Localized Weathering: Implications for Theoretical and Applied Studies

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In situ quantification of localized weathering processes on basalt flows in New Mexico and Hawaii demonstrates that small-area factors can be more important than other more readily observable factors. Further, it demonstrates that the factorial concept of the Pope Boundary-Layer weathering model is partially solvable, that organic weathering can accentuate glass weathering (with implications for climate models and storage of nuclear waste), and that silica coatings are not a simple solution for the preservation of stone monuments. Enhancement of glass weathering by lichens on the McCartys flow, El Malpais National Monument, New Mexico, remains restricted to a half-millimeter directly underneath the lichen-covered surface. In contrast, although the inorganic rock coating of silica glaze reduces weathering directly underneath the coating by up to nine times rates found in uncoated locales, silica glaze can almost double variability in weathering along its margins. **Key Words: geomorphology, Hawaii, lichen, rate, weathering.**

Introduction

Rock and mineral decay has long been taught and studied at vastly different spatial scales. Geographers and colleagues in cognate fields focus on micron-scale changes (Pope 1995a, b; Banfield et al. 1999; Brantley and Mellott 2000), relate those changes to field-notable features such as weathering rinds (Dixon et al. 2002), soils (Dixon, Thorn, and Darmody 1984), and differential weathering (Turkington 1998), and then utilize weathering concepts in interpreting landscapes (Allen et al. 2001; Twidale 2002) and global change (Brady and Caroll 1994).

Recent trends in weathering research emphasize the importance of clear and precise upscaling of micron-scale processes (Viles 2001) to link the micron scale with such large-area concerns as landform development (Viles 1995; Thorn et al. 2001) as well as applications to societal concerns such as understanding watersheds (Brantley and Velbel 1993; Aghamiri and Schwartzman 2002), stone monument conservation (Krumbein 1988; Paradise 1995; Prieto, Edwards, and Seaward 2000) and rock art conservation (Ford, MacLeod, and Haydock 1994; Dorn 1998). But as Whalley and Turkington (2001, 2) write, "difficulties in relating small-scale, short-term studies of weathering to longer-term landform change in a plethora of environments represents one of the most important and long-standing problems facing geomorphology: how to link small-scale process studies to larger-scale landscape evolution."

We explore here a small piece of the effort to link scales—the effects of localized weathering agents on rock decay—by asking, "How much do these localized agents influence weathering, and over what distance?" By localized weathering agents, we mean features that have a limited and spatially irregular distribution over scales of centimeters to meters. We focus on lichens and the rock coating of silica glaze.

Abundant prior research has explored the role of lichens in enhancing weathering (Wilson and Jones 1983; Viles and Pentacost 1994; Banfield et al. 1999; Aghamiri and Schwartzman 2002), but not in situ and not controlling for time over thousands of years. Similarly, prior research identified the ability of coatings of silica glaze to reduce weathering (Curtiss, Adams, and Ghiorso 1985; Vincente et al. 1993; Dorn 1998; Smith 1998), but not in situ, not quantitatively, and not

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over thousands of years. Our focus, thus, rests in understanding the effects of localized weathering agents on weathering and in quantifying differences with adjacent weathering contexts.

This research has both theoretical and applied implications. Further, we seek to quantify some terms in the previously qualitative-only Boundary-Layer Weathering model of Pope and others (Pope, Dorn, and Dixon 1995). In terms of theory building, we argue that scale linkages must address spatial heterogeneity of weathering factors—for it is extraordinarily easy to include localized weathering agents in a larger sampling unit and not account for their effects. In terms of applied research, localized weathering agents are often critical in preserving priceless stone monuments (Price 1996), affect the regulation of atmospheric CO_2 over geologic timescales (Berner 1995), and relate to the stability of glass hosts for high-level nuclear waste in geologic repositories (Ewing and Haaker 1979).

Study Sites and Sample Collection

We selected basalt flows in New Mexico and Hawaii to conduct this study for three main reasons. First, the basalt flows are young enough to avoid problems associated with inherited weathering effects. Increasing evidence indicates that studies attempting to calculate weathering rates suffer from questions over construct validity due to "inheritance" of weathering, evident in a variety of circumstances (Dorn 1997; Pope 2000; Allen et al. 2001; Phillips 2001). Thus, studies of weathering rates should have a clear starting point that permits adjustment for initial conditions. Basalt flows up to a few thousand years old permit just such an assumption. Second, we wanted sites that could be considered clear case studies for the controlling variables. Third, the selected localized weathering agents of lichens (New Mexico) and silica glaze (Hawaii) allowed us to address topics of environmental concern to society, in storage of nuclear waste, and in stone monument conservation.

El Malpais National Monument

El Malpais National Monument rests near the town of Grants in west-central New Mexico. The area contains a number of dated basalt flows that have repeatedly flooded the Rio San Jose Valley over the past 16 mya (mya = million years before present; kya = thousand years before present) (Laughlin, Perry, et al. 1993). Eruptions take place along a major crustal flaw, the Jemez Lineament (Mayo 1958). Flows within the monument itself range in age from $\sim$3 kya to over 100 kya (Laughlin, Charles, et al. 1993; Laughlin, Perry, et al. 1993; Laughlin et al. 1994; Laughlin and WoldeGabriel 1997), with the youngest ($\sim$ 3 kya) called the McCartys flow (Laughlin, Charles, et al. 1993).

The McCartys flow (Figure 1) provides a natural laboratory in which to conduct a long-term experiment to assess the influence of lichens. Thumbnail-sized chips of basalt were collected from three locations along the McCartys flow within the monument boundaries, each at a different elevation (Figure 1).

The source of the flow, McCartys Crater (Laughlin and WoldeGabriel 1997), forms the highest sample site (2164 m, Site A), while the lowest elevation sample site (1939 m, Site C) rests at the terminus of the flow, near the junction of I-40 and NM-117. An intermediate elevation near the Zuni-Acoma Trail hosts the third sample collection site (2094 m, Site B). Elevation is important, because it serves as a proxy for temperature in studies of weathering rates of glass in the McCartys flow (Gordon and Brady 2002). Care was taken to select original flow surfaces at local topographic highs (tumuli) to normalize solar exposure and precipitation runoff and/or infiltration. Samples were collected from the surface of the flow in areas that exhibited both lichen cover and original flow features (e.g., pahoehoe texture, glassy sheen). The McCartys flow is sporadically covered by lichens, and therefore, sampling was highly specific to basalt pieces with lichens on them. The most common lichens on basalts at the Malpais are saxicolous, foliose lichens. The most common species are *Xanthoparmelia lineola* and *X. plittii* (Lightfoot et al. 1994).

Samples of basalt covered by surface lichens were collected for the purpose of comparison with weathering rates for lichen-free samples (Gordon 1999; Gordon and Brady 2002) at the same locations. Generally, lichens on the surface of the flow remove the glassy "sheen" from the surface and leave small "pits" on the pahoehoe texture. This makes it easy to avoid collecting "non-lichen" samples that had been previously covered with lichens for an appreciable

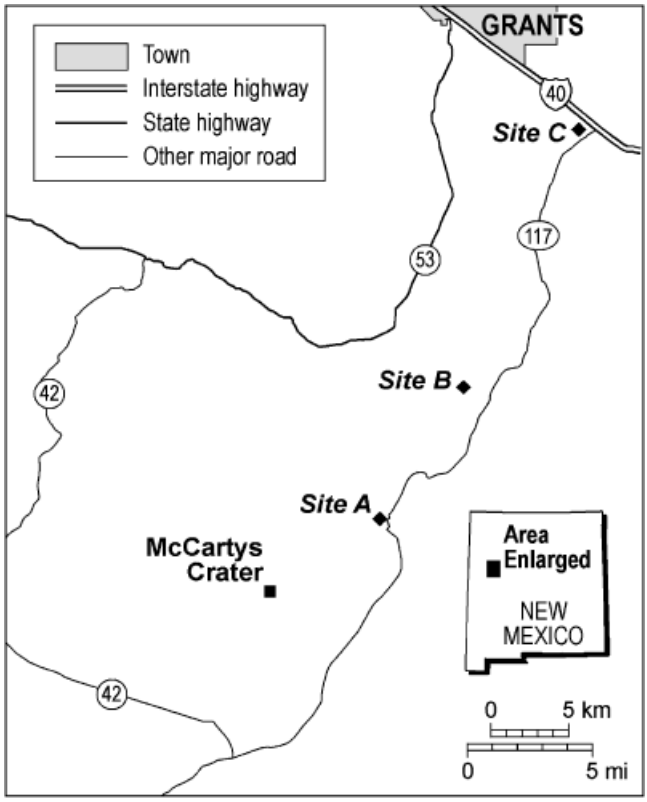

Figure 1 *Sample sites on the McCartys flow, El Malpais National Monument.*

time. It is highly probable that lichens colonized the surface of the basalt flow some time after cooling (not immediately), and therefore, any observed acceleration of weathering rates by lichens are *minimum* enhancements.

Island of Hawaii

The Island of Hawaii provides a natural laboratory for conducting a long-term experiment to assess the protective ability of silica coatings. Basalt lava flows of known age are coated by natural silica glazes (Curtiss, Adams, and Ghiorso 1985; Dorn 1998). Prior research on these lava flows reveals a variety of qualitative and quantitative observations on natural weathering where rock coatings are *not* present (Wasklewicz 1994; Dorn 1995; Cochran and Berner 1996; Brady et al. 1999). This article revisits these same sites, quantifying dissolution rates of matrix minerals resting under and near natural silica glazes.

Naturally coated lava flows range in age from historic to thousands of years where prehistoric ages derive from radiocarbon dates on subflow charcoal (Rubin, Gargulinksi, and McGeehin 1987; Moore and Clague 1991) and cosmogenic ^{3}He and ^{36}Cl ages on glacial polish atop Mauna Kea (Dorn et al. 1991). Lava flow youth facilitates preservation of original flow structures (Kurz et al. 1990), and the presence of glacial polish makes reasonable the assumption that cosmogenic ages reflect the onset of weathering. Furthermore, sampled lava flows are chemically and mineralogically similar (Moore et al. 1987; Moore and Clague 1991), with energy dispersive X-ray measurements ensuring that the analyzed plagioclase minerals have similar chemical compositions as measured by wavelength dispersive electron microprobe.

Four general types of surface weathering microenvironments occur on Hawaii (Cochran and Berner 1993; Wasklewicz 1994): (1) minerals in contact with vascular land plants; (2) minerals in contact with epilithic organisms such as lichens; (3) minerals under or directly adjacent to inorganic rock coatings such as silica glaze;

and (4) minerals not proximate to the above influences where "chemical weathering is severely limited because introduction of acids to the profiles is limited by rainfall" (Nesbitt and Wilson 1992). Prior weathering research studied all of the above factors, except the role of inorganic rock coatings such as silica glaze (Cochran and Berner 1993, 1996; Wasklewicz 1994; Brady et al. 1999). Brady et al. (1999) explain that "rock coating sites were avoided, because the weathering response is complicated by the thermal and moisture characteristics of surface films."

Three general types of measurements aim to understand effects of the overlying silica glaze on weathering: (1) percent weathering of plagioclase feldspars directly underneath silica glaze; (2) percent weathering of plagioclase feldspars within one millimeter of the edge of silica glaze, but not directly coated; and (3) the percent of silica glaze that precipitated within the basalt flow vesicles directly underneath silica glaze. Vesicle-infilling measurements were made because such infilled silica glaze may also play a role in rock conservation as a case-hardening agent.

Collection sites (Figure 2) represent a range of ages, from a recent lava flow at Mauna Ulu (Decker and Decker 1992) to glacial polish exposed on Mauna Kea about 15,000 years ago (Dorn et al. 1991). The Mauna Loa 1800–1801 C.E. flow was sampled 190 years after eruption; three flows on Hualalai erupted ~700 C.E. (f7dh7.9), 2030 ± 80 ^{14}C years (f5dc8.2), and 2885 ± 150 ^{14}C years (f5d3.5) ago (Figure 3). The Mauna Ulu flow was sampled twenty-six years after its eruption.

Quantification of In Situ Weathering

All samples were set in cross-section in circular molds of casting resin. Entombment of a cross-section of the sample and the surface lichen(s) or silica glaze allows analysis of weathering directly underneath the lichen or silica glaze and at depth. The exposed face was polished to a mirror finish using successively finer laps from 60 grit to 0.05 microns in preparation for microprobe analysis. Backscattered electron (BSE) photomicrographs were collected using a JEOL-8600 microprobe at the Arizona State University Microprobe Laboratory. Magnification of the lichen/glass images was held constant at 200x.

Lichens and silica glazes were identified on the microprobe using a combination of the SEI (surface) and BSE (chemical) detectors. Organic material is generally invisible in backscatter mode, except for some bright spots indicative of heavier-element concentrations within the organism. In SEI mode, however, the lichen is visible as a bright surface covering. Silica glazes were detected with BSE and energy-dispersive X-ray analysis.

Dissolution was quantified using digital image processing of BSE images (Dorn 1995; Gordon and Brady 2002). An example is given in Figure 3.

The method for measuring weathering under lichens in New Mexico follows. First, BSE images were scanned at 75 dots per inch. *Scion-Image*, an image processing program available from the Scion Corporation and the National Institute of Health, was then used to digitally "cut out" materials from the image that is neither unweathered material nor weathering void space (e.g., mineral phenocrysts, polish imperfections). Each pixel in the "cut" image was then classified as either fresh material or void space, based upon the brightness value (0–255) of each pixel. Pixels brighter than a threshold were classified as fresh material while pixels darker than the threshold were classified as void space. The threshold used for this study is the default in the program, calculated for each image using an iterative analysis of the brightness histogram (Ridler and Calvard 1978), based upon an algorithm by Ridler and Calvard (1978). The number of pixels classified as porosity was divided by the total number of pixels in the image to yield a percent porosity of the BSE image. Division of percent porosity by length of exposure determines a weathering "rate" in units such as percent per thousand years.

Nine BSE photomicrographs were imaged underneath lichens. Three of the "surface" BSE micrographs also served as starting points for depth transects from the lichen-covered surface of the sample into the interior of the sample. Transects ranged from the lichen-covered surface to approximately 2,500 microns underneath the basalt surface.

The eighty-two BSE images of basalt surfaces free of lichen (Gordon and Brady 2002) were collected using the procedure outlined above. Lichen-free (abiotic) images were not, however, collected either specifically at the surface or

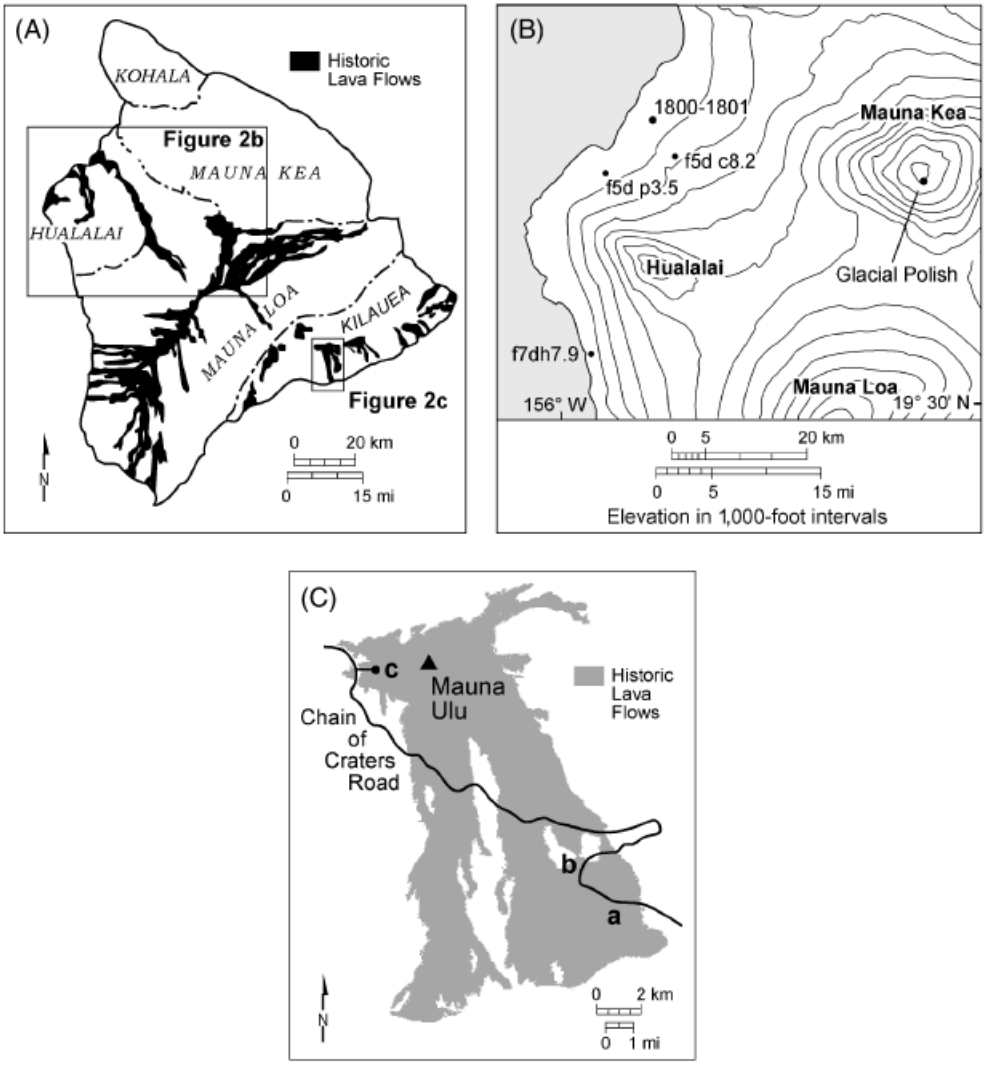

Figure 2 *Sample sites on Hawaii.*

along depth transects. The same method of quantifying weathering was employed on both "biotic" (lichen-covered) and "abiotic" (lichen-free) samples.

To preserve compatibility with previous work, percent porosities of the lichen/glass samples were converted to weathering rates stated in percent per thousand years, by dividing the porosity by the age of the McCartys flow. The rate of weathering per thousand years is best interpreted as a minimum measurement, because (a) lichens probably did not cover the surface for the entire three-thousand-year exposure of the flow, (b) pixels may be misclassified by the image processing threshold, (c) weathering products may be counted as unweathered glass, (d) glass may have preweathering porosity from formation, and (e) the technique employs a two-dimensional representation of a three-dimensional reality (Dorn 1995; Gordon 1996).

Difference of means tests (2-tailed paired sample t-test) at the $\alpha = 0.05$ and $\alpha = 0.01$ confidence intervals evaluates the difference

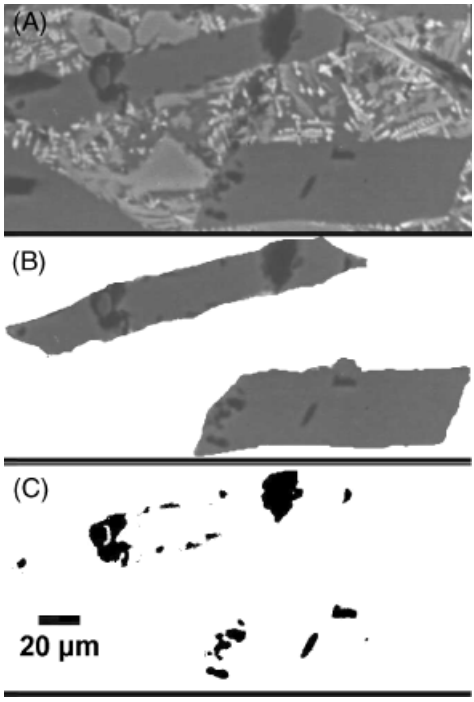

Figure 3 *Generalized sequence of image processing to quantify weathering. Frame (A) shows a backscattered electron micrograph of a small section of the matrix of flow f5dp3.5 where no silica glaze coats the rock surface. Frame (B) then illustrates plagioclase minerals ''cut out'' of the image in Frame A. Frame (C) thresholds dissolved plagioclase, a step that facilitates counting of weathered pixels.*

between the mean weathering rates of glass in biotic (lichen-covered) conditions and abiotic (lichen-free) conditions. Distributions of both biotic and abiotic weathering rates showed departure from normality, based upon values of skewness and kurtosis (Table 1) (Rummel 1970). To address the departure from normality, the expression:

$$x_t = \log_{10} x_i$$

transformed both values where x_t is the transformed value and x_i is the original value.

A total of ten BSE images underneath silica glaze comprise the dataset for each Hawaii site. A similar method to the one used for the McCartys flow, outlined in Dorn (1995), calculated porosity values and silica-glaze infilling percentages for the Hawaii sites.

Results

Lichens and Glass at El Malpais

The mean rate of glass weathering directly underneath surface lichens is 3.57% ± 1.97% per kya ($n = 9$, Table 1). In contrast, the weathering rate for glass without lichen cover decreases to 2.08% ± 1.80% per kya ($n = 82$, Table 1). Differences in mean weathering rates are statistically significant at $\alpha = 0.01$ levels. The presence of lichens enhances the rate of glass dissolution at least 1.7x over weathering in the absence of lichens.

The rate of glass weathering is highest directly underneath lichen cover (Figure 4). The rate drops sharply from the surface to a distance of 0.5 mm, at which point the weathering rate is similar to that of the abiotic samples.

Silica Glaze and Plagioclase in Hawaii

We measured plagioclase weathering in three contexts (Table 2): not under silica glaze; under silica glaze; and directly adjacent to silica glaze. Measurements in Table 2 for not under silica

Table 1 *Weathering Rates for Basaltic Glass from the McCartys Flow, Lichen Free and Lichen Covered*

	Lichen-Free Wx Rate[1,2]	Lichen-Covered Wx Rate[1,2]	Lichen-Free Wx Rate (trans)[1,3]	Lichen-Covered Wx Rate (trans)[1,3]
Mean	2.08	3.57	−0.86	−0.40
N	82	9	82	9
Min	0.08	0.94	−2.10	−0.92
Max	10.35	7.81	0.00	0.00
Std. Dev.	1.80	1.97	0.41	0.26
Kurtosis[4]	*5.36*	*2.23*	0.71	1.21
Skewness[4]	1.95	1.12	−0.62	−0.67

[1] *weathering rates in percent per thousand years.*
[2] *transformed values using* $\log_{10} x$.
[3] *reported in Gordon and Brady (2002).*
[4] *values in italics represent perceived departure from normality.*

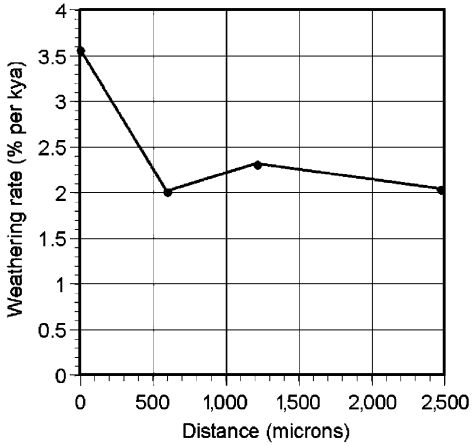

Figure 4 *Change in glass weathering rate with distance into the McCartys flow directly underneath lichen cover. The sudden rate change at about 500 μm reflects a drop to values similar to abiotic samples (Gordon and Brady 2002).*

glaze derive from a prior study (Brady et al. 1999) and form the basis of comparison for the effects of silica glaze. Differences between weathering under silica glaze and weathering on the edges or away from silica glaze are statistically significant at $\alpha = 0.05$ for all *t*-tests except: Mauna Ulu-c for under versus not under; and flow 5dp3.5, flow f5d c8, and Mauna Kea glacial polish for not under versus adjacent (see Table 2).

Silica glaze shows an average capability of increasing weathering at only one site near the cone of the Mauna Ulu flow (Figure 5). For all other sites, silica glaze decreases weathering rates by factors that range from under two to over eight. In addition to greatly reducing weathering of plagioclase feldspars within the basalt matrix, Figure 6 reveals that silica glaze can penetrate into basalt vesicles in semiarid locations. The amount of silica glaze filling in pores increases slightly over time.

The influence of silica glaze changes dramatically on its margins—within a millimeter of silica glaze, but not directly coated (Figure 5). All sites exemplify more variability in weathering rates adjacent to silica glazes, with the greatest range associated with the youngest lava flow, Mauna Ulu, sampled when the flow was about twenty-six years old. Flow f7dh7.9 at about seven hundred years old showed more variability than the two (f5dc8.2)- and three (f5d3.5)-thousand-year-old lava flows. However, even near the top of Mauna Kea, microsites adjacent to silica glaze showed more variability in weathering rates than microsites under the rock coatings.

Discussion

Lichens, Glass Weathering, and Waste Disposal

The rate of basaltic glass weathering increases by at least 1.7 times directly underneath lichens compared with rates from directly underneath a surface free of lichens. This is a minimum value, since it assumes ongoing lichen weathering for the three-thousand-year age for the host basalt flow—an assumption that is difficult to test. Additional uncertainties in these results could be resolved with larger sample sizes ($n \geq 30$ BSE images), a larger number of depth transects from surface to interior of samples ($n \geq 15$) to refine curves of loss of strength of lichen

Table 2 *Weathering of Plagioclase Grains in Different Weathering Contexts on Different Hawaiian Surfaces Identified in Figure 2*

Surface	Not Under Silica Glaze		Under Silica Glaze		Adjacent to Silica Glaze	
	Grain Area	Porosity	Grain Area	Porosity	Grain Area	Porosity
Mauna Ulu-a	217,500	0.071 ± .018	160,500	0.009 ± 0.018	239,000	1.65 ± 1.42
Mauna Ulu-b	216,000	0.058 ± .014	216,500	0.008 ± 0.011	205,500	1.18 ± 0.92
Mauna Ulu-c	202,500	0.007 ± .004	247,000	0.010 ± 0.022	193,000	1.72 ± 0.92
flow f5d c8.2	303,000	1.63 ± 0.15	160,500	0.39 ± 0.23	202,000	1.87 ± 1.76
flow f5d p3.5	141,000	2.90 ± 0.25	185,500	0.54 ± 0.33	175,500	2.59 ± 3.17
flow f7d h7.9	238,500	0.94 ± 0.17	183,500	0.13 ± 0.19	175,500	2.42 ± 2.96
Mauna Kea Glacial Polish	201,500	26.20 ± 10.33	154,000	15.71 ± 5.82	179,500	27.04 ± 17.58

Note: Each value indicates the average and standard deviation of the porosity measurements. Grain area is measured in square micrometers as a total for all grains. The plagioclase minerals have a representative composition in oxide weight percent of 3.22% Na_2O, 0.22% MgO, 29.12% Al_2O_3, 48.22% SiO_2, 18.10% CaO, 0,12% TiO_2, 0.40% MnO, and 0.54% FeO.

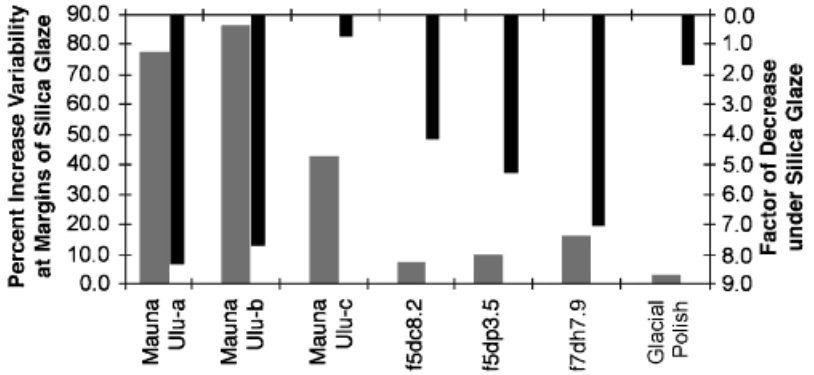

Figure 5 *Influence of silica glaze on weathering rates of plagioclase at Hawaii sites. The left hand scale (light gray, thicker bars) shows increasing variability as measured by the ratio of [standard deviation of weathering adjacent to silica glaze/standard deviation of weathering directly underneath silica glaze]. The right hand scale (black, thin bars) presents factors of decreases in weathering rates directly under silica glaze as compared to plagioclase not coated by silica glaze, as measured by the ratio of [average weathering of uncoated grains/average weathering of grains directly underneath silica glaze].*

enhancement, and transects deeper than 2,500 microns to determine if weathering rates reach a steady state, increase, or decrease at greater depths. Despite these uncertainties, these results are unique in providing both in situ and long-term rates of biotic enhancement of weathering.

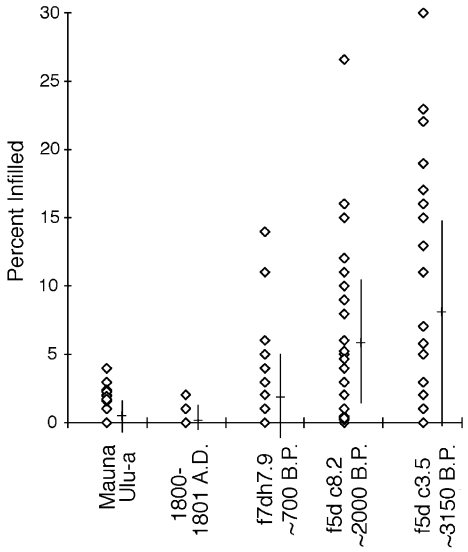

Figure 6 *Percent silica glaze filling in vesicles of Hawaii lava flows, based on measurements made in 30 vesicles for each lava flow. Although average and standard deviations are shown by the bar and cross, these data are not normally distributed.*

Previous workers report enhancement of weathering rates by epilithic organisms that vary widely. In laboratory experiments, bacteria act to etch glass surfaces and enhance weathering rates of waste glasses (Staudigel et al. 1995), and enhance weathering rates of basaltic glass tenfold (Thorseth, Furnes, and Tumyr 1995). Work on recent Hawaiian lava flows suggest that lichens enhance rates of weathering-rind formation 10–100 times faster than sites not colonized by lichens (Jackson and Keller 1970), and this is used calculate enhancement factors of 100–1,000 times (Schwartzman and Volk 1989). While data in Table 1 and Figure 4 do support epilithic enhancements of weathering rates, such in situ, long-term rates rest toward the lower end of the range from these other studies.

Data obtained in this study compare well to rates obtained using chemical data from drainage basins. Runoff calculations for tropical drainage basins suggest biotic enhancements of weathering 1.3 to 5 times above abiotic weathering rates (Benedetti et al. 1994), while nontropical runoff studies suggest two- to five-fold enhancements (Cawley, Burruss, and Holland 1969; Cochran and Berner 1992; Drever 1994; Moulton and Berner 1998). This appears to strengthen the watershed-based technique of weathering quantification, at least in the biotic

enhancement context, or, conversely, strengthen the micron-scale technique outlined in this article. Supporters of cost-effective research will therefore see the value in tests such as ours, with results that allow researchers and funding agencies to choose the most cost-effective technique that suits their purpose.

This in situ study indicates that rates of basaltic glass are highest directly underneath lichens and then drop off substantially (Figure 4), just 0.5 mm to 2.5 mm beneath lichens. In fact, these 0.5 to 2.5 mm values are statistically indistinguishable from sites on the same flow lacking lichen cover (Gordon and Brady 2002). The magnitude of the effect of lichen growth on basaltic weathering rates is, therefore, scale and location dependent. In nature, lichens and other epilithic organisms do not completely cover surfaces of basalt flows. Biotic enhancements are, therefore, localized to colonized locales.

This scale dependency issue is not trivial and needs to be factored into the literature. Assume a perfectly flat, 100 percent lichen-covered cube of basalt. Using a depth of 500 μm as a limit for biotic enhancement, a one-meter cube of basalt has 0.05 percent of its total volume affected by lichens; a one-centimeter cube of basalt has 5.0 percent of its total volume affected by lichens; and a one-millimeter cube of basalt has 50 percent of its total volume affected by lichens. The role of lichen growth in the removal of mass at a given time, therefore, is minor on the scale of a lava flow several meters thick, but very important on the scale of a knob or crack on the surface of that same flow, and critical on the scale of root hairs, rock coatings, and thin layers of basaltic glass present on the surface fringe of lava flows.

This work has implications for carbon dioxide models and high-level nuclear waste storage. The enhancement factor of 1.7 supports previous arguments that the effect of primitive plants on global silicate weathering and carbon dioxide regulation is small (Berner 1992; Moulton and Berner 1998). Further, primitive plants would have only influenced silicate weathering rates for a miniscule portion of all exposed silicates at the surface (following the above analogy). Therefore, climate models that rely upon a strong function of CO_2 drawdown from the colonization of the land surface by primitive organisms may overestimate this effect.

The scale dependency is also important for high-level nuclear waste storage (Ewing and Haaker 1979; Werme et al. 1990; Bates et al. 1992; Lutze 1998), as the breakdown of small glass hosts (e.g., beads or wafers) will be subject to the effects of epilithic organisms more than larger glass hosts (e.g., long rods or large pieces).

Silica Glaze and Stone Conservation

A focus of considerable recent research rests in the potential of different coatings for preserving stone structures and monuments (Krumbein 1988; Urmeneta et al. 1993; Paradise 1995; Price 1996; Bescher et al. 2000; Borgia et al. 2001; Kurtz and Netoff 2001). Some of this discussion turns on the topic of "progressive mineral matrix dissolution" and the potential for different coatings to reduce this slow decay process (Tiano, Biagiotti, and Mastromei 1999, 139). "Ornamental slabs used by architects and monumental masons might last longer by minimizing mechanical abrasion during sawing and polishing and by silicifying the surface" (Smith 1998, 3366).

Our findings reveal that the protective effect of silica glaze, although substantial in Hawaii, is far more complicated than simply slowing weathering. By analogous reasoning, a bad job of painting a house could create conditions of enhanced decay underneath the paint or on the margins of the paint, or decay could extend underneath the paint. However, to not paint your house when you learn it preserves the house is not intelligent. This section details the long-term preservative effects of silica glaze and associated complications.

Silica glaze shows the potential for invading pores in the host rock (Figure 6). This impregnation of the host rock over time may have important effects on stone-surface stability since natural silica glaze may hold together decayed and friable materials, much in the way that lithobionts can protect sandstone (Kurtz and Netoff 2001). Calculating the amount of silica glaze that fills in pores is more complicated than simply counting porosity in plagioclase. These infilled pores contain other types of rock coatings (Figure 7D) along with considerable submicron porosity—requiring careful digital "cutting out" of just the silica glaze for area calculations.

Silica glaze reduces weathering of matrix minerals in the rock directly underneath silica

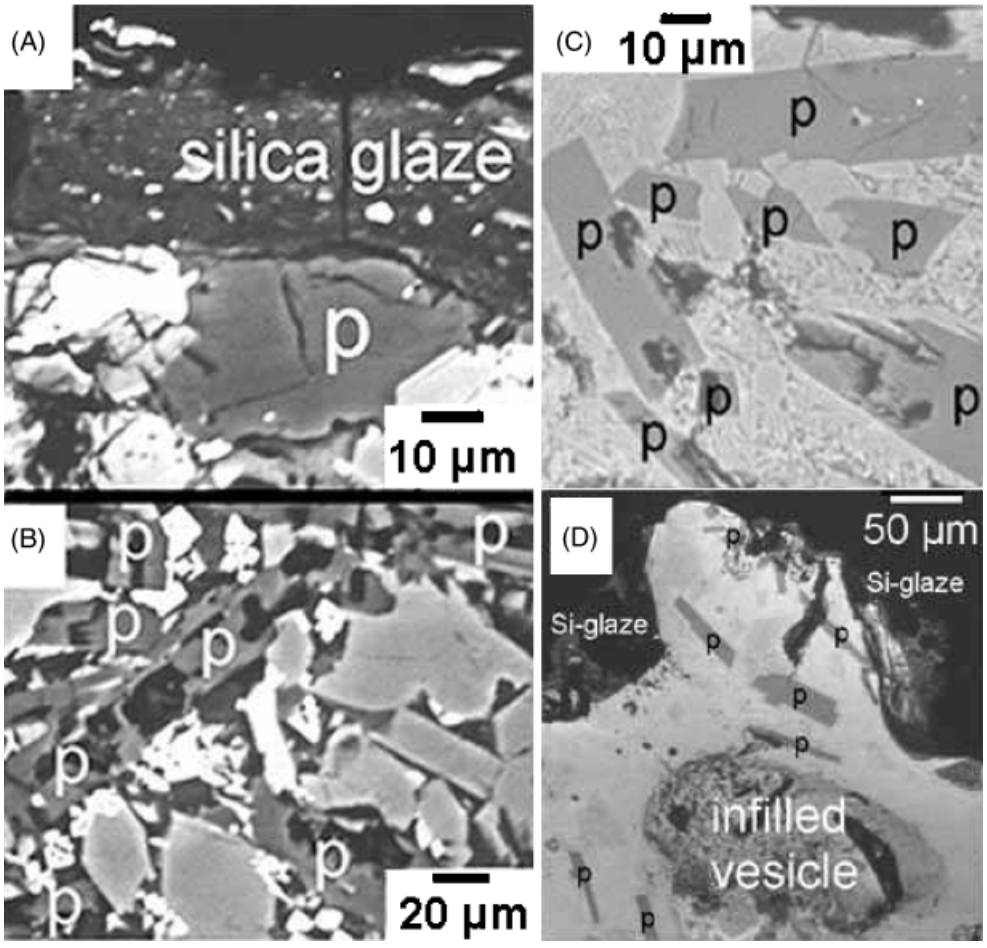

Figure 7 *Plagioclase weathering seen in different geographic circumstances. Letter p identifies plagioclase feldspar minerals in all images. Images A and B display plagioclase weathering of Mauna Kea glacial polish, where weathering underneath silica glaze (A) is far less than weathering of surfaces not coated by silica glaze (B). Image C illustrates the sort of variability seen in plagioclase weathering at the margins of silica glaze, in this case exemplified from flow f5dc8.2. Image D shows dark-colored silica glaze on the surface of flow f5d3.5, where about 30 percent of a vesicle has been filled by silica glaze. In addition to silica glaze, other precipitates (e.g., iron skins, rock varnish, carbonate) formed inside the vesicle.*

glaze (Figure 5). Figures 7A and 7B illustrate an example from fifteen-thousand-year-old glacial polish on Mauna Kea where the mineral porosity away from the silica glaze contrasts with grains protected by this rock coating. This study thus documents the potential of silica glaze to slow stone decay on time scales of hundreds to thousands of years.

One uncertainty in these results relates to the tremendous variability in "weathering protection" seen in Figure 5. The cause of this variability is not known, but it may relate to different properties of silica glaze and different types of silica glaze coatings. There are many different types of silica glazes, even in Hawaii. The general type of silica glaze found in Hawaii (Curtiss, Adams, and Ghiorso 1985; Dorn 1998) is chemically and texturally different from silica glazes found in other settings (Weed and Norton 1991; Matsukura,

Kimata, and Yokoyama 1994; Dorn 1998; Smith 1998).

A key cause of the variable protective effects seen in Figure 5 may relate to permeability of different silica glazes. Available data reveal that rock coatings do influence permeability (Fuller and Sharp 1992) and hence, the potential for rock decay. Qualitative observations of back-scattered electron imagery reveal differences in silica glazes that may influence permeability (Curtiss, Adams, and Ghiorso 1985; Dorn 1998). We speculate that porous silica glazes would have a greater protective effect through the ability of capillary moisture to escape rock-weathering zones more rapidly. However, research controlling permeability in different silica glazes, keeping the rock surface constant, would be necessary to determine the importance of coating permeability in protecting stones.

The protection afforded by silica glaze contains only one exception, site Mauna Ulu-C. We speculate that this exception may relate to its location near the flow vent (Figure 2) and effects of acidic deposition downwind from ongoing Kilauea eruptive centers (Siegel, Nachbarhapai, and Siegel 1990). In other words, the greater acidity at this site may counter protection afforded by silica glaze——with implications for silica-glaze-coated stones in acidic regions and locations suffering from acidic rain.

A large complication in attempts to use silica glaze to stabilize stone monuments would be weathering margins of silica glaze. Enhanced variability seen in Figure 5 is illustrated in Figure 7C, where some grains show no detectable porosity, while other grains show lots of holes. The cause of the great variability in weathering rates found directly adjacent to silica glazes (Figure 5) could have profound implications for conservation activities using silica coatings and for individuals interested in calculating weathering rates.

Consider a hypothetical situation of two microsites on the sides of silica glaze: one marginal site to where water ponded behind the silica glaze is channeled and the other, a marginal site receiving less moisture. For the coating-marginal microsite where ponded water emerges, there should be greater flow rates and a more rapid translocation of hygroscopic water away from weathering sites. But in another marginal location, the redirection of water could have the opposite effect, slowing weathering. Such a scenario could explain the greater variability in weathering rates at microsites near silica glazes.

Given the century-to-millennium time scales of many stone monuments, observations on conservation powers of natural silica glazes would seem important data for consideration. Unfortunately, little quantitative data exists on whether silica glaze protects or attacks underlying stone minerals over time scales of the hundreds to thousands of years that we all hope our stone monuments will last. This article therefore provides unique quantitative insight on the influence of natural silica coatings on mineral matrix dissolution.

Readers should note the lithological and climatic limitations of our study. The rock type studied is basalt, and the overall climatic regime is semiarid. No data exists on whether conclusions reached here transfer accurately to different lithologies, different climates, or different types of rock coatings. Additional research on different rock types in different environmental contexts, for example, sandstone in Petra, Jordan (Paradise 1995), is the only way that researchers will learn whether these findings can be generalized. Still, we hope that this approach is a starting point for long-term studies of matrix mineral decay influenced by rock coatings.

It might be possible to use digital image processing of back-scattered electron imagery to assess whether or not this millimeter-scale effect translates to meter-scale or even centimeter-scale variability in real-world applications of silica glaze to stone monuments. Key remaining uncertainties include whether rock coatings facilitate weathering by retaining water, whether rock coatings strengthen a rock by holding highly porous rock together, or whether both responses occur in different contexts and different lithologies. Even though considerable uncertainties remain over the importance of sampling locale, the role of coating permeability, the influence of local acidity, and, especially, of large sample-to-sample variability, these findings provide the first long-term data that silica glaze conserves stone surfaces.

Factorial Model and Scaling Considerations

Given the critical nature of linking scales (Whalley and Turkington 2001), we note that general geochemical models of weathering (Lasaga et al. 1994; Berner 1995) are not designed for use in applied research at varied spatial

scales—with the exception of the Pope Boundary-Layer Weathering model (Pope 1994; Pope, Dorn, and Dixon 1995). In this factorial model, weathering rate (W_r) is a function of several synergistic factors:

- (R_a) availability and proximity to abiotic weathering agents (abiotic reactant chemistry)
- (R_b) availability and proximity to biotic weathering agents (biotic reactant chemistry)
- (C_p) mineralogy and petrology (chemistry) of the parent material
- (C_e) mineralogy (chemistry) of evolved products
- (L) Lithology of the parent material
- (S_t) Structure (jointing, foliation, bedding) of the parent material
- (T) Temperature at the reaction site
- (H) Hydraulics of water movement
- (−M) removal of weathered material via gravity water or capillary water
- (e) Eolian input or deflation of organic and inorganic fines
- (mT) microtopography of the land surface
- (A_s) exposed surface area
- (A_c) accreted coating area (armoring)
- (s) scale
- (t) time (E_c) Environmental change over time, including biota, climate, landscape, erosion, and weathering products
- (. . .) variables still undefined, including anthropomorphic influences

such that:

$$W_r = f(R_a, R_b, C_p, C_e, L, S_t, T, H, -M, e, mT, A_s, A_c, s, t, E_c, \ldots)$$

By isolating the role of biotic weathering agents (R_b) and accreted coatings (A_c), this article illustrates that the factorial concept of the model is solvable. Furthermore, we illustrate that upscaling (Casey et al. 1993; Banfield et al. 1999; Viles 2001) can contain specific spatial thresholds, such as 0.5 mm underneath Malpais lichens and over a few millimeters of Hawaiian silica glazes.

The Malpais research, at first glance, reveals a "yes/no" operator immediately underneath the lichen cover. A minimum weathering rate enhancement of at least 1.7 times is dependent upon distance from the lichen cover into the interior of the flow. At depths between 500 μm and 2,500 μm, this relationship is not effective and all glass rates (for lichen-covered glass or not) resemble abiotic rates. This suggests that any quantification of the "R_b" term in the above model is itself a scalable function, dependent upon depth from the lichen-covered surface, instead of simply a static factor of $1.7\times$ if lichens are present. The values range from a multiplier of approximately $1.7\times$ when depth = 0 and decreases to 1.0x as depth approaches some threshold ($\sim$ 500 μm in this study). Similarly, the rock coating term has variable rate implications as seen in Table 2, whereby silica glaze both reduces plagioclase weathering rates up to eight times and can almost double variability in weathering rates at coating margins (Figure 5).

Researchers interested in using field weathering rates in their research (Dorn 1995; Banfield et al. 1999; Dixon et al. 2002; Gordon and Brady 2002) must be extraordinarily careful in the selection of samples for analysis and be aware of these spatial thresholds. Even though the investigator may think a particular rock sample lacks organic contact or an inorganic coating, the coating could have been polished off or not appear to be polished deep enough to the investigator looking at a two-dimensional section. Spatial thresholds of these localized effects could be a critical confounding factor in work trying to resolve observed discrepancies between field and laboratory studies (Swoboda-Colberg and Drever 1993; Brantley and Mellott 2000; Kump, Brantley, and Arthur 2000).

Conclusion

This article addresses the importance of localized, highly site-specific factors (lichen growth, silica glaze) on rates of weathering of basalts. We determine that lichens enhance glass dissolution approximately 1.7 times over similar glass without lichen cover. Further, the enhancement of dissolution by lichen cover is greatest directly underneath the lichens and rapidly diminishes to a negligible value $\sim$500 μm from the surface. Silica glaze, on the other hand, generally protects plagioclase phenocrysts from dissolution by a factor of up to 9x directly underneath the coating, versus uncoated samples. Variability in dissolution is greatest at the margins of the silica

glaze coating and is low directly underneath the coating as well as far from the coating.

Our work addresses weathering theory by illustrating that the Boundary-Layer model of Pope, Dorn, and Dixon (1995) can be quantitatively solvable, at least in part. This lends applicability to the model, and our work suggests that the use of silica coatings in stone structure and monument conservation, while an effective practice, must be exercised with the caution that weathering may actually *increase* at the edges of the coating.

Studies of global climate that employ a silicate weathering negative feedback to regulate atmospheric CO_2, coupled with a strong increase in weathering rate after the rise of primitive plants, must also exercise caution. Our results, compared to some published works, suggest that lichen enhancement of silicates weathering rates is small and that enhancement is highly localized to microsites directly underneath the lichens. Dramatic CO_2 drawdown via this mechanism is, therefore, unlikely. ■

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