Abstract—Long-term ( > 10^5 years) weathering can be quantified by measuring microscopic dissolution of minerals in exposed rock surfaces. Digital backscattered (BSE) electron microscope images of plagioclase porosity in field exposures of known age resolves weathering at finer scales and over longer time spans than conventional solute budget and laboratory studies. Rock-based BSE imaging is therefore a potentially useful tool for quantifying steady-state weathering fluxes occurring over geologic time. Here, we compare results of the rock-based method against solute-budget and experimental data, using plagioclase weathering rates from ^14C-dated basalt flows on Hualalai Volcano in Hawaii, USA. A rock-based field activation energy of 26.2 kcal mol^-1 is somewhat higher than solute-budget and laboratory measurements of plagioclase weathering.

INTRODUCTION

Controls on chemical fluxes must be quantified in order to understand more fully the complex and interlocking biogeochemical cycles which determine habitability of the Earth's surface. The fluxes most important to global climate control are those which regulate atmospheric CO₂, including outgassing from volcanic activity (Berner et al., 1983; Urey, 1952), metamorphic decarbonation (Nesbitt et al., 1995), and the consumption of CO₂ through silicate weathering (Berner et al., 1983; Brady and Caroll, 1994; Caldeira, 1992; Lovelock and Whitfield, 1982; Probst et al., 1994; Raymo, 1994; Schwartzman and Volk, 1989; Sundquist, 1991; Velbel, 1993; Walker et al., 1981). Weathering is particularly important because, unlike mantle-controlled volcanic and metamorphic activity, silicate consumption of CO₂ is controlled by a myriad of competing and potentially coupled surface factors that include biotic activity, global temperature, extent of glaciation, elevation, and runoff rates. As a result, over timescales greater than the mean residence time of HCO₃⁻ in the ocean (t > 10^5 years), the response of silicate weathering to global environmental change is one of the primary determinants of atmospheric CO₂ levels, and through the Greenhouse Effect, global climate.

The effect of temperature on silicate weathering has been highlighted as one of the more important controls on long-term climate stability (Berner, 1992; Brady, 1991; Velbel, 1993; Walker et al., 1981). A positive temperature sensitivity of global silicate minerals exposed to weathering would stabilize climate. Historically, the susceptibility of minerals to chemical weathering has been qualitatively examined by relative abundance in the field (Goldich, 1938). Traditionally, weathering fluxes have been quantified by analyses of river solutes, focusing on the output of fluid-rock interactions on the scale of drainage basins (Drever and Zobrist, 1992; Garrels, 1967; Garrels and MacKenzie, 1967; Paces, 1983; Stal-
limited by rainfall” (plant cover and litter is limited) (Nesbitt and Wilson, 1992, p. 771).

Samples were collected from ten different tops of constructional lava flow features at four different elevations on the 500 mm isohyet (Fig. 1; Table 1). Mean annual temperatures were calculated from local lapse rates (Armstrong, 1973). However, the upper site on Hualalai is usually above the trade-wind inversion (Grubisic, 1995), resulting in an adjustment of +2–3°C (cf. Armstrong, 1973). These sites receive only precipitation (no runoff), and samples were not collected from flow structures colonized by lichens or other epilithic organisms (except bacteria, which are impossible to avoid) and at least 3 mm distant and upslope from the margins of rock coatings (Dorn et al., 1992).

Polished cross-sections from each sample were examined with BSE, which reveals variations in sample composition (Dilks and Graham, 1985). Transects were made in the upper 50 μm of weathering rinds in each cross-section; the first twenty plagioclase feldspars in a transect were imaged by BSE, and digitally “cut out.” Unweathered plagioclase grains from different flows have similar compositions measured by wavelength dispersive electron microprobe of Na2O ~ 3.5%, MgO ~ 0.3%, Al2O3 ~ 29%, SiO2 ~ 49%, K2O ~ 0.3%, CaO ~ 17, TiO2 ~ 0.2, and FeO ~ 0.7. Digital image processing was used to measure the cross-sectional area (square micrometers) of dark dissolved areas and bright unweathered plagioclase for each grain (Fig. 2). These values were totalled for each section, and averaged for each isohyet position. The methodology of quantifying weathering with digital image processing of BSE imagery is detailed elsewhere (Dorn, 1995).

RESULT AND ANALYSIS OF UNCERTAINTIES

The natural temperature sensitivity of plagioclase weathering on ~2000–2700 14C year-old basalt flow surfaces of Hualalai, based on data in Table 1, is an $E_a$ of 26.2 kcal/mol (Fig. 3). This value is somewhat higher than the laboratory-based measurement on albite of 21.2 ± 3.5 kcal/mol (Helmmann, 1994) and watershed-based calculations for plagioclase of ~ 18.4 kcal/mol (Velbel, 1993).

Several complications were encountered that are difficult to quantify, but may impact the confidence of the reader in our measurement of plagioclase $E_a$:

1) Sample pretreatment can mimic weathering effects (Creemans et al., 1987). Therefore, only distilled water and ultrasonic cleaning were used. Grooves and shallow pits cre-

Table 1. Data on plagioclase weathering on Hualalai, where samples were collected at different elevations along the 500 mm isohyet (Giambelluca, 1986). Temperature is based on local lapse rate data and trade-wind inversion (Armstrong, 1973).

<table>
<thead>
<tr>
<th>Site</th>
<th>Flow</th>
<th>Age (14C yr)</th>
<th>Elev.</th>
<th>Mean Annual Temp (°C)</th>
<th>Total Area (m²)</th>
<th>Percent Dissolved Weighted Mean</th>
<th>Percent Dissolved 10 sections</th>
<th>Percent Weathered per 10³ yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>fsc 07</td>
<td>2200-2300</td>
<td>20</td>
<td>23.3</td>
<td>281,500</td>
<td>2.48</td>
<td>2.43</td>
<td>1.08±0.07</td>
</tr>
<tr>
<td>2</td>
<td>f5d p9.2</td>
<td>2140±100</td>
<td>100</td>
<td>22.8</td>
<td>308,500</td>
<td>2.21</td>
<td>2.22</td>
<td>0.99±0.06</td>
</tr>
<tr>
<td>3</td>
<td>f5d e8.2</td>
<td>2030±80</td>
<td>500</td>
<td>20.6</td>
<td>303,000</td>
<td>1.64</td>
<td>1.63</td>
<td>0.72±0.07</td>
</tr>
<tr>
<td>4</td>
<td>f5e b0.7</td>
<td>2670±80</td>
<td>2380</td>
<td>12.5</td>
<td>306,000</td>
<td>0.48</td>
<td>0.45</td>
<td>0.20±0.06</td>
</tr>
</tbody>
</table>

1as identified on Fig. 1
2 from MOORE and CLAGUE (1991)
3 in square micrometers of 200 plagioclase crystals
4 average weighted by area of plagioclase crystals in each section
Temperature dependence of plagioclase weathering

FIG. 2. Matrix plagioclase in weathering rinds on Hualalai Volcano, Hawaii, USA, weathers by dissolution—rather than alteration to secondary products. Scale bars in micrometres. (a) BSE images of polished cross section from the f5d c8.2 flow (Moore and Clague, 1991), where smaller arrows identify plagioclase grains. The large arrow identifies the locale of a typical electron microprobe analysis of the unweathered section of the plagioclase grain: Na₂O 3.48; MgO 0.26; Al₂O₃ 27.84; SiO₂ 48.45; K₂O 0.32; CaO 16.28; TiO₂ 0.18; MnO 0.00; FeO 0.86. (b) BSE image of a broken (not polished) weathering rind from the same site as A. Arrows identify plagioclase crystals (determined by EDS analysis).

2) Scale effects. Porosity values can vary at different magnifications. Our solution was to apply the magnification (2000×) necessary to resolve the smallest plagioclase pores in our samples that we could observed with BSE. Still, we cannot account for pores below the ~0.1 μm limit of resolution for detecting pores with BSE (Krinsley et al., 1993).

3) Potential misidentification of altered vs. fresh minerals. This was tested with the electron microprobe for pores and adjacent fresh plagioclase; probe totals dropped from >95% to <15% (X-rays generated from pore walls) when the boundary between bright unweathered plagioclase and dark dissolved areas was crossed. A related issue is the nature of plagioclase weathering. The larger phenocrysts of plagioclase weather by congruent dissolution, as well as the formation of clay mineral secondary weathering products. The smaller plagioclase grains within basalt matrix weather only by dissolution—making "holes." Clay minerals are not seen in these pores. Although the reason for this dichotomy is unclear, the "style" of weathering of the matrix plagioclase is to make "holes." Our observations are similar to those of Cochran and Berner (1993) and Wasklewicz (1994), who also worked in Hawaii. This begs the question of whether this style is at all representative of weathering in general. We have used BSE to examine of the surface weathering rinds of basalts from Mauna Kea and Haleakala (Hawaii, USA), the Cima volcanic
Hawaii (Gavenda, 1992), we can only assume that considered per thousand years at the subscripted temperature. The only quantitative study we know would result in even more weathering. Little data, how-

don in situ weathering of basalts over time scales similar to ever, exist on this topic. The magnitude and direction, for the last 2700 14C years on Hualalai.

The growth of epilithic organisms (Jackson, 1971); organisms and away from acid-secreting (Bryson, 1993; COHMAP, 1988), and perhaps in organics-poor microenvironments, away from rock coatings, are the only microsites studied. Data are from Table 1. The line is the Arrhenius fit to the data as per

\[
\frac{\% \text{ Weathered}_t}{\% \text{ Weathered}_0} = \exp \left( \frac{E_a}{R} \left( \frac{1}{T_t} - \frac{1}{T_0} \right) \right),
\]

where \( \% \text{ Weathered}_t \) is the percent of the plagioclase surface weathered per thousand years at the subscripted temperature. \( T \) is temperature (K), and \( R \) is the gas constant.

field (California, USA), the Sierra Pianate volcanic field (Sonora, Mexico), and San Francisco Peaks volcanic field (Arizona, USA). For all these samples, the matrix plagioclase weathered by dissolution with the product of dark holes (Fig. 2), readily quantified by digital image processing of BSE im-

\[
M(\% \text{ weathered}) = M_0 + \frac{E_a}{RT} \ln(1 + \frac{1}{T_0})
\]

where \( M(\% \text{ weathered}) \) is the percent of the plagioclase surface weathered, \( M_0 \) is the initial matrix plagioclase, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T_0 \) is the reference temperature.

4) Assumptions regarding environmental change. Our in situ samples record weathering over 2000–2700 14C years, which we assume integrates climatic variability. While the late Holocene has been a relatively stable climatic period globally (Bryson, 1993; COHMAP, 1988), and perhaps in Hawaii (Gavenda, 1992), we can only assume that contemporary isohyet and isotherm relationships were valid for this period. It is likely that surface microenvironments have changed, for example by changes in rock coating (Dorn et al., 1992) and the growth of epilithic organisms (Jackson, 1971); we assume that the sampled microenvironments have remained constant, or have experienced changes of similar magnitude and direction, for the last 2700 14C years on Hualalai. Lastly, we assume that our average measurement for two hundred grains at ten outcrops is truly representative of the general state of plagioclase dissolution for the last Holocene — and not an artifact of some environmental change or site-specific factor (White and Hochella, 1992).

5) A positive feedback may occur to amplify our measurement, because more pores should retain more water, which in turn would result in more weathering. Little data, however, exist on this topic. The only quantitative study we know of on in situ weathering of basalts over time scales similar to our study is an examination of weathering rinds over 10^3 to 10^4 years, showing a decrease in weathering rates over time (Colman, 1982). This relationship should not occur if a positive feedback occurs by this mechanism. To test a positive feedback, we examined samples from five different outcrops from the highest elevation site (coldest) and lowest elevation site (warmest). They were weighed. These ten samples were placed outside (in Arizona, at ambient temperatures) and 2 mm water was sprinkled on them. Samples from the lowest site (most porosity) returned to their air dry weight faster than the samples from the highest site (least porosity). The experiment was conducted again with four millimeters and six millimeters of simulated precipitation, with the same results. This preliminary study suggests that a positive feedback, due to more water retention, probably does not occur for our samples. We suspect that this is because our samples were collected from topographic highs (pinnacles) in basalt flows. Water drains well in these places, and capillary water evaporates more rapidly from the larger holes, just like water evaporates more rapidly from a sandy soil than a clay soil.

6) Mesoscale climatic values may not necessarily approximate moisture and temperature conditions. We used available mean annual isohyet and lapse-rate data in Table 1, but these values may not portray seasons when more weathering occurs, or true hydraulic and thermodynamic conditions of weathering (Pope et al., 1995). Boundary-layer microclimatic research is in progress to refine the moisture and temperature variables for the sampled sites, but the values we report are best available approximations at this time.

**PALEOCLIMATIC SIGNIFICANCE**

Depending upon geomorphic setting and hydrogeology, natural weathering can be termed "bare rock," "regolith covered," or some combination. Bare-rock weathering occurs when physical erosion exposes unaltered minerals at a rate faster than the latter can be weathered. Solute-fluxes (and CO₂ consumption) tend to reflect the mineralogical abundance of the most-rapidly dissolved components (Stallard, 1985). Regolith-covered weathering happens when high rates of soil formation lead to burial of primary minerals whose dissolution is subsequently limited by transport of the reactants into, and products out of soil profiles. Hydrologic processes control solute fluxes in the endmember case of regolith-limited weathering (Stallard, 1985).

The distinction between weathering-limited landscapes (bare rock) and transport-limited landscapes (regolith covered) has long been recognized as an important dichotomy in geomorphology (Gilbert, 1877). An important question is: Which limiting case best describes weathering globally? In the transport-limited regime, hydrologic factors outweigh the specific weathering susceptibilities of the minerals. In other words, the weathering dependencies we measure in Hawaii, where there is no regolith, can only be used in global carbon cycle models if bare-rock weathering consumption of CO₂ dominates globally (Lasaga et al., 1994).

Weathering-limited geomorphic regimes are likely to be extremely important in the consumption of CO₂. Lithologic susceptibility to weathering varies by orders of magnitude; in the laboratory, cation-rich olivines weather over 1000 times faster than cation-poor kaolinite and quartz (Brady and Walther, 1989). This is important because dissolution of Ca-and Mg-silicates is the primary means of CO₂ removal (Urey, 1952; Berner, 1992), and these minerals are continuously exposed to weathering solutions when erosion dominates. In the
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transport-limited regime, the same minerals will dissolve out in their exposed proportion. Therefore, if the field is analogous to the lab, there must be substantially greater acidity consumption in the weathering-limited regime. This analysis assumes that the exposed surface area and mineralogy of the rock being weathered are the same. Obviously, there will be much more surface exposed in the thick regolith of a transport-limited geomorphic regime. However, the transport-limited soil should possess an appreciably smaller proportion of cation-rich minerals because of the aforenoted instability. For these reasons we apply our “bare rock” results from Hualalai to consider weathering controls on climate.

Our long-term (2000–2700 14C years) in situ measurement of plagioclase $E_a$ ($\sim 26.2 \text{ kcal/mol}$) is somewhat higher than the short term (a few years) watershed study ($\sim 18.4 \text{ kcal/mol}$) of Velbel (1993) and the laboratory study of albite $E_a$ (21.2 ± 3.5 kcal/mol) by Hellmann (1994). These three studies exemplify measurement of $E_a$ in very different conditions: in the laboratory (e.g., Brady, 1991); in situ examination of bare-rock weathering (this study); and watershed studies of flow through a regolith-covered landscape (Velbel, 1993).

These three $E_a$ measurements are appreciably higher than activation energies used in climate models (Berner, 1991, 1993; Berner et al., 1983; Brady, 1991; Lasaga et al., 1994; Schwartzman and Volk, 1989; Volk, 1987; Walker et al., 1981) indicating that weathering has a somewhat tighter control over climate than previously thought. If we use our in situ measurement of $\sim 26.2 \text{ kcal/mol}$, a substantial effect is shown in Fig. 4, where our results are used as input in the global carbon cycle model of Berner (1991) to calculate CO2 levels over the past 80 million years. To put these numbers in perspective, a temperature change of 2°C was sufficient to trigger the most recent ice age, and at that time atmospheric CO2 levels were only one-third less than those at present (Berner et al., 1979).

Our results are preliminary, for the foregoing reasons. Nevertheless, there are areas critical to the accurate modeling of climate evolution where field measurements are lacking and lab measurements are inappropriate. Obvious directions to apply rock-based measurements of weathering are to quantify the temperature dependence of weathering by organic acids, and the temperature dependence of Mg-silicate weathering, a large component of weathering-induced CO2 consumption. Because the rock-based approach we propose is focused on the reactivity of specific mineral surfaces, we should be able to better link mineralogy and organic activity to CO2 consumption by weathering in the field over geological timescales. This approach may also assist in establishing the extent to which the transition from bare-rock weathering to regolith-covered weathering affects the consumption of CO2 by global silicate weathering.

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REFERENCES


FIG. 4. Calculated global temperatures and atmospheric $p_{CO_2}$ values as a function of weathering input function using the global carbon cycle model of Berner (1991). We have used all of the geophysical forcing functions of the latter and varied only the temperature dependency of weathering. 15 kcal/mol is the weathering function used by Berner (1993) and based on Brady (1991). The temperature dependency derived in this study of plagioclase weathering is 26.2 kcal/mol. The 10 kcal/mol value is shown to illustrate the importance of the temperature dependence.