Thickness of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks

A. Joshua West*
Department of Earth Sciences, University of Southern California, 3651 Trousdale Parkway, Los Angeles, California 90089, USA

ABSTRACT
Quantitative understanding of variability in weathering fluxes on the modern Earth is limited because little is known about where the most important weathering reactions take place. This is partly because the locus of weathering is difficult to measure empirically. Inverse analysis of a parametric model presented here provides first-order constraints on variability in the thickness of the zone of active weathering. Results suggest that the effective thickness of the weathering zone varies relatively little across several orders of magnitude of denudation rate. At low to moderate denudation rates, reactions in soils may dominate weathering fluxes at the catchment scale, but the contribution from soil weathering decreases at higher denudation rates. Consequently, increased erosion leads to higher weathering fluxes, sustained by progressively greater contributions from weathering in bedrock. The effect of climate (temperature and runoff) on weathering fluxes is apparently weaker at low denudation rates than at high denudation rates, such that erosion, and potentially associated bedrock weathering, may be important for maintaining climate-stabilizing feedbacks in Earth’s carbon cycle.

INTRODUCTION
Mineral weathering plays a central role in mass exchange between the solid Earth and its life-sustaining surface. Weathering produces soils and nutrients for ecosystems (Vitousek et al., 2003), and regulates the long-term carbon cycle and global climate (Berner, 2004). This lends fundamental importance to quantitatively understanding variability in weathering, but such understanding has remained elusive. There are a number of reasons for this, one of which is that it is difficult to assess where weathering takes place, for example how important the regolith and soil environment is in determining total fluxes transported by rivers. Weathering fluxes are determined by the amount of dissolution that occurs over the duration of time that mineral material spends passing through the weathering zone (e.g., Chamberlain et al., 2005), but the scale of this weathering zone is not well defined. Steady-state denudation implies a relationship between fluxes from chemical weathering ($\chi$, mass area$^{-1}$ time$^{-1}$) and total denudation rate ($\epsilon$, mass area$^{-1}$ time$^{-1}$) of the form (Gabet and Mudd, 2009; Hilley et al., 2010):

$$\chi = \epsilon R_k [1 - \exp(-R \cdot z/\epsilon)],$$

where $\chi_k$ is the mass fraction of chemically mobile material in the bedrock (unitless), $z$ is the effective depth of the weathering zone (mass area$^{-1}$), and $R$ is the rate of reaction (time$^{-1}$). There are two major challenges to applying the general expression in Equation 1 to quantifying weathering rates across the Earth’s surface: (1) determining the parametric controls on reaction rate, and (2) defining the weathering depth. Here, a general formulation for $R$ is adopted based on principles of reaction kinetics, and variability in $z$ is explored by inverse analysis. A key aspect of this formulation is the distinction between the reaction rate of chemical weathering and the total flux from chemical weathering.

REACTION RATES
Explicitly considering variation in reaction rate distinguishes this approach from previous geomorphic models, which assume that this is fixed. Hilley et al. (2010), who provided the most general exploration of Equation 1, did not account for any changes in the rate of weathering. Gabet and Mudd (2009) accounted for changes in weathering rate with time, but not for other variation in weathering rate, and they provided a solution only for one specific relationship between $z$ and $\epsilon$.

Using as a basis the general expression for mineral dissolution rate derived from kinetic theory and laboratory experiments (Lasaga et al., 1994), the following relation (developed in the GSA Data Repository1) describes total weathering fluxes as a function of denudation rate ($\epsilon$), runoff ($Q$), and temperature ($T$):

$$\chi = \epsilon \chi_0 \left[1 - \exp\left(-K \left(1 - \exp\left(-k_w \cdot Q\right)\right) \exp\left(\frac{E_o - E_a}{RT} \cdot \left(\frac{z}{\epsilon^{\sigma+1}}\right)\right)\right]\right],$$

where $K$ describes the inherent characteristics of mineral weathering and the dependence on grain size, $k_w$ describes the role of water flow, $\sigma$ describes the effect of time on weathering rate, and $E_o$ is the activation energy. Equation 2 is proposed as a general parametric form for predicting weathering fluxes. It provides a deterministic relationship based on the principles of steady-state denudation and reaction kinetics, with somewhat crude simplifications of kinetic terms permitting practical use for predicting large-scale variability in weathering fluxes. Models accounting for details not captured by Equation 2 (e.g., solution composition, including variability in inorganic and organic acid concentrations, soil mineralogy, and catchment hydrology) are likely to provide a more accurate and complete quantitative representation (Godderis et al., 2009; Lebedeva et al., 2010). Such models may be ideal for some applications, for example in specific catchment systems where many of the key hydrologic and mineralogic characteristics are well known. However it is likely to be difficult if not impossible to realistically infer detailed variation in the range of parameters in these models, for example in soil hydrology, at the spatial and temporal scale necessary to apply to many problems, such as modeling the global carbon cycle over geologic time.

PARAMETERIZING WEATHERING ZONE THICKNESS
A major challenge to evaluating Equation 2 is defining $z$, since variability in the thickness of the weathering zone across the Earth’s surface is poorly constrained. While there is information about the depth of observable regolith, defined either in terms of chemical depletion (e.g., Brantley and Lebedeva, 2011) or physical mobility (e.g., Heimstath et al., 1997), it remains unclear how either of these depths relate to the zone of active weathering. Given this, parameterizing weathering thickness is not straightforward. One approach is to assume that weathering thickness

1GSA Data Repository item 2012229, supplementary information, is available online at www.geosociety.org/pubs/G33041.htm or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
A similar approach may be possible with data from other lithologies, such as felsic metamorphics, such that lithological variations are minimized. From solute fluxes corrected for atmospheric deposition and contribution 2 (see the Data Repository). Values of to determine parameter values based on the best statistical fit of Equation 4. Appropriate parameter values, for example, for particle size. Instead, data to predict weathering fluxes, but it is difficult to confidently assign appropriate parameter values, for example, for particle size. Instead, data on weathering fluxes at the catchment scale (West et al., 2005) are used to determine parameter values based on the best statistical fit of Equation 2 (see the Data Repository). Values of in this dataset reflect weathering-derived cation fluxes from silicate mineral dissolution, calculated from solute fluxes corrected for atmospheric deposition and contribution from carbonate and evaporite minerals. The data come exclusively from catchments with bedrock of granitic to granodioritic composition, including felsic metamorphics, such that lithological variations are minimized. A similar approach may be possible with data from other lithologies, using the same functional form but expecting parameter values to vary. Denudation rates (e) associated with each data point are derived from measured riverine fluxes (sediment plus total chemical erosion fluxes), or from the inventory of cosmogenic nuclides (e.g., 10Be in quartz) from river sediments (for details, see West et al., 2005).

Best-fit parameter combinations and associated uncertainties were calculated for Equation 2 using each of Equations 3, 4, and 6 for z, as well as using arbitrary functions; for example, linear dependence on e. In each case, the implied thickness of the weathering zone varies little (<50%) across the four orders of magnitude in denudation rate in the data set (Fig. 1). There is at present no robust basis for determining the most appropriate functional form for describing z, and no clear general solution to this problem, but the striking constancy of inferred z based on the inverse analysis appears to be independent of chosen form. Given this, a general best-fit solution was determined for Equation 2 based on the assumption that z remains constant; the resulting best-fit parameter values are shown in Table 1. In principle, the calculated thickness of the weathering zone can be converted into an equivalent vertical depth based on density. Weathering may take place in both regolith and soil, with differing densities; for a reasonable range of ρ = 1.5–2.5 g cm⁻³, the inferred thickness would be h = 3.5–5.9 m (66% confidence interval = 0.11–27.4 m). Despite the large uncertainty, these represent sensible values, with intriguing implications. One implication is that the weathering zone is not always contained entirely within the regolith, particularly at the highest denudation rates. As denudation rate increases, the depths of both chemically depleted and physically mobile regolith are known to thin dramatically from field observations (eventually giving way to bare bedrock landscapes with scales inversely with erosion rate, following the logarithmic function empirically observed for the production of physically mobile soil (Heimsath et al., 1997):

$$z_s = -\frac{1}{c_s} \ln \left( \frac{e}{c_s} \right),$$  

(3)

where $z_s$ is the soil depth, $c_s$ is the rate of soil production when $z_s = 0$, and $c_s$ is a constant. If the overall thickness of the weathering zone follows a similar scaling relationship, then $z_s$ in Equation 3 can be used as depth $z$ to solve Equation 2. This soil depth may also vary as a function of climate, and a kinetic dependence of zero-depth weathering can be introduced, so that

$$z = -\frac{1}{c_s} \ln \left( \frac{e}{c_s} R(T,Q) \right),$$  

(4)

where

$$R(T,Q) = \left[1 - \exp(-k_w \cdot Q) \right] \exp \left( \frac{E_s}{RT} - \frac{E_s}{RT} \right),$$  

(5)

based on the simplified kinetic terms (as in Equation 2).

Another approach is to assume that the thickness of the weathering zone is dictated by the extent to which waters penetrate into the subsurface, which in turn may be controlled by relief (Hilley et al., 2010). Relief $S$ is a power-law function of denudation rate ($e = aS^b$, where a and b are empirical constants; Montgomery and Brandon, 2002); so, if weathering thickness is directly proportional to relief-driven water penetration, and ignoring other effects such as lithology-dependent permeability structure, then:

$$z = \left( \frac{e}{a} \right)^{\frac{1}{b}}$$  

(6)

Equation 2 can then be solved using $z$ from Equation 6.

**INVERSE ANALYSIS OF WEATHERING THICKNESS**

It is theoretically possible to calculate a forward solution to Equation 2 to predict weathering fluxes, but it is difficult to confidently assign appropriate parameter values, for example, for particle size. Instead, data on weathering fluxes at the catchment scale (West et al., 2005) are used to determine parameter values based on the best statistical fit of Equation 2 (see the Data Repository). Values of in this dataset reflect weathering-derived cation fluxes from silicate mineral dissolution, calculated from solute fluxes corrected for atmospheric deposition and contribution from carbonate and evaporite minerals. The data come exclusively from catchments with bedrock of granitic to granodioritic composition, including felsic metamorphics, such that lithological variations are minimized. A similar approach may be possible with data from other lithologies, using the same functional form but expecting parameter values to vary.

**TABLE 1: BEST-FIT PARAMETER VALUES FOR EQUATION 2 BASED ON CONSTANT SOIL DEPTH**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best-fit value (66% confidence range)</th>
<th>Range of expected values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_s$</td>
<td>0.09 (0.04–0.13)</td>
<td>0.08–0.11</td>
</tr>
<tr>
<td>$K_w$</td>
<td>2.6 x 10⁻¹ (7.6 x 10⁻¹–1.2 x 10⁻¹)</td>
<td>Unknown (dependent on particle size)</td>
</tr>
<tr>
<td>$k_w$</td>
<td>7.6 x 10⁻¹ (1.5 x 10⁻¹–3.0 x 10⁻¹)</td>
<td>Unknown (dependent on hydrology)</td>
</tr>
<tr>
<td>$E_s$</td>
<td>45.3 (14.6–79.2) kJ mol⁻¹</td>
<td>41.8–125.5 kJ mol⁻¹</td>
</tr>
<tr>
<td>$z$</td>
<td>8.9 (0.26–41.0) t m⁻³</td>
<td>Unknown (see text)</td>
</tr>
<tr>
<td>$\sigma + 1$</td>
<td>0.89 (0.66–1.13)</td>
<td>0.553–0.636³</td>
</tr>
</tbody>
</table>

*Note: Symbols as in text.
1Fraction of cations in fresh rock (Rudnick and Gao, 2003).
2Activation energy of silicate mineral dissolution (Brantley, 2003).
3Time dependence of weathering rate (Gabet and Mudd, 2009).
zero regolith depth), but calculated weathering zone thicknesses do not decrease in tandem. This suggests that much of the weathering must be taking place outside of the soil zone, consistent with the observation of significant contribution of solutes from deep groundwater to rivers in actively eroding mountains, such as in the Himalaya (Tipper et al., 2006) and Taiwan (Calmels et al., 2011).

At the same time, the analysis equally suggests that weathering thicknesses in some cases are smaller than observed regolith depths (i.e., the best-fit \( h_w \sim 4 \) m is considerably smaller than the full depth of chemically depleted regolith in many locations, particularly in the tropics). This implies that there may be a restricted zone of active chemical reaction within an otherwise relatively inert but chemically depleted regolith, which cannot surprise anyone familiar with the regolith mineral dissolution fronts that often define narrow bands in which individual minerals disappear (cf. Brantley and Lebedeva, 2011).

The extent to which either of these two effects is more globally prevalent is difficult to assess given that the present analysis only weakly constrains \( z \) and thus \( h_w \). If \( h_w \) is at the higher end of the uncertainty range (tens of meters), then the weathering zone will extend beyond the regolith in many environments. However, if \( h_w \) is at the lower end of this range (tens of centimeters), then this would only be true in landscapes with very thin soils or bare bedrock.

There is clearly much yet to be learned about the thickness of the weathering zone. There remains considerable need for direct observational data, aiming to test the model predictions presented here. Making measurements of weathering thicknesses will require careful attention to identify what area in the subsurface is actually contributing to active chemical reaction. Moreover, care is required in interpreting the meaning of weathering thickness as defined by \( h_w \); this is unlikely to represent a simple thickness observable in one-dimensional physical terms such as in a single mineral dissolution front, or in the depth of mobile material. Instead, \( z \) and \( h_w \) reflect an integration of the area undergoing active chemical reaction, including, for example, the summation of multiple dissolution fronts in soil profiles as well as weathering along bedrock fractures. The key point is that there must be an explicit distinction between the overall thickness of this zone in which active chemical weathering processes are taking place, and the readily observed depth of regolith, whether defined in chemical terms by depletion or in physical terms by mobility.

**VARIATION IN WEATHERING FLUX**

In addition to information about the weathering zone thickness, the calculated parameters provide some insights into global controls on weathering fluxes. The best-fit values are compared with ranges expected from independent evidence in Table 1. \( \chi_c \) is the fraction of weatherable mass (Ca + Mg + Na + K for \( \delta \) defined by cation fluxes) in fresh rock and is consistent with the composition of felsic (granitic to granodioritic) rocks. \( E_r \) reflects an integrated activation energy of the multimineralic assemblage undergoing dissolution, and is within the range observed in experiments with individual silicate minerals. These agreements suggest that the model provides a physically reasonable description of weathering fluxes. The parameter \( \sigma \) reflects the time dependence of mineral dissolution; the best-fit value reflects weaker time dependence than previously inferred (White and Brantley, 2003), but this effect remains to be understood mechanistically, so it is difficult to assess whether this discrepancy is important.

Figure 2 shows the relationship between weathering flux and denudation rate \( \epsilon \), runoff \( Q \), and temperature \( T \). An important feature in Figure 2A is the break in slope of the model curve in the weathering-denudation space. For small values of \( \epsilon \) (i.e., at low denudation rates), the weathering flux is linearly related to denudation rate, with Equation 2 effectively simplifying to:

\[
\sigma = \epsilon \chi_c.
\]

Equation 7 defines the supply-limited condition where all cations are leached from rock material that is supplied by erosion (West et al., 2005). The flux from weathering is determined by the amount of material supplied by erosion and cannot exceed this limit at steady state (shaded region in Fig. 2A). At higher denudation rates, weathering flux varies nonlinearly with denudation rate, with Equation 2 effectively reducing to the reaction-rate term in the exponent (i.e., the weathering-limited regime). The terms “weathering” and “supply” limits are used here instead of “kinetic” and “transport” limits (Stallard and Edmond, 1983; West et al., 2005) to avoid confusion with terminology used in reactive-transport modeling (e.g., Maher, 2010).

The implication of the best-fit solution shown in Figure 2A is that weathering fluxes continue to increase even at Earth’s highest denudation rates. Such sustained increases in weathering fluxes at high denudation rates contrast with proposed humped dependence of weathering flux on denudation rate, in which weathering fluxes reach a peak value and decrease at the very highest denudation rates (Gabet and Mudd, 2009; Hilley et al., 2010; Ferrier and Kirchner, 2008). The humped outcome results from fixing the value of \( \epsilon \) in Equation 3 to yield progressively thinner soils (and, in association, thin weathering depths) at high denudation rates. Rates of soil weathering specifically (i.e., weathering taking place just within the soil zone) should follow a humped dependence on denudation rate, precisely because soils get thinner and thinner as denudation rates increase. However, at the same time, weathering within the soil zone makes up a progressively smaller portion of the total weathering flux within catchments, and the weathering flux derived from outside the soil zone becomes more and more important, thus continuing to generate high weathering fluxes at the catchment scale.

Given the large uncertainty in parameter values, this data set is not sufficient to conclusively distinguish between increasing and decreasing weathering fluxes at the very highest denudation rates (cf. Fig. 2A). More
data from the most rapidly eroding terrains may help to reduce the uncertainties, and make it possible to more confidently assess the key relationships at these highest denudation rates. However, the highly nonlinear model and correlated parameters make it difficult to significantly reduce uncertainties, and more focused mechanistic studies may be required to unravel the exact nature of the relationship between erosion and weathering in these environments.

**ROLE OF CLIMATE AND IMPLICATIONS FOR CARBON-CYCLE FEEDBACKS**

One important implication of the model presented here is that, at relatively low denudation rates, runoff and temperature both become less relevant in determining weathering fluxes, because the role of material supply becomes dominant (Fig. 3). A weathering feedback in the global carbon cycle requires change in weathering flux as a function of temperature and/or runoff (Berner and Caldeira, 1997). At low erosion rates, as temperature and runoff exert progressively less influence on weathering rates, the direct weathering feedback becomes weak to nonexistent. The parameterization presented here provides a basis for quantitatively assessing how such supply-limited weathering fluxes may have influenced direct carbon cycle feedbacks in Earth’s past. It is possible that higher runoff may increase long-term denudation rates and supply new material for dissolution, generating an indirect feedback, but this effect needs to be better quantified for stable, slowly eroding landscapes.

**REFERENCES CITED**


Manuscript received 22 November 2011
Revised manuscript received 24 March 2012
Manuscript accepted 30 March 2012
Printed in USA