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Direct measurement of the combined effects of lichen, rainfall, and temperature onsilicate weathering

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Abstract—A key uncertainty in models of the global carbonate–silicate cycle and long-term climate is the way that silicates weather under different climatologic conditions, and in the presence or absence of organic activity. Digital imaging of basalts in Hawaii resolves the coupling between temperature, rainfall, and weathering in the presence and absence of lichens. Activation energies for abiotic dissolution of plagioclase (23.1 ± 2.5 kcal/mol) and olivine (21.3 ± 2.7 kcal/mol) are similar to those measured in the laboratory, and are roughly double those measured from samples taken underneath lichen. Abiotic weathering rates appear to be proportional to rainfall. Dissolution of plagioclase and olivine underneath lichen is far more sensitive to rainfall. *Copyright © 1999 Elsevier Science Ltd*

1. INTRODUCTION

By casting the Earth, oceans, and atmosphere as participants in a vast chemical reaction whose elementary steps can be largely understood through coordination chemistry, Werner Stumm focused the efforts of at least two generations of scientists on unraveling the inner secrets of global geochemical cycling. No geochemical cycle has received more attention in recent decades than that of carbon, primarily because of concerns about global warming. To paraphrase Werner, "Although we are clearly performing a massive titration of CO_2 into the atmosphere, our limited understanding of the carbon cycle makes it difficult to predict the outcome of the experiment." Presumably, a clearer understanding of the complex linkages involved would provide a more certain view of future climate shifts, as well as a means for understanding global change in the geologic past.

Over geologic time spans ($>10^5$ year), silicate weathering reactions control the movement of carbon between the atmosphere and oceans, and during the past 400 million years, biota have played an important role in the process. Weathering of Ca and Mg silicates is the primary sink for atmospheric CO_2 over geologic time, and the amplification of weathering caused by the appearance of biota in the Precambrian almost certainly caused a decrease in atmospheric CO_2 levels (Lovelock and Whitfield, 1982). Although the cause-and-effect linkages are fairly straightforward, the actual magnitude of the shift from abiotic to organically mediated weathering is unclear. Biotic enhancement has been argued to be "on the order of at least 100 to perhaps more than 1000" (Schwartzman and Volk, 1989). Drever (1994) argued for a much smaller effect. The uncertain biotic enhancement is a critical unknown in models of early climate as large-scale shifts in atmospheric CO_2 levels would likely result, owing to the greenhouse effect, in temperature excursions. A minor enhancement of weathering by biota would imply that global temperature changed relatively little with the colonization of land by the biota. A high biotic weathering enhancement would point to a substantial lowering of temperature. For example, Schwartzman and Volk (1989) calculated an abiotic Earth 15°C warmer than the present if biotic weathering is 10 times faster than abiotic weathering. The abiotic Earth temperature was calculated to be 30°C warmer if biotic weathering is 100 times greater than the abiotic case. The order of magnitude uncertainty in the biotic effect makes it difficult to model global habitability over geologic time.

It would be useful to know to within at least an order of magnitude, to what degree soil microorganisms, lichens, and vascular plants accelerate weathering. This is not an easy question to answer because the factors that control the weathering of the Earth's crust are complex, often coupled, and, as a result, understood at the field scale only in a semiquantitative sense. Soils rich in organic matter often have high CO_2 pressures and abundant organic acids, and are often warmer than soils that are not. Soils exposed to heavy rainfall often have high organic activity. Any, or all, could result in accelerated weathering. To separate the various effects, watershed studies have focused on denudation fluxes from multiple basins, differing primarily in the variables of interest (e.g., temperature or runoff) (Velbel, 1993; White and Blum, 1995). Weathering rates increase with temperature, ambient moisture, and organic activity, although the derived dependencies are somewhat approximate because no two basins are the same in a mineralogic, hydrologic, or biological sense.

To resolve more precisely the controls on weathering, we looked directly at the silicate minerals, as opposed to the solutions in contact with them, and built a model based on measurements made at a single mineralogically and hydraulically similar field site. We digitally imaged weathering rates of plagioclase and olivine as a function of mean temperature, organic activity, and rainfall on a series of basalt flows in Hawaii. This allows us to gauge the role of temperature and

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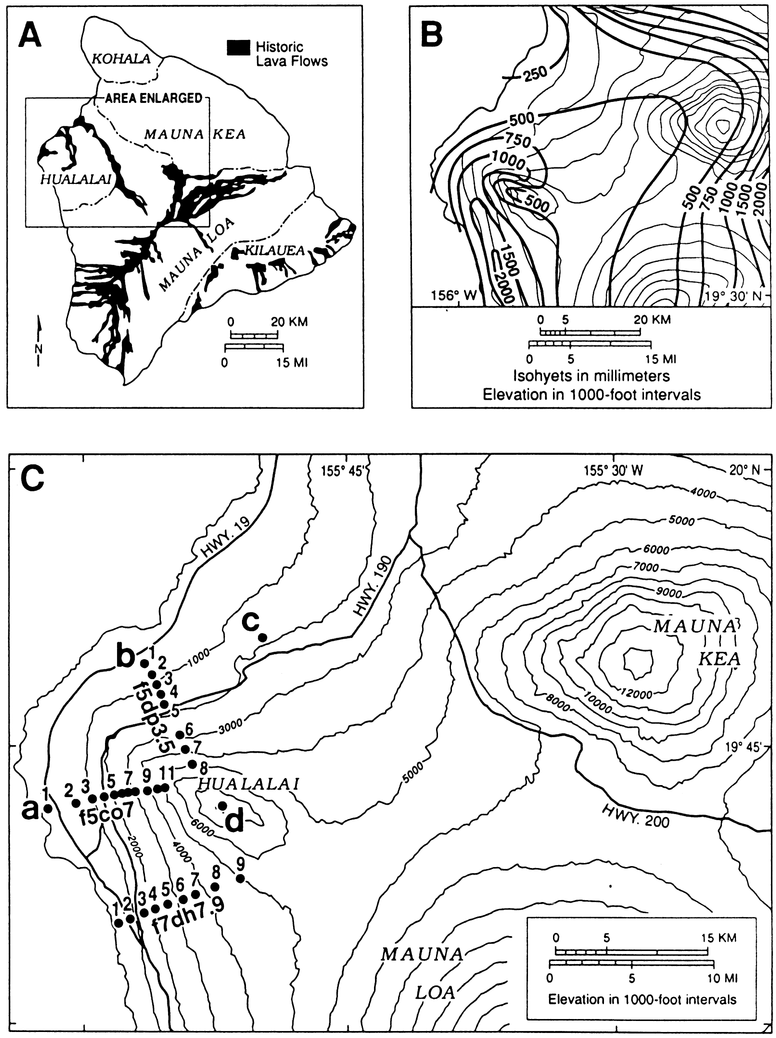

Fig. 1. Map of field area showing flow locations (A), elevations (B), isohyets and sampling sites (C). a, b, c, and d represent original data collection sites, see Table 1.

rainfall on Ca–silicate (plagioclase) and Mg–silicate (olivine) weathering in the presence and absence of lichen.

2. FIELD METHODS

Constant lithology, climate with a low seasonality, and good age control on lava flows makes the island of Hawaii an ideal site to study the role of climate and microenvironment on mineral transformations and soil formation (Chadwick et al., 1994). In particular, Hualalai Volcano permits us to observe varying temperature and rainfall (Fig. 1), whereas time is controlled on 700–2700-year-old basalt flows (Rubin et al., 1987; Moore and Clague, 1991). The youth of the flows means that the original flow surfaces are preserved (Kurz et al., 1990; Dorn et al., 1992) and thus ^{14}C lava flow ages approximate the onset of weathering.

The lava flows sampled (Table 1) are chemically and mineralogically similar and are of similar age (Moore et al., 1987; Moore and Clague, 1991). Unweathered plagioclase grains from the matrix of the various flows have similar compositions measured by wavelength dispersive electron microprobe (Table 2), but olivine grains vary considerably in composition. We consider here only matrix olivines where the MgO/FeO ratio is between 1.5 and 2, as determined by a wavelength dispersive electron microprobe. For Hualalai volcano (Fig. 1) mean annual temperature, rainfall, and evaporation were interpolated along the length of transects from previously mapped data (Juvik et al., 1978; Giambelluca et al., 1986; Giambelluca and Sanderson, 1993; Bean et al., 1994). The interpolation process yields trends of data that are the best available, and higher precision is possible only with additional field observations on which interpretation of the energy and moisture budgets of the sampled rock surfaces might be based. We believe the outcrops sampled have comparable microclimates, because basalt was collected only from microtopographic highs, where emitted terrestrial energy would not be received from adjacent rock surfaces and where water runs off the surface instead of ponding on it.

Because the temperatures in Table 1 were calculated from air

Table 1. Weathering intensities of plagioclase and olivine.

Map	Elevation	Isohyet (mm)	Temp. (°C)	Plagioclase Weathered (% per KYr)		Olivine Weathered (% per KYr)	
				Abiotic	Lichen	Abiotic	Lichen
Flow f5d p3.5 (3150 ± 140 yr B.P.)							
1	61	350	23.6	0.92 ± 0.08[a]	2.29 ± 0.33	0.64 ± 0.13	1.85 ± 0.64
2	143	500	23.1	0.90 ± 0.05	2.24 ± 0.27	0.72 ± 0.07	2.35 ± 0.70
3	300	600	22.1	0.92 ± 0.09	2.57 ± 0.23	0.74 ± 0.12	2.63 ± 1.00
4	450	700	21.1	0.94 ± 0.06	2.67 ± 0.20	0.76 ± 0.12	3.15 ± 0.84
5	580	750	20.2	0.96 ± 0.05	3.72 ± 0.36	0.77 ± 0.14	4.32 ± 1.06
6	975	1000	17.6	1.24 ± 0.10	5.72 ± 0.45	1.00 ± 0.16	6.50 ± 1.11
7	1250	1100	15.9	1.41 ± 0.14	7.99 ± 0.73	1.11 ± 0.17	9.41 ± 1.29
8	1539	1200	14.3	1.52 ± 0.11	8.93 ± 0.52	1.21 ± 0.16	10.55 ± 1.68
Flow f7dh7.9 (710 ± 50 yr B.P.)							
1	60	1000	23.6	1.36 ± 0.15	8.97 ± 0.71	0.90 ± 0.58	7.50 ± 2.09
2	300	1250	22.1	1.48 ± 0.26	12.77 ± 0.50	1.10 ± 0.48	13.43 ± 2.34
3	490	1500	20.8	1.67 ± 0.25	13.31 ± 0.38	1.31 ± 0.42	15.81 ± 2.10
4	610	2000	20.0	1.92 ± 0.15	14.55 ± 0.55	1.54 ± 0.68	17.63 ± 3.65
5	790	2000	18.8	1.68 ± 0.23	14.00 ± 0.52	1.39 ± 0.45	17.22 ± 2.89
6	1040	1500	17.2	1.19 ± 0.15	11.73 ± 0.50	0.70 ± 0.45	10.80 ± 3.34
7	1160	1250	16.4	0.69 ± 0.16	10.65 ± 0.31	0.61 ± 0.39	10.10 ± 1.46
8	1280	1000	15.8	0.51 ± 0.13	6.21 ± 0.23	0.46 ± 0.25	4.38 ± 1.55
9	1520	750	14.4	0.32 ± 0.07	4.24 ± 0.29	0.20 ± 0.10	2.12 ± 1.07
Flow f5co7 (2200–2300 yr B.P.)							
a&1	20	500	23.9	1.07 ± 0.07	3.40 ± 0.20	0.85 ± 0.20	4.17 ± 1.00
2	180	700	22.8	1.20 ± 0.14	6.02 ± 0.36	1.01 ± 0.12	6.27 ± 1.44
3	300	1000	22.1	1.43 ± 0.15	9.50 ± 0.56	1.18 ± 0.19	9.88 ± 1.56
4	450	1200	21.1	1.60 ± 0.13	11.85 ± 0.70	1.21 ± 0.18	11.43 ± 1.61
5	600	1500	20.1	1.71 ± 0.15	13.22 ± 0.73	1.40 ± 0.19	15.11 ± 2.52
6	700	1500	19.4	1.59 ± 0.15	12.94 ± 1.01	1.21 ± 0.18	13.34 ± 2.05
7	820	1500	18.6	1.44 ± 0.15	12.57 ± 1.19	1.21 ± 0.15	14.25 ± 1.80
8	910	1500	18.0	1.33 ± 0.13	12.33 ± 1.06	1.04 ± 0.18	12.19 ± 2.31
9	1200	1350	16.2	0.87 ± 0.09	11.03 ± 0.75	0.71 ± 0.21	9.62 ± 1.94
10	1370	1200	15.3	0.62 ± 0.11	9.57 ± 0.93	0.52 ± 0.21	7.90 ± 1.76
11	1520	1000	14.4	0.41 ± 0.07	7.42 ± 0.95	0.30 ± 0.17	4.99 ± 1.73
Flow f5dp9.2 (2160 ± 100 yr B.P.)							
b	100	500	23.4	1.03 ± 0.06	2.26 ± 0.24	0.78 ± 0.12	3.28 ± 0.64
Flow f5d c8.2 (2010 ± 80 yr B.P.)							
c	500	500	20.7	0.81 ± 0.08	1.36 ± 0.20	0.67 ± 0.10	1.55 ± 0.41
Flow f5eb0.7 (2800 ± 80 yr B.P.)							
d	2377	500	9.8	0.16 ± 0.05	0.29 ± 0.08	0.18 ± 0.04	0.51 ± 0.21

[a] Standard deviations reported here are based on analyses of the average porosity for the different sites at each elevation. Standard deviations for porosity variability in any given thin section are much larger, typically ranging from 20 to 60%. The site-disaggregated dataset will be posted on the web at http://www.sandia.gov/eesector/gs/gc/hawaii.html

temperature trends, they may not accurately represent the temperature of the rock during weathering. Rock surface temperatures can depend on a number of additional factors, including humidity and exposure. Because detailed field observations of year-round surface temperatures are unavailable, computer simulations were done to determine any differences between mean surface and air temperature trends with elevation. We modeled surface temperature gradients after the method of Outcalt (1972) using as inputs Earth–sun relations, surface (albedo, moisture), and atmospheric conditions. We used standard albedo ranges of fresh and old lava (α of 6–10%), air mass variables of wind, temperature, humidity, and simulated solar input appropriate for Hawaii (Giambelluca and Sanderson, 1993; Nullet and Sanderson, 1993). Basalt surface temperatures were calculated for corresponding air temperatures of 8–25°C.

Figure 2 shows surface temperature gradients for wet surfaces with active trade winds, wet surfaces under calm conditions, dry surfaces with active trade winds, and dry surfaces under calm conditions. Surface temperatures differ the most from air temperatures under dry, calm conditions. The offset is on the order of 1–2°C over the 18–25°C air temperature range, where the bulk of the data were collected. Wet surfaces under cloudy, windy conditions below the trade wind inversion (TWI) are calculated to be similarly close to air temperatures. These are also the conditions we expect to typify the bulk of weathering. The offset between air and surface temperatures shown in Fig. 2 for these conditions suggests that the temperatures in Table 1 are best interpreted as close minimum values.

Air temperatures in Hawaii depend on elevation, position of the TWI (~1200–2000 msl), and lee versus windward positioning with respect to the moisture-bearing trade winds. The Hualalai sites are leeward sites, and two of the transects (f5co7

Table 2. Representative mineral compositions.

Oxide	Plagioclase	Olivine
Na_2O	3.22	0.05
MgO	0.22	37.83
Al_2O_3	29.12	0.05
SiO_2	48.22	39.20
CaO	18.10	0.25
TiO_2	0.12	0.11
MnO	0.40	0.25
FeO	0.54	22.14
Total	99.94	99.88

and f7dh7.9) reach the TWI. The TWI is important here because rainfall decreases and evaporation increases at and above the inversion. Thus, we collected samples along isohyets (lines of equal rainfall) at warmer (lower) and colder (higher) locales to identify the trends in temperature effects on weathering.

At various elevations on the lava flows (Fig. 1), we collected samples from 10 different microtopographic highs from all lava flows, except f7dh7.9, where five positions were sampled. If the flow was aa, we collected from a knob that had a relatively smooth surface, on the scale of millimeters, to mimic the pahoehoe surface characteristics as much as possible. Aa is extremely permeable, but pahoehoe has a smooth glassy surface that sheds water.

There are four basic types of surface weathering microenvironments on Hualalai, Hawaii (Cochran and Berner, 1993; Wasklewicz, 1994): (1) those colonized by vascular land plants (Berner, 1995); (2) those covered by inorganic rock coatings; (3) those colonized by lichens, and other epilithic organisms (Jackson and Keller, 1970); and (4) "abiotic" microenvironments where "chemical weathering is severely limited because introduction of acids to the profiles is limited by rainfall" (Nesbitt and Wilson, 1992).

We studied only the latter two microenvironments (10 lichen covered surfaces and 10 abiotic ones) at each site. Rock coating sites were avoided, because the weathering response is complicated by the thermal and moisture characteristics of surface films (Warke et al., 1996). Vascular land plants could potentially be studied with our in situ approach, but the millennial age of the lava flows makes the assumption of constant vascular land plant weathering over time less certain. Although lichen colonization times are relatively rapid (Jackson and Keller, 1970), they probably varied among the lava flows and sampling locales; we are assuming that this complexity is reflected in the higher standard deviations of the measurements for the lichen sites (Table 1).

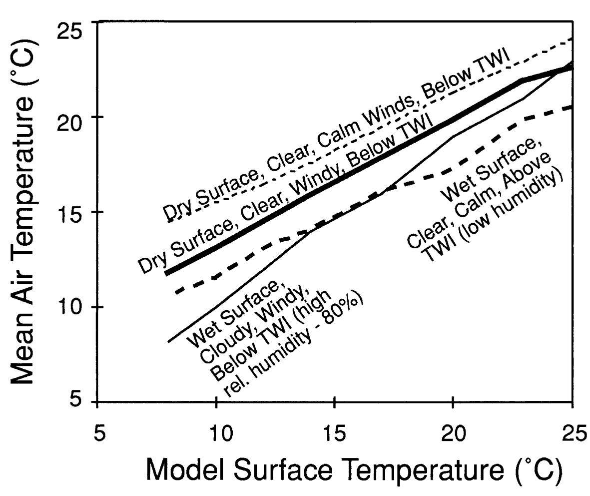

Fig. 2. Relationship between mean air temperature and surface temperature as calculated by the energy balance model discussed in the text. The surface state that would simulate weathering conditions (wet surface, cloudy, windy, high humidity found below the trade wind inversion) is very close to the mean air temperature.

One critical uncertainty in our analysis is the assumption that today's abiotic sites were abiotic over the lifetime of the respective flow. A parallel assumption is that the sites covered by lichen today were covered by lichen for the lifetime of the flow. If, in fact, the lichen only arrived recently, the rates listed in Table 1 are lower than true lichen-controlled rates. Concomitantly, if the abiotic sites were once colonized by lichen that has since departed, the rates listed in Table 1 are higher than true abiotic weathering rates. Therefore, we can only interpret the abiotic data as "maximum" and biotic data as "minimum" weathering rates. Another uncertainty arises from the fact that lichen may in fact prefer to colonize areas where porosity is greater and, presumably, nutrient uptake by roots is easier. This would tend to exaggerate the biotic effect. Moreover, we have only imaged the outer rind of weathering, yet weathering proceeds at greater depth as well, where there is less of a biotic signature. Total weathering dependencies integrate both deep and surficial weathering, and the biotic effect we determine in the upper section almost certainly overestimates the total impact of biota on solute export. Lastly, it must be emphasized that we image dissolution of phenocrysts, not ground mass.

Although many different types of epilithic organisms occur on Hawaiian lava flows, we focused on the lichen *Stereocaulon vulcani*, because it is common and has previously been identified as a weathering agent (Jackson and Keller, 1970). We also chose to study a single species to avoid mixing the effects of multiple epilithic organisms. There may be synergistic or negative feedbacks with multiple organisms and interactions with vascular flora. Furthermore, the weathering effects likely vary from organism to organism. Comprehensive coverage of these multiple interactions is beyond the scope of this study. Our focus rests on understanding, in an order of magnitude sense, how effectively epilithic lichens, likely among the earlier organisms to colonize the land surface in the Precambrian (Taylor et al., 1995; Taylor and Osborn, 1996), enhanced the drawdown of CO_2 by silicate weathering. Lichen may have even existed at earlier times, but not have been preserved. Modern lichens might roughly approximate terrestrial vegetation before the late Silurian (Cochran and Berner, 1993).

Polished cross-sections were made from directly underneath the lichen *Stereocaulon vulcani* and at abiotic locales; for each of the ten positions (five positions at f7dh7.9); and at each site shown in Fig. 1. In each polished cross section, transects were made in the upper 50 μm of weathering rinds. Thirty plagioclase feldspars and olivine grains with MgO/FeO ratios of 1.5–2 were imaged by back scattered electron (BSE) microscopy, and digitally cut out. In the case of lichen weathering, often fewer than 30 grains (per cross section) were directly

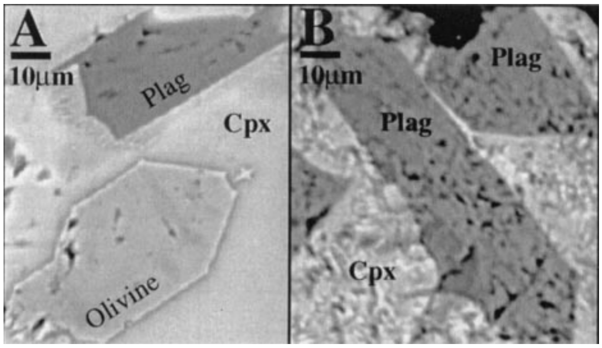

Fig. 3. Backscattered electron microscopy imagery of weathering of flow f7dh7.9 both away from lichens (image A) and directly beneath *Stereocaulon vulcani* (image B). Note how porosity (dark 'holes') is enhanced under lichen. Cpx stands for clinopyroxene; and plag for plagioclase, as identified by microprobe analyses.

underneath a lichen, in which case all minerals at the rock/lichen interface were imaged. The tandem of BSE and secondary electron microscopy reveals the presence of pores in minerals (Watts., 1985; Berner, 1992), where the BSE images can be analyzed to quantify mineral porosity (Ehrlich et al., 1991; Bruand et al., 1996). Digital image processing of BSE images measures the cross-sectional area (tabulated as square micrometers) of dark dissolved regions and bright unweathered mineral material for each grain (Fig. 3). The values were summed to give a total porosity and cross-sectional area studied for each section. Then, these section values were averaged for each site in Fig. 1 (Table 1). The method for quantifying weathering with digital image processing of BSE imagery is detailed elsewhere (Dorn, 1995), and the full data set will be made available at the web site http://www.sandia.gov/eesector/gs/gc/hawaii.html.

3. ABIOTIC VS. LICHEN-CONTROLLED WEATHERING

Figure 4 serves to illustrate the combined effects of temperature, rainfall, and organic activity on weathering, by showing two transects (the f5co7 and f7dh7.9) along which abiotic and lichen sites were sampled from low to high elevation. Temperature decreases with elevation, whereas rainfall initially increases, then decreases. Three points stand out: (1) plagioclase and olivine weather faster when lichen are present; (2) weathering increases with rainfall; and (3) higher temperatures favor weathering as well.

The presence of *Stereocaulon vulcani* appears to be more

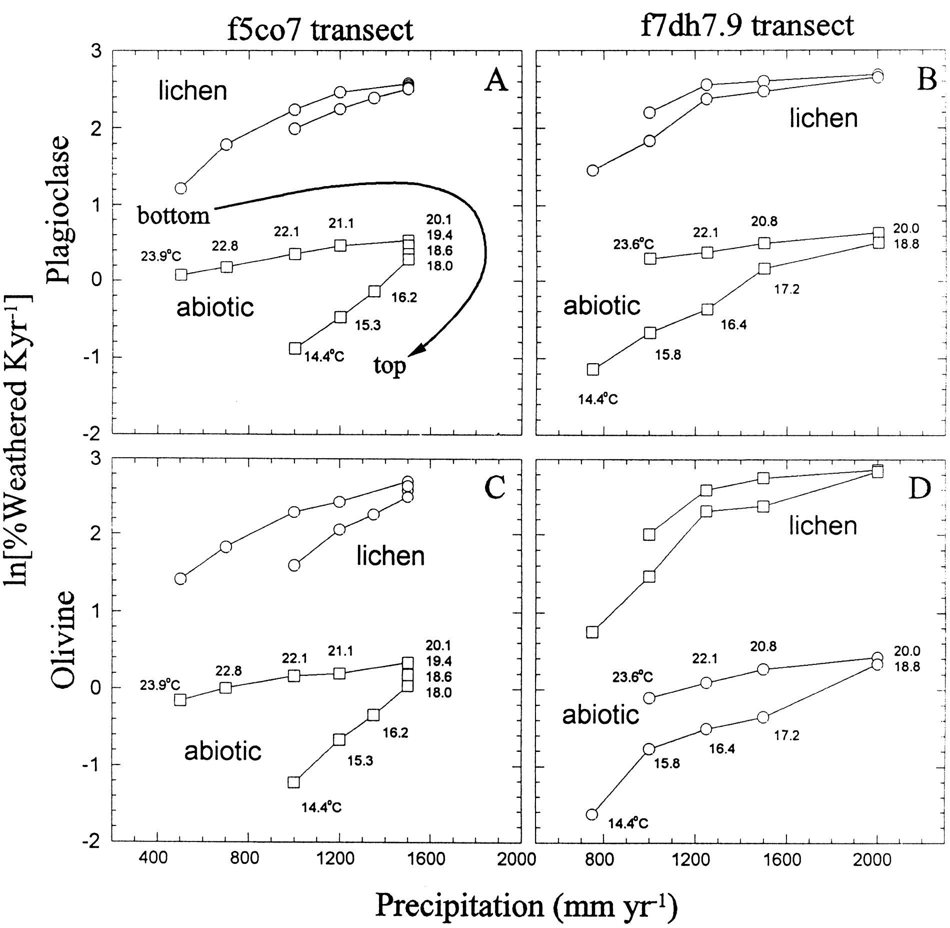

Fig. 4. Weathering measured along the f5co7 (circles) and f7dh7.9 (triangles) (Moore and Clague, 1991) transects through the trade wind inversion as a function of rainfall for plagioclase (A and B) and olivine (C and D). Temperatures are shown for the abiotic sites, but are the same for the lichen sites directly above them on the graph.

important than rainfall, which in turn has a greater effect on weathering than temperature, and *S. vulcani* amplifies the weathering of olivine slightly more than plagioclase (see Table 1). Weathering intensity under lichens is routinely 2–18 times greater than the abiotic case. This is broadly consistent with the enhancements of 12–72 and 25–50 measured by Jackson and Keller (1970) and McCarroll and Viles (1995) on, respectively, lichen-covered basalt and lichen-covered gabbros. Note that the aforementioned in situ studies measure weathering products, which is only an indirect measure of mass lost and CO_2 drawdown. Watershed studies (Berner; 1992; Benedetti et al., 1994; Drever, 1994) generally point to enhancement factors of 2–5. Also, watershed studies measure a weighted sum of organic + abiotic weathering, and therefore, can only predict a biology-specific component to weathering.

Soil weathering by biota is thought to proceed through some combination of organic acid/chelator (and proton) secretion (Graustein et al., 1977; Hiebert and Bennett, 1992), physical exposure of surface area by fungal hyphae (Berthelin, 1988), and recycling of water (Drever, 1994). Previous studies have provided important snapshots that point to runoff and organic activity as the primary controls over weathering on Hawaii. Our results, by including climatic data and covering wide ranges in temperature and rainfall, go further. The fact that all of the data were gathered in a single, well-constrained field area severely limits the amount of scatter seen in weathering trends, making the specific effects much more apparent.

Our object is to model the primary controls on CO_2 consumption by mass loss of Ca– and Mg–silicate weathering (our approach ignores any formation of secondary phases that would take up solutes). We express abiotic and biotic weathering rates, $W_{P,T}$, the percentage of plagioclase weathered per thousand years at a particular rainfall rate, P (mm/yr), and temperature (K) divided by a reference value, at P = 1 mm/yr and 273.15 K as:

$$W_{P,T}/W_{1,273.15} = f\{\text{Rainfall, Temperature}\} \qquad (1)$$

$$= \exp[E_a/_R(1/_{273.15} - 1/_T)]P^n$$

The constant P effect of T on weathering is modeled with an Arrhenius expression, the exponential term in Eqn. 1 (Brady, 1991; White and Blum, 1995), whereas we fit the constant temperature effect of rainfall on weathering as a power function. Dunne (1978), and subsequently Berner (1994), expressed runoff effects on weathering with a power function. Because in tropical watersheds, runoff correlates in a nearly 1:1 fashion with rainfall, but correlates only weakly with temperature (White and Blum, 1995), we follow the same approach here. Note that rainfall and temperature subsume variables such as microbial production of complexing agents, and protons, as well.

Equation 1 was fitted to the abiotic and biotic datasets in Table 1 using a nonlinear regression. The calculated activation energies and rainfall–weathering coefficients (E_a and n, respectively) are listed in Table 3. Measured and calculated weathering rates are shown in Fig. 5 to illustrate the adequacy of Eqn. 1 in describing weathering. The abiotic plagioclase activation energy (23.1 ± 2.7 kcal/mol) is quite close to that measured in the laboratory, 21.2 kcal/mol by Hellmann (1994). The abiotic olivine E_a (21.3 ± 2.7 kcal/mol) approximates the laboratory-measured value of 19.5 kcal/mol (Wogelius, 1992). Organic activation energies for plagioclase and olivine weathering (Berner, 1992) (respectively, 13.3 ± 3.8 and 11.5 ± 2.7 kcal/mol) are substantially smaller than abiotic values. Welch (1996) showed that oxalate and gluconate lower the activation energy of plagioclase dissolution by ~7 kcal mol, suggesting that the catalysis of mineral dissolution by organic acids might account for some of the relative lowering of biotic activation energies. The comparison is not completely equivalent as the activation energy for lichen weathering may include a term describing the effect of temperature on dissolution-affecting organic activity (e.g., acid production, hyphal extension).

Abiotic weathering at any given temperature is nearly proportional to rainfall; n = 0.81–0.85(±0.1). Weathering underneath lichen is a great deal more sensitive to rainfall; n = 1.65–1.83(±0.1–0.2). The runoff exponents, n, may have some mechanistic underpinning. For the abiotic case, n is sufficiently close to 1 that weathering fluxes might simply be proportional to the amount of rainfall the rock receives. In effect, weathering is limited by the availability of weathering solutions. Weathering by lichen, in contrast, is nearly proportional to the square of the rainfall rate. Lichens are obviously able to weather a much greater volume of rock relative to the abiotic case given the same amount of rainfall. A first explanation for the differ-

Table 3. Mineral weathering parameters.

Mineral	E_a (kcal/mol)	n	$\ln W_o$
Plagioclase			
(Abiotic)	23.1 ± 2.5	0.85 ± 0.1	−8.59 ± 0.8
(Lichen)	13.3 ± 3.8	1.83 ± 0.2	12.38 ± 1.3
Olivine			
(Abiotic)	21.3 ± 2.7	0.81 ± 0.1	−8.36 ± 0.9
(Lichen)	11.5 ± 2.7	1.68 ± 0.1	−11.09 ± 0.9

Errors represent standard errors of the regression coefficients.

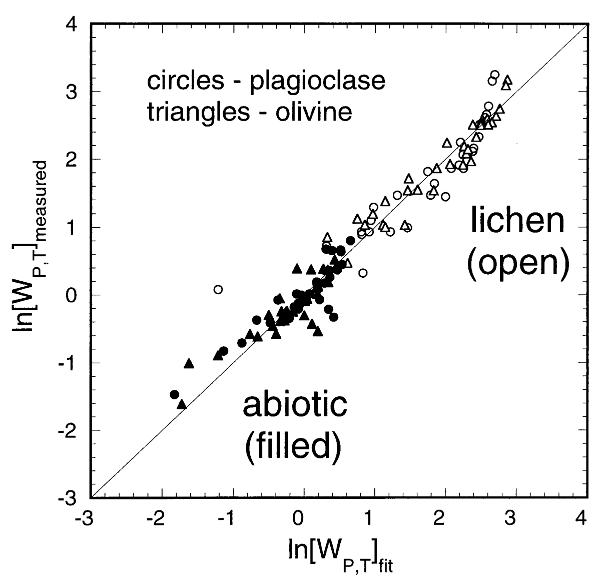

Fig. 5. Measured weathering rates and rates predicted from fitting of equation 1 to all of the measurements. The line has a slope of 1.

ences involves water availability maximizing the secretion of organic acids or hyphal activity. The latter has the potential to amplify chemical denudation by increasing the amount of rock surface area being weathered. A second explanation is that the presence of lichen and other microflora extends the stay of moisture in the pore walls, increasing the impact of weathering solutions. A third explanation involves the "poisoning" of weathering by mineral components (Al, Na, Si, Mg, etc.) dissolved in solution. High levels of the latter are observed to inhibit silicate dissolution in the lab (Oelkers et al., 1994). Assuming that increased rainfall increases organic acid levels in pore fluids adjacent to fungal hyphae, an acceleration of weathering might occur relative to the abiotic case because of the complexing ability of the aforementioned organic acids. Presumably, this effect would be more apparent where flushing of solutions was minimal.

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REFERENCES

Bean C., Juvik J. O., and Nullet D., (1994) Mountain evaporation profiles on the island of Hawaii. *J. Hydrology* **156,** 181–192.

Benedetti M., Mernard O., Noack Y., Carvalho A., and Nahon D. (1994) Water–rock interactions in tropical catchments: Field rates of weathering and biomass impact. *Chem. Geol* **118,** 203–220.

Berner R. A. (1992) Weathering, plants and the long-term carbon cycle. *Geochim. Cosmochim. Acta* **56,** 3225–3231.

Berner R. A. (1994) GEOCARB II: A revised model for atmospheric CO_2 over Phanerozoic time. *Amer. J. Sci.* **294,** 56–91.

Berner R. A. (1995) Chemical weathering and its effect on atmospheric CO_2 and climate. In *Chemical Weathering Rates of Silicate Minerals* (ed. A. F. White, S. L. Brantley) Reviews in Mineralogy, Vol. 3 pp. 565–583. Mineralogical Society of America, Washington D.C.

Berner R. A. (1997) The rise of plants and their effect on weathering and atmospheric CO_2. *Science* **276,** 545–546.

Berner R. A., Lasaga A. C., and Garrels R. M. (1983) The carbonate–silicate cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Amer. J. Sci.* **283,** 641–683.

Berthelin J. (1988) Microbial weathering processes in natural environments. In *Physical and Chemical Weathering Cycles* (ed. A. Lerman, M. Meybeck), pp. 33–59. Kluwer, Dordrecht.

Brady P. V. (1991) The effect of silicate weathering on global temperature and atmospheric CO_2. *J. Geophysical Res.* **96,** 101–106.

Bruand A., Cousin I., Nicoullaud B., Duval O., and Begon J. C. (1996) Backscattered electron scanning images of soil porosity for analyzing soil compaction around roots. *Soil Sci. Soc. Amer. J.* **60,** 895–901.

Chadwick O. A., Hendricks D. M., Kelly E. F., Gavenda R. T. and Olson C. G. (1994) Soil genesis along an arid to humid climate transect in Hawaii, I. Weathering and mineral transformations. *Geol. Soc. Amer. Abstracts Programs* **26,** A-88.

Cochran M. F. and Berner R. A. (1993) Enhancement of silicate weathering rates by vascular land plants: quantifying the effect. *Chem. Geol.* **107,** 213–215.

Dorn R. I. (1995) Digital processing of back-scatter electron imagery: A microscopic approach to quantifying chemical weathering. *Geol. Soc. Amer. Bull.* **107,** 725–741.

Drever J. I. (1994) The effect of land plants on weathering rates of silicate minerals. *Geochim. Cosmochim. Acta* **58,** 2325–2332.

Dunne T. (1978) Rate of chemical denudation of silicate rocks in tropical catchments. *Science* **274,** 244–246.

Ehrlich R., Crabtree S. J., Horkowitz K. O., and Korkowitz J. P. (1991) Petrology and reservoir physics, I. Objective classification of reservoir porosity. *Amer. Assoc. Petroleum Geol. Bull.* **75,** 1547–1562.

Giambelluca T. and Sanderson M. (1993) The water balance and climate classification. In *Prevailing Trade Winds. Weather and Climate in Hawaii* (ed. M. Sanderson), pp. 56–72. University of Hawaii Press, Honolulu.

Giambelluca T. W., Mullet M. A., and Schroder T. A., 1986. *Rainfall Atlas of Hawaii*. Department of Land and Natural Resources, Honolulu.

Graustein W. C., Cromack K., and Sollins P. (1977) Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles. *Science* **198,** 1252–1254.

Hellmann R. (1994) The albite–water system: Part I. The kinetics of dissolution as a function of pH at 100, 200, and 300°C. *Geochim. Cosmochim. Acta* **58,** 595–611.

Hiebert F. K. and Bennett P. C. (1992) Microbial control of silicate weathering in organic-rich ground water. *Science* **258,** 278–282.

Jackson T. A. (1975) "Humic" matter in the bitumen of pre-Phanerozoic and phanerozoic sediments and its paleobiological significance. *Amer. J. Sci.* **275,** 906–953.

Jackson T. A. and Keller W. D. (1970) A comparative study of the role of lichens and "inorganic" processes in the chemical weathering of recent Hawaiian lava flows. *Amer. J. Sci.* **269,** 446–466.

Juvik J. O., Singleton D. C., and Clarke G. C. (1978) Climate and water balance on the island of Hawaii. In Mauna Loa Observatory. Twentieth Anniversary Report (ed. J. Miller), pp. 129–139. U.S. Department of Commerce, Washington D.C.

Kurz M. D. Colodner D., Toull T. W., Sampson D. E., Moore R. B., and O'Brien K. (1990) Cosmic ray exposure age dating with in situ produced cosmogenic He-3: Results from young Hawaiian lava flows. *Earth Planetary Sci. Lett.* **97,** 177–189.

Lovelock J. E. and Whitfield M. (1982) Lifespan of the biosphere. *Nature* **296,** 561–563.

McCarroll D. and Viles H. A. (1995) Rock weathering by the lichen *Lecidea auriculata* in an arctic alpine environment. *Earth Surface Processes and Landforms* **20,** 199–206.

Moore R. B. and Clague D. A. (1991) Geologic map of Hualalai Volcano, Hawaii. U.S. Geological Survey Miscellaneous Investigation Series Map, I-2133: (Scale 1:50,000).

Moore R. B., Clague D., Rubin M., and Bohrson W. A. (1987) Hualalai volcano: A preliminary summary of geologic, petrologic and geophysical data. U.S. Geological Survey Professional Paper **1350,** 571–585.

Nesbitt H. W. and Wilson R. E. (1992) Recent chemical weathering of basalts. *Amer. J. Sci.* **292,** 740–777.

Nullet D. and Sanderson M. (1993) Radiation and energy balance and air temperature. In *Prevailing Trade Winds: Weather and Climate in Hawaii.* (ed. M. Sanderson) University of Hawaii Press, Honolulu, HI.

Oelkers E. H., Schott J., and Devidal J. L. (1994) The effect of aluminum, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. *Geochim. Cosmochim. Acta* **58,** 2011–2024.

Outcalt S. I. (1972) The development and application of a simple digital surface climate simulation. *J. Appl. Meteorol.* **11,** 629–636.

Rubin M., Gargulinksi L. K., and McGeehin J. P. (1987) Hawaiian radiocarbon dates. *U.S. Geological Survey Professional Paper* **1350,** 213–242.

Schwartzman D. W. and Volk T. (1989) Biotic enhancement of weathering and the habitability of Earth. *Nature* **340,** 457–460.

Taylor T. N., Hass H., Remy W., and Kerp H. (1995) The oldest fossil lichen. *Nature* **378,** 244.

Taylor T. N. and Osborn J. M. (1996) The importance of fungi in shaping the paleoecosystem. *Rev. Palaeobotany Palynol.* **90,** 249–262.

Velbel M. A. (1993) Temperature dependence on silicate weathering in nature: how strong a negative feedback on long-term accumulation of atmospheric CO_2 and global greenhouse warming? *Geology* **21,** 1059–1062.

Volk T. (1989) Rise of angiosperms as a factor in long-term climatic cooling. *Geology* **17,** 107–110.

Warke P. A., Smith B. J., and Magee R. W. (1996) Thermal response characteristics of stone: Implications for weathering of soiled surfaces in urban environments. *Earth Surface Processes and Landforms* **21,** 295–306.

Wasklewicz T. (1994) Importance of environment on the order of mineral weathering in olivine basalts, Hawaii. *Earth Surface Processes and Landforms* **19,** 715–735.

Watts S. H. (1985) A scanning electron microscope study of bedrock microfractures in granites under high arctic conditions. *Earth Surface Processes and Landforms* **10,** 161–172.

Welch S. A. (1996) PhD. thesis, Univ. Delaware.

White A. F. and Blum A. E. (1995) Effects of climate on chemical weathering in watersheds. *Geochim. Cosmochim. Acta* **59,** 1729–1747.

Wogelius R. A. (1992) Olivine dissolution kinetics at near surface conditions. *Chem. Geol.* **97,** 101–112.