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LETTER

Rock-based measurement of temperature-dependent plagioclase weatheringRONALD I. DORN¹ and PATRICK V. BRADY²¹Department of Geography, Arizona State University, Tempe, AZ 85287-0104, USA²Geochemical Research, MS 750, Sandia National Laboratories, Albuquerque, NM 87185, USA

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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 ^{14}C -dated basalt flows on Hualalai Volcano in Hawaii, USA. A rock-based field activation energy of $26.2 \text{ kcal mol}^{-1}$ 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 CO_2 , including outgassing from volcanic activity (Berner et al., 1983; Urey, 1952), metamorphic decarbonation (Nesbitt et al., 1995), and the consumption of CO_2 through silicate weathering (Berner et al., 1983; Brady and Carroll, 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 CO_2 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 HCO_3^- in the ocean ($t > 10^5$ years), the response of silicate weathering to global environmental change is one of the primary determinants of atmospheric CO_2 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-

lard, 1985; Velbel, 1985, 1993). Recent work indicates that basinal solute fluxes reflect short-term (10^2 – 10^3 y) hydro-geochemical steady-states (Gwiazda and Broecker, 1994), and are sensitive to recent natural and anthropogenic changes (Probst et al., 1994). Measurement of weathering over longer timescales may require a sensor with a longer time constant. An alternative to water-based analyses is to cut out the "middle person" and look directly at the rocks themselves. Here, we outline a method for quantifying weathering dependencies in the field using digital processing of BSE images, and apply it to examine temperature-dependent weathering of basalt flows from Hualalai Volcano, Hawaii, USA.

STUDY SITE AND METHOD

The field area was chosen to minimize the effects of organic activity (Berthelin, 1988) and differences in moisture, and to measure a temperature-dependency of weathering which, for the sake of calibration, should be similar to those measured in solute-budget and experimental studies. Hualalai Volcano, Hawaii, is an ideal site to study the influence of temperature on weathering rates because chemically, temporally, and mineralogically similar lava flows (Moore et al., 1987; Moore and Clague, 1991) intersect isohyets which bend uphill to lower mean annual temperatures (Armstrong, 1973; Giambelluca et al., 1986; Fig. 1). We sampled 2000–2700-year-old basalt flows (Rubin et al., 1987) along the 500 mm isohyet (Giambelluca et al., 1986). These flows retain constructional surfaces (Dorn et al., 1992; Kurz et al., 1990); thus, ^{14}C lava flow ages (Moore and Clague, 1991; Rubin et al., 1987) approximate the onset of weathering.

On Hawaii it is possible to "find an area of constant rock type and climate where one portion of the rock is vegetated and another is not" (Berner, 1992, p. 3230). There are three basic types of weathering microenvironments on Hualalai, Hawaii (Wasklewicz, 1994) that we used to discriminate samples at the millimeter to micrometer scale: those rich in organic acids released by lichens and other epilithic organisms (Jackson and Keller, 1970); those covered by silica glaze and other rock coatings (Curtiss et al., 1985; Dorn et al., 1992); and the microenvironments we sampled, namely those lacking organisms and rock coatings. At these xeric sites "chemical weathering is severely limited because introduction of acids to the profiles is

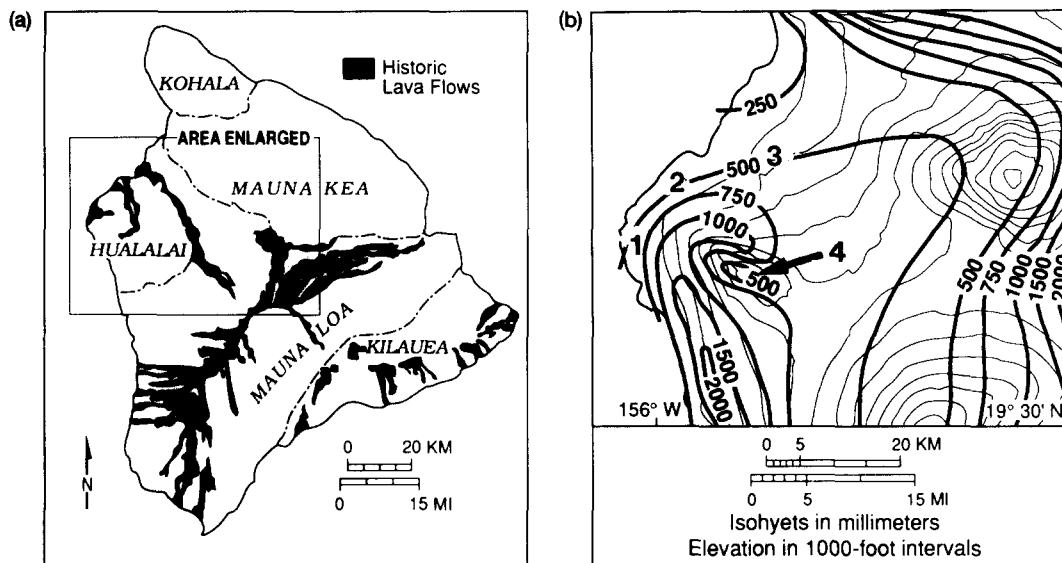


FIG. 1. Maps of (a) the Hualalai study area, and (b) isohyets (Giambelluca et al., 1986) in relationship to elevation and study sites.

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 $\text{Na}_2\text{O} \sim 3.5\%$, $\text{MgO} \sim 0.3\%$, $\text{Al}_2\text{O}_3 \sim 29\%$, $\text{SiO}_2 \sim 49\%$, $\text{K}_2\text{O} \sim 0.3\%$, $\text{CaO} \sim 17$, $\text{TiO}_2 \sim 0.2$, and $\text{FeO} \sim 0.7$. 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 ^{14}C 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 (Hellmann, 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 (Creameens 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).

Site	Flow ²	Age ² (^{14}C yr)	Elev. (m)	Mean Annual Temp ($^{\circ}\text{C}$)	Total Area ³	Percent Dissolved Weighted Mean ⁴	Percent Dissolved Mean 10 sections	Percent Weathered per 10^3 yr
1 ¹	f5c o7	2200-2300	20	23.3	281,500	2.48	2.43	1.08 \pm 0.07
2	f5d p9.2	2140 \pm 100	100	22.8	308,500	2.21	2.22	0.99 \pm 0.06
3	f5d c8.2	2030 \pm 80	500	20.6	303,000	1.64	1.63	0.72 \pm 0.07
4	f5e b0.7	2670 \pm 80	2380	12.5	306,000	0.48	0.45	0.20 \pm 0.06

¹as identified on Fig. 1

²from MOORE and CLAGUE (1991)

³in square micrometres of 200 plagioclase crystals

⁴average weighted by area of plagioclase crystals in each section

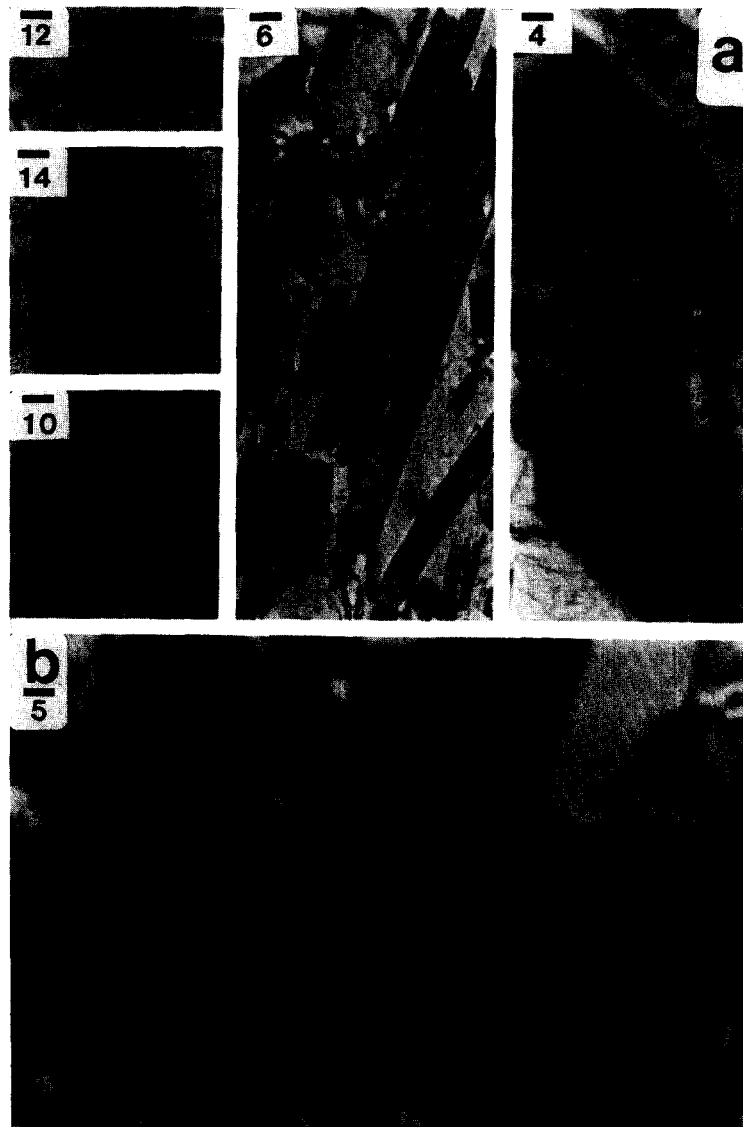


FIG. 2. Matrix plagioclase in weathering rinds on Hualalai Volcano, Hawaii, USA, weathers by dissolution—rather than alteration to secondary products. Scale bars in micrometres. (a) BSE images of *polished* cross section from the f5d c8.2 flow (Moore and Clague, 1991), where smaller arrows identify plagioclase 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).

ated by submicron aluminum polishing grit are seen with secondary electrons (SE), but do not affect the BSE images—although they can be seen on SE images. Thus, it is possible to determine the difference between pitting made by polishing and natural dissolution using both SE and BSE.

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 observe with BSE. Still, we cannot account for pores below the ~0.1 μm limit of resolution for detecting pores with BSE (Kransley 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 the surface weathering rinds of basalts from Mauna Kea and Haleakala (Hawaii, USA), the Cima volcanic

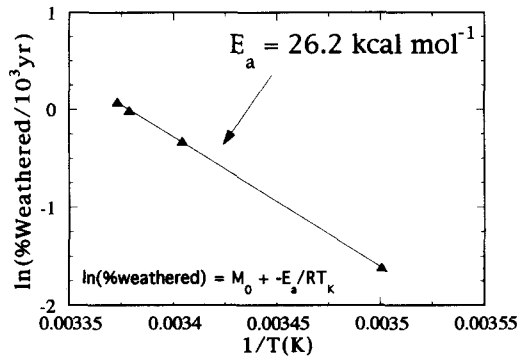


FIG. 3. Rock-based activation energy for plagioclase weathering trends along the 500 mm isohyet on Hualalai, collected from flows that range in age from 2000 to 2700 ^{14}C years (Moore and Clague, 1991). Organic-poor microenvironments, away from acid-secreting organisms and away from rock coatings, are the only microsites studied. Data are from Table 1. The line is the Arrhenius fit to the data as per

$$\frac{\% \text{Weathered}_{T_2}}{\% \text{Weathered}_{T_1}} = \exp \left[\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right],$$

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

4) *Assumptions regarding environmental change.* Our in situ samples record weathering over 2000–2700 ^{14}C 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 ^{14}C 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 late 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 even 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 10^5 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 CO_2 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 the 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 CO_2 dominates globally (Lasaga et al., 1994).

Weathering-limited geomorphic regimes are likely to be extremely important in the consumption of CO_2 . 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 CO_2 removal (Urey, 1952; Berner, 1992), and these minerals are continuously exposed to weathering solutions when erosion dominates. In the

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 aforementioned instability. For these reasons we apply our "bare rock" results from Hualalai to consider weathering controls on climate.

Our long-term (2000–2700 ^{14}C years) in situ measurement of plagioclase E_a (~ 26.2 kcal/mol) is somewhat higher than the short term (a few years) watershed study (~ 18.4 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 ~ 26.2 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 CO_2 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 CO_2

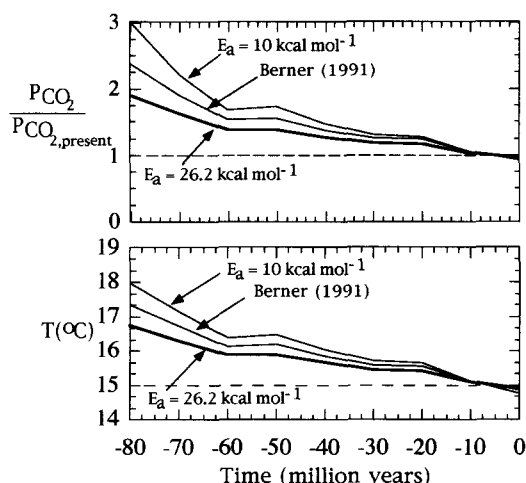


FIG. 4. Calculated global temperatures and atmospheric $p\text{CO}_2$ values as a function of weathering input function using the global carbon cycle model of Berner (Berner, 1991). We have used all of the geophysical forcing functions of the latter and varied only the temperature dependency of weathering. 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.

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 CO_2 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 CO_2 consumption by weathering in the field over geological time-scales. 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 CO_2 by global silicate weathering.

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