free crust yielded a small peak at 7.2 A which was unaffected by calcination at 400°C

TABLE 3

X-ray diffraction pattern of the lichen-covered weathering crust. Lines ascribed to contaminants (particles of basalt and lichen tissue) are shown in parentheses.

Crust from lava of 1907			Crust from lava of 1926		
d (A)	I	Remarks	d (A)	I	Remarks
(4.47)	ms	Lichen ("lichen acid")	(4.43)	ms	Lichen ("lichen acid")
(4.02)	ms	Lichen ("lichen acid"); basalt mineral	(4.04)	ms	Lichen ("lichen acid"); basalt mineral
(3.20)	w	Basalt minerals	3.54*	m	
(2.96*)	v	Basalt minerals	(3.20)	s	Basalt minerals
2.71*	v		(2.96)	m	Basalt minerals
2.52	ms	Rather broad and diffuse	2.51	s	Slightly diffuse
2.23	ms	Rather broad and diffuse	2.23	ms	Broad and slightly diffuse
1.98	vw	Broad, diffuse	(2.14)	mw	Basalt mineral
1.70	w	Broad, diffuse	1.98	vw	Very broad
1.47	m	Very broad and diffuse; sharper at lower d-value side, and increasingly diffuse toward higher d-spacings	1.83*	v	
			1.70	vw	Very broad, diffuse
			(1.62)	w	Basalt mineral
			1.47	m	Very broad and diffuse; sharper at lower d-value side, and increasingly diffuse toward higher d-spacings
			1.41*	vw	Secondary mineral or basalt mineral?

* Not detected in all samples.

for 1 hour; in addition, there was a faint band centered at 9.75 A, which partially disintegrated during calcination, leaving a tiny hump at about 10 A. Probably these two reflections represent halloysite and a trace of poorly crystallized mica-like material.

In contrast, the lichen-covered weathering crust consists principally of an unidentified, poorly crystallized form of ferric oxide which is metastable with respect to hematite, and no layer-lattice silicates were detected. The X-ray diffraction data for samples of lichen-covered weathering crust from the lavas of 1907 and 1926 are recorded in table 3. We may disregard the lines representing d-spacings of 4.47 (or 4.43), 4.02 (or 4.04), 3.20, 2.96, 2.14, and 1.62 A (and possibly 1.41 A), because they arise from bits of lichen tissue[2] and from minerals contained in fragments of unaltered basalt.[3] The remaining reflections evidently arise from weathering products. The rather diffuse bands at 2.52 (or 2.51), 2.23, 1.70, and 1.47 A correspond to some of the stronger lines of α–Fe_2O_3 (hematite); they also correspond to the four strongest lines of "δ–ferric oxide," a synthetic oxyhydroxide (Glemser and Gwinner, 1939;

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[2] The reflections due to lichen tissue evidently arise from the organism's "lichen acid" (see discussion), which was extracted with acetone, recrystallized, and X-rayed separately.

[3] The X-ray patterns of the lichen tissue, lichen acid, and basalt minerals are recorded separately in the appendix (p. 000).

Bernal, Dasgupta, and MacKay, 1959; Francombe and Rooksby, 1959; Petit, 1961; Mackenzie, 1957; Brown, 1961), but additional evidence tended to rule out the presence of δ–FeOOH. The X-ray pattern shows some similarities to that of the ferric oxide in ferritin and the radular teeth of chitons (Towe and Lowenstam, 1967). The bands at 2.52 and 1.47 A also match the two strongest lines of γ–Fe_2O_3, but it is doubtful whether this polymorph is present. The four reflections probably represent a poorly crystallized polymorph of ferric oxide whose atomic structure is similar to that of α–Fe_2O_3 in some respects. The barely visible line at 2.71 A (and possibly the line at 1.83 A) may represent a trace of hematite. The peak at 1.98 A (and possibly the peak at 1.41 A) may arise from poorly crystallized colloidal aluminum oxide (Newsome and others, 1960). The line at 3.54 A may represent a polymorph of titanium oxide (Brown, 1961, p. 475).

X-ray diffraction by the lichen-covered crust after heating to 1000°C yielded strong, sharp lines of hematite. There were also much fainter lines at 4.93, 3.48, and 2.74 A corresponding to the three strongest lines of pseudobrookite (Pauling, 1930). In addition, there were faint lines at 1.97 and 1.41 A, possibly corresponding to the two strongest lines of γ– or η–Al_2O_3 (Newsome and others, 1960); these lines could also be interpreted as pseudobrookite lines, but the case for Al_2O_3 is strengthened by the presence of a line at 2.32 A and the absence of several pseudobrookite lines whose intensities are equal to or greater than that of the line at 1.41 A. There was also a very weak line at 2.04 A, which suggests the presence of α–Al_2O_3.

Electron diffraction yielded additional information about the minor minerals in the lichen-covered weathering crust but not about the identity of the ferric oxide polymorph. One of the patterns consists solely of lines at 3.34 and 2.75 A, corresponding more or less closely to the

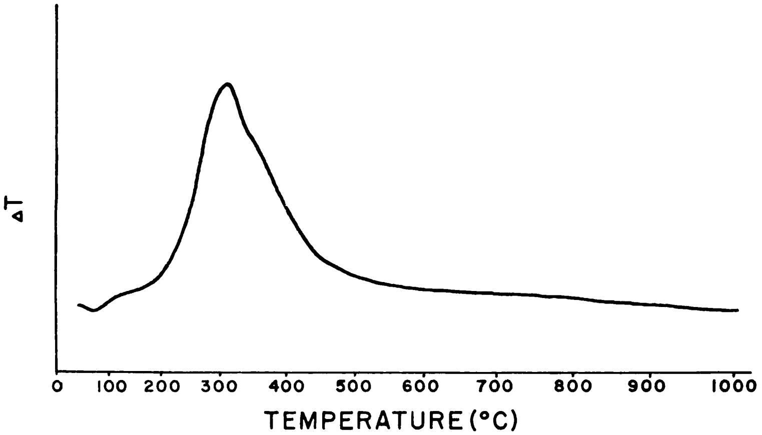

Fig. 3. Differential thermal curve of lichen-covered weathering crust from the lava of 1907.

two strongest lines of pseudobrookite and probably representing an Fe (III)–Ti oxide gel. Several other patterns having very strong lines at 1.96 to 2.00 A and strong to medium lines at 1.36 to 1.39 A resembled the patterns given by γ– and η–Al_2O_3, especially the former (Newsome and others, 1960). Thus, the X-ray lines at 1.98 A and 1.41 A probably represent poorly crystallized γ–Al_2O_3.

Differential thermal analysis of the lichen-covered crust showed a small endotherm at less than 100°C, which is attributable to expulsion of water, and a large, broad exotherm at about 300°C, which, according to the X-ray data, is due to crystallization (and possibly recrystallization) of hematite (fig. 3). This DTA curve is similar to the DTA curves of β–FeOOH and certain artificial and naturally occurring "amorphous" or poorly crystallized hydrated ferric oxides (Gheith, 1952; Mackenzie,

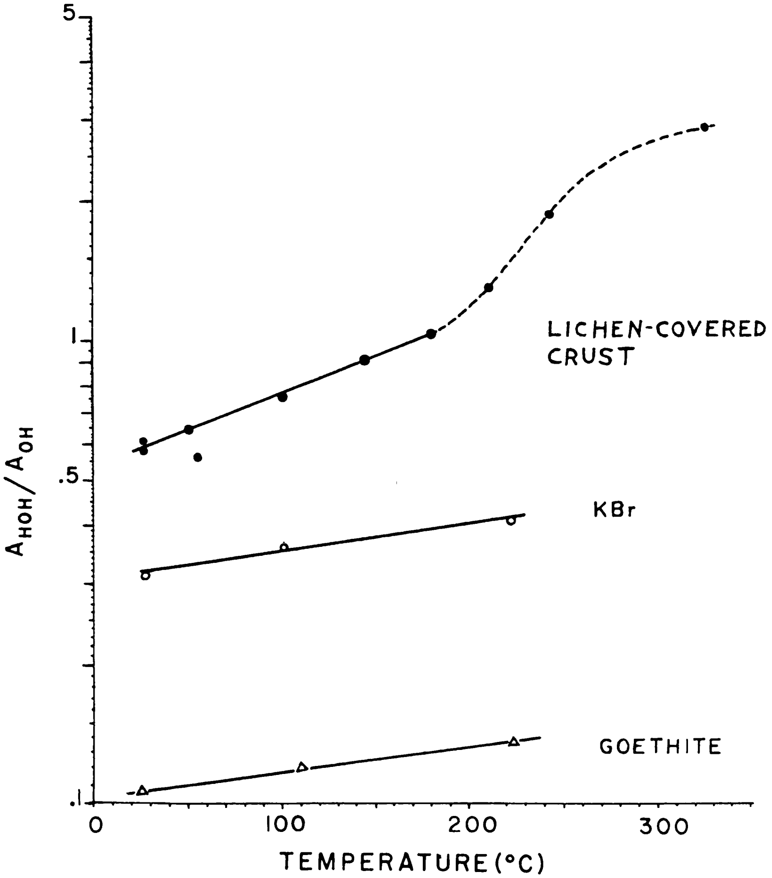

Fig. 4. Dehydration curve for lichen-covered weathering crust from the lava of 1907, based on infrared spectrophotometric data: ratio of absorbance for HOH bending mode to absorbance for OH stretching mode plotted against temperature (semi-log plot). Curves for reference substances are shown.

1949, 1952, and 1957), as well as "ferric nitrate hydrolyzate" and the ferric oxide associated with ferritin (Towe and Bradley, 1967), but it is altogether different from the DTA curve of δ–FeOOH (Mackenzie, 1957). No interference by the traces of lichen tissue and basalt present as impurities was indicated.

The dehydration curve of the lichen-covered crust is shown in figure 4. Curves for geothite (below the temperature of dehydroxylation) and the sorbed water of KBr are included for comparison. In the temperature range 27° to 180°C the smoothness of the exponential curve for the weathered material rules out the possibility that the endotherm in the differential thermogram was caused by dehydroxylation; the endotherm must, therefore, be due to loss of adsorbed water molecules. Hence, the iron oxide must consist of Fe_2O_3, not FeOOH. The break in the curve coincides with the onset of the exotherm and probably results from the transformation of the unknown iron oxide to hematite.

Owing to limited supply of purified material, measurement of the magnetic susceptibility of the lichen-covered crust was made on a crude preparation heavily contaminated with rock and lichen fragments, and this value was compared qualitatively with measurements made on fresh rock and lichen tissue (table 4). Although the results are tenuous, it would seem that the ferric oxide of the crust is paramagnetic. This militates against the presence of δ–ferric oxide, since the latter is ferromagnetic (Glemser and Gwinner, 1939; Francombe and Rooksby, 1959; Bernal, Dasgupta, and Mackay, 1959).

Moessbauer spectroscopy of the crude preparation of lichen-covered crust indicated an isomer shift of 0.37 mm/sec and a quadrupole splitting of 0.68 ± 0.04 mm/sec with respect to iron. These values are similar to those obtained for β–FeOOH (Rossiter and Hodgson, 1965; Rudloff, personal commun.).

Summarizing the ferric oxide mineralogy of the lichen-covered weathering crust, the X-ray data suggest the presence of a poorly crystallized polymorph somewhat similar to α–Fe_2O_3, or possibly a poorly crystallized form of α–Fe_2O_3, but the differential thermal curve and Moessbauer spectrum suggest the presence of a β–ferric oxide phase; the presence of δ–ferric oxide can probably be ruled out. Possibly the ferric oxide associated with the lichen is a nearly "amorphous" β–ferric oxide

TABLE 4

Magnetic susceptibility, on a weight basis, of crude preparation of lichen-covered weathering crust, and fresh rock and lichen tissue, from the lava of 1907.

Sample	mean 10^6X_w
Lichen-covered weathering crust (impure)	78.1
Rock	110
Lichen	1.18

gel which, during aging and dehydration, has partially recrystallized to α–Fe_2O_3. Similar gels are known to be widespread in nature (Mackenzie, 1949 and 1952). Alternatively, the X-ray, DTA, and IR data could be interpreted as indicating that the mineral is similar to the biogenic ferric oxide found in ferritin and the radular teeth of chitons (Towe and Lowenstam, 1967; Towe and Bradley, 1967).

TABLE 5

Fe, Al, and Si content of *Stereocaulon vulcani* samples from different lava flows (on basis of air-dry wt). The arithmetic means and the 95 percent confidence intervals on the means ($t_{0.95}s/\sqrt{n}$) are given.

Lava flow	Type of data	Element concentration in millimoles/100 gm of lichen		
		Fe	Al	Si
1955	Raw data	0.453	0.715	0.549
		0.647	1.48	0.835
		0.491	1.23	0.876
	$\bar{X}$	0.530 ± 0.261	1.14 ± 0.627	0.753 ± 0.465
1950	Raw data	0.424	0.526	0.993
		0.413	0.727	0.843
		0.371	0.686	1.31
			0.785	1.05
	$\bar{X}$	0.403 ± 0.0785	0.680 ± 0.181	1.05 ± 0.318
1926	Raw data	3.06	5.44	12.1
		1.76	3.12	7.73
		4.17	7.00	16.3
			7.56	16.4
	$\bar{X}$	3.00 ± 2.98	5.78 ± 3.18	13.1 ± 6.55
1919	Raw data	0.614	0.964	1.38
		0.276	0.426	0.908
		0.810	1.70	1.66
			1.31	2.04
	$\bar{X}$	0.567 ± 0.673	1.10 ± 0.858	1.50 ± 0.746
1907	Raw data	0.883	1.59	3.67*
		1.15*	1.37*	3.81
		1.19	3.85*	4.70
		1.58*	1.98	6.27*
		1.11*	2.90	4.77
		1.39	2.30*	4.09*
			2.13	5.13
			1.57*	4.29*
	$\bar{X}$	1.22 ± 0.257	2.21 ± 0.685	4.59 ± 0.774
1859	Raw data	1.63	4.67	5.02
		2.03	5.78	6.20
		1.63	4.04	4.67
	$\bar{X}$	1.76 ± 0.581	4.83 ± 2.15	5.30 ± 1.84

* Samples from the Route 11 sampling station.

The chemistry of the lichens.—The Al, Si, and Fe content of *Stereocaulon vulcani* is shown in table 5. The concentration of each element in the lichen tends to increase with increasing age of the substrate, although the pattern of variation is too irregular to permit analysis of the kinetics of accumulation. On the average, the relative abundances of the elements in the lichen are Si > Al > Fe, the reverse of their order of abundance in the underlying weathering crust. Nevertheless, the Fe/Al ratio of the lichen is not significantly different from the Fe/Al ratio of the rock on which it grows (not counting the lava of 1859); this conclusion is supported by the following statistical tests: the Mann-Whitney U-test ($U = 42$ in a one-sided test with $\alpha = 0.05$), the t-test ($t = 0.109$, with 21 degrees of freedom, which, in a one-tailed test, permits rejection of the research hypothesis at an α–value as high as 0.45), and the paired t-test ($t = 0.19$, with 17 degrees of freedom, permitting rejection of the research hypothesis in a one-sided test at an α-value as high as 0.40). The Fe/Al ratio of the lichen remains nearly constant with time, despite appreciable variation in the absolute values for Fe and Al concentration; thus, in the linear regression of Fe/Al ratio of the lichen on age of lava flow, $a_y = 0.561$, and $b_{yx} = 0.00021$. Moreover, the Al/Si ratio of the lichen is consistently higher than that of the underlying rock; the difference was obvious from the raw data, so that statistical analysis was unnecessary.

Leaching the lichen with water yielded solutions in which the mean Fe/Al ratio was 0.711, which lies within the range of Fe/Al values for the lichen. Thus, the Fe/Al ratio in the lichen is probably determined chiefly by uptake from the substrate and is not appreciably affected by the leaching action of rain water. The mean Al/Si ratio of the leachates was 2.16, which is considerably higher than that of the lichen (0.488), suggesting that the high Al/Si ratio of the lichen relative to the rock is due to differential uptake rather than differential leaching from the lichen by rain water.

DISCUSSION

The differences between the weathering crusts of lichen-covered and lichen-free rock samples in terms of chemistry, mineralogy, and thickness indicate that *Stereocaulon vulcani,* or its associated microflora, or both together, actively participate in the chemical weathering of basalt and the formation of incipient lateritic "soil".

The greater thickness of the weathering crust beneath the lichen thalli than on bare rock suggests acceleration of weathering by the organisms. Alternative explanations are theoretically possible, though improbable. Conceivably, the secondary minerals could accumulate more rapidly under the lichens merely because the lichens shield them from erosion. However, this possibility is very unlikely; if it is true, then the weathering products should tend to accumulate in the irregular invaginations and vesicles that pit the lichen-free rock surfaces, but petrographic examination yielded no evidence for such accumulation. Another possibility is that the thicker weathering crusts are formed by especially rapid inorganic weathering of certain unstable iron-rich minerals, and that the lichen is simply better able to grow in these areas. Petrographic examination, however, revealed no visible difference in mineralogy between lichen-covered rocks and bare rocks. A third possibility is that the organisms create a chemical microenvironment which favors flocculation of the weathering products, but this is purely hypothetical and must await further evidence. The evidence available, especially when considered in the light of the chemical and mineralogical data discussed below, favors the view that the organisms greatly accelerate chemical weathering. The apparent absence of appreciable biochemical weathering on the lava of 1859 implies that the process requires moderately high rainfall, presumably because rain water stimulates biological activity (Jackson, ms) in addition to leaching dissolved weathering products.

The fact that the lichen-covered weathering crust is greatly enriched in Fe but impoverished in Si, Ti, and Ca relative to the lichen-free crust indicates that chemical weathering is considerably more intense in the presence than in the absence of the lichen. Owing to this difference in weathering intensity, the lichen-covered crust differs much more profoundly from the unaltered parent rock in terms of elemental composition than does the lichen-free crust. In the lichen-covered crust, the order of resistance of the elements to leaching is similar to that found in lateritic materials (Mohr and van Baren, 1954), including severely weathered Hawaiian soils (Hough, Gile, and Foster, 1941); thus, it would seem that the weathering action of the *Stereocaulon vulcani* ecosystem is remarkably intense, though on a very small scale.

The proportions in which the elements occur in the lichen-covered crust could have resulted primarily from the action of CO_2, H_2O, and O_2 (and H^+ ions from organic acids) as indicated by the experiments of Pedro (1961), in which the elements in artificially "laterized" basalt showed the following order of resistance to leaching: $Fe > Ti > Al > Si > Ca$. The data also suggest that chelation is one of the mechanisms of biochemical weathering. The fact that the lichen thalli accumulate Fe and Al in the same proportion in which those elements occur in the underlying rock cannot be explained by the action of CO_2, H_2O, and O_2, but it could well be due to the action of an organic complexing agent involved in the uptake of Fe and Al. Huang (ms) found that certain elements in silicates could be solubilized congruently by chelating agents but not by CO_2 and H_2O, and it has been shown that plants absorb Fe in the form of a chelate complex (Wallace and others, 1955; Carlisle and Cleveland, 1958); moreover, the theory that active uptake of cations by plants is mediated by specialized organic complexing agents ("carrier molecules") is widely accepted (Epstein, 1956). In addition, lichens excrete powerful chelating agents ("lichen acids") which are thought to play a role in chemical weathering (Schatz, 1963). Thus, the acceleration of chemical weathering by the lichen could be due largely to localized reduction in pH caused by generation of respiratory CO_2 and organic acids (possibly accompanied by localized increase in E_h due to photosynthetic O_2), and additional effects may be produced by chelating agents. The relative importance of pH and chelation was not evaluated in the present study, but their combined effect on the rate of chemical weathering is much greater than that of the acidity due to atmospheric CO_2 as shown by the contrast between the lichen-covered and lichen-free weathering crusts.

The observation that the order of abundance of Fe, Al, and Si in the lichen thalli is the opposite to that in the underlying weathering crust might seem to indicate that differential uptake of these elements is one of the mechanisms whereby the lichen accelerates lateritic weathering (Lovering, 1958). This hypothesis, however, is disproven by the Fe/Al and Al/Si ratios, which indicate that the lichen tissue is not enriched in Al with respect to Fe nor in Si with respect to Al relative to the substrate rock. Hence, a considerable proportion of the Al and Si released from the rock by the weathering action of the lichen must be washed away by rain water.

In the lichen-free weathering crusts, the apparent relative mobilities of the elements, computed by taking the composition of the rock as a norm (p. 449-452) cannot be accepted, as they are in conflict with the known results of natural and artificial lateritic weathering (Mohr and van Baren, 1954; Pedro, 1961; Keller and Reesman, 1963). A plausible interpretation of the analytical data is that the composition of the lichen-free crust reflects the composition of the parent minerals rather than the differential mobilization of elements by weathering processes, though the latter doubtless exerted some influence. The low ratio of Al to Si and Ca in the crust compared with the rock strongly suggests that the lichen-free crust (at least the areas analyzed) was formed by alteration of the rock's groundmass, which is rich in ferromagnesian minerals such as clinopyroxenes that have a lower ratio of Al to Si and Ca than the rock as a whole (Macdonald, 1949b). If this is true, the "order of resistance of the elements to leaching" for the lichen-free crust is misleading, since the bulk composition of the rock was used as a norm. The thinness of the crust might give rise to suspicion that the microprobe beam overlapped the fresh rock, but particular care was taken to avoid such overlap, a 1μ beam having been used, and so we are reasonably confident that this did not happen—at least not to any appreciable extent. Another possible source of the difficulty is that the crust may contain incompletely altered remnants of the primary parent minerals, but we have no information about this. In any case, our basic conclusion that the bare rock is weathered much less intensely than the lichen-covered rock presumably remains valid, since the analytical data leave little doubt that from the standpoint of chemical composition the lichen-free weathering crust differs much less profoundly from the primary parent minerals than does the lichen-covered crust.

The absence of detectable clay minerals in the lichen-covered weathering crust and the presence of halloysite together with a trace of mica-like mineral in the lichen-free weathering crust on the 1907 lava constitute additional evidence that chemical weathering is more intense in the presence than in the absence of the lichen. The absence of clay minerals and gibbsite in the lichen-covered crust is noteworthy, considering that halloysite, gibbsite, nontronite, and allophane are among the most abundant weathering products on the Hawaiian Islands (Bates, 1960a, b). Probably the leaching of Si caused by the combined effects of biogenic CO_2 and organic solubilizing agents, frequent rainfall, and excellent drainage prevents synthesis of clay minerals, resulting in the formation of an assemblage of residual oxides—a kind of "primary laterite" (Harrison, 1934; Keller, 1958 and 1964). However, clay minerals and gibbsite probably precipitate in the subsurface, where the dissolved Si and Al are carried by percolating water (compare, Keller, 1964). Abbott (1958) and Sherman and Ikawa (1959) found gibbsite deposits and Bates (1960b) found deposits of clay minerals and mineral gel in fractures and vesicles in Hawaiian lava overlain by soil; these secondary minerals had evidently been transported downward in solution or colloidal dispersion from the soil.

The fact that the lichen-covered and lichen-free weathering crusts differ in iron oxide mineralogy provides a further indication that the lichen creates a geochemical microenvironment quite different from the ambient "inorganic" environment. There is little doubt that the ferric oxide in the lichen-free crust is composed entirely, or almost entirely, of hematite. The ferric oxide in the lichen-covered crust is distinctly different, but further work is needed to establish its identity. Possibly this oxide consists of a nearly amorphous β–ferric oxide gel which has largely dehydrated and has started to recrystallize to α–Fe_2O_3. Thus, the ferric oxide gel associated with the lichen may be akin to the "cold precipitated hydrated ferric oxide" described by Mackenzie (1949 and 1952). Alternatively, the mineral may be akin to the ferric oxide polymorph in ferritin and the radular teeth of chitons (Towe and Lowenstam, 1967; Towe and Bradley, 1967). That the mineral is biogenic is shown by its exclusive association with the lichen. Possibly the formation of this mineral is an epitaxial phenomenon in which some organic compound excreted by the lichen (or by its microflora) predetermines the crystal structure of the ferric oxide nuclei. Mackenzie (1952) and Schwertmann, Fisher, and Papendorf (1968) have demonstrated that organic compounds can influence the crystallization of ferric oxide, and Mackenzie suggested that a mechanism of this sort may be responsible for the nucleation of cold precipitated hydrated ferric oxide in nature.

The observation that the iron and aluminum oxides of the weathering crusts are anhydrous oxides rather than oxyhydroxides can be explained by the continual exposure of the rock surfaces to the drying action of the air (Sherman, Kanehiro, and Matsusaka, 1953).

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Appendix A

X-ray pattern of unweathered lava

Lava of 1907		Lava of 1926	
d(A)	I	d(A)	I
6.45	m	6.37	m
4.66	vw	4.65	v
4.41	vw	4.41	v
4.07	v	4.02	m
4.00	m	3.88	vw
3.87	w	3.73	m
3.74	m	3.61	m
3.62	m	3.46	vw
3.47	vw	3.34	w
3.34	w	3.18	vs
3.19	vs	3.12	w
3.12	w	2.99	vs
3.00	vs	2.92	m
2.92	ms	2.83	w
2.83	w	2.64	w
2.77	vw	2.56	ms
2.65	w	2.50	ms
2.56	ms	2.28	w
2.51	ms	2.20	w
2.45	w	2.13	m
2.28	w	2.10	mw
2.21	w	2.03	m
2.13	ms	1.99	v
2.10	w	1.92	vw
2.03	m	1.88	w
1.99	vw	1.83	w
1.93	w	1.80	w
1.88	w	1.77	w
1.84	w	1.75	w
1.80	w	1.72	vw
1.77	m	1.68	vw
1.75	m	1.63	ms
1.71	w	1.54	mw
1.67	w	1.50	w
1.63	ms	1.49	m
1.54	w	1.45	vw
1.51	w	1.41	m
1.49	m	1.39	w
1.45	vw	1.37	w
1.41	m	1.35	w
1.39	w	1.34	w
1.37	vw	1.32	w
1.35	w		
1.34	w		
1.32	w		

APPENDIX B

X-ray diffraction pattern of *Stereocaulon vulcani*

S. vulcani from lava of 1907, west branch, at 3000 ft.			*S. vulcani* from lava of 1926		
d(A)	I	Remarks	d(A)	I	Remarks
20.5	w		14.9	m	
10.2	w		10.2	m	
8.86	m		8.75	m	
7.53	ms		7.53	s	
5.98	w		5.92	m	
5.07	mw*		5.20	m	
4.45	vs		4.88	m	
3.98	s		4.46	vs	thick line
3.75	mw		3.99	vs	rather thick line
3.53	mw		3.73	m	
3.31	ms		3.53	m	
3.01	w		3.31	ms	
2.72	vw		3.10	vw	
2.53	w		2.99	w	
2.40	w		2.80	vw	
2.18	w	broad	2.72	vw	
			2.61	vw	
			2.50	vw	
			2.41	w	
			2.20	w	
			1.99	vw	
			1.94	vw	
			1.80	vw	
			1.72	vw	
			1.66	vw	

* broad band (doublet?)

APPENDIX C

X-ray diffraction pattern of "lichen acid" of *Stereocaulon vulcani* (extracted with acetone and purified by recrystallization)

d(A)	I.
19.1	m
15.1	m
7.48	vw
6.77	m
4.49	vs
4.38	s
3.99	vs
3.71	vw
2.42	m
2.20	w
1.72	v
1.58	v