GSA DATA REPOSITORY 2012229

Supplementary Information for "The depth of the chemical weathering zone and implications for erosional and climatic drivers of weathering and for carbon-cycle feedbacks"

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Part 1. Defining the Rate of Reaction in the Model

In order to account for variation in *R*, the rate of reaction, the general expression that describes mineral dissolution rate based on kinetic theory and laboratory experiments (Lasaga et al., 1994) is used as a starting point:

$$\mathcal{R}_{th} = k_0 A_{min} e^{-\frac{E_a}{RT}} f(a) f(\Delta G) \qquad \text{[DR1]}$$

where R_{th} describes the theoretical reaction rate, A_{min} is the mineral surface area, E_a is the Arrhenius activation energy, *R* is the gas constant, *T* is the temperature, *f(a)* describes the dependence of reaction rate on the activity of aqueous species in solution, and $f(\Delta G_r)$ is the dependence of reaction rate the distance from equilibrium. The kinetic rate constant, k_o, is related to intrinsic mineral characteristics. This may change with the time that minerals are exposed to the weathering environment, though this effect is difficult to quantify (White and Brantley, 2003).

Equation DR1 provides a fundamental mechanistic framework. In principle, it is possible to solve this using detailed knowledge of catchment hydrology and soil mineralogy, in order to predict weathering fluxes in catchment systems (e.g., Godderis et al., 2009). Such implementation is difficult to apply broadly, particularly in the geologic past or over large spatial extent where hydrology and mineralogy are effectively unconstrained. A series of basic simplifications are made here in order to capture the variability in *R* without requiring detailed knowledge of specific environments. Firstly, *f(a)*, the relative activities of species in solution, are considered constant, and this term is ignored. This does not account for the wide heterogeneity in the composition of soil and groundwater solutions that are actively involved in weathering, including the variable presence of organic and inorganic acids. It could be possible in future work to add simplified expressions describing such effects, for example to include strong acids or biological activity, but these are not included here.

The influence of deviation from equilibrium, $f(\Delta G_r)$ in Equation DR1, is treated based on the fluid-transport control on weathering in natural environments (Lasaga et al., 1994; Maher, 2010):

$$\mathcal{R} \propto [1 - \exp(-k_w . q)] \qquad \text{[DR2]}$$

where k_w is an constant and *q* is the flow rate of water ($m.yr^{-1}$), on the basis that increasing flow rate leads to solutions that are farther from equilibrium. The actual behavior of $f(\Delta G_r)$ is likely to vary by mineral type, dissolution mechanism, and saturation state (cf. Lasaga et al., 1994), and is likely to be more complicated than Equation DR2, but this form may provide a reasonable first-order simplification. In fact, Equation DR2 can reasonably describe the bulk empirical behavior

of natural systems with approximately uniform flow, such as lab experiments and soil solutions (Maher, 2010). To provide a globally-scalable relationship, the assumption here is that river runoff Q reflects the average flow rate q in catchment systems. This ignores the obvious range of flow rates along different flowpaths in catchment systems, which are difficult to parameterize in a simple manner given the limited current understanding of how flow path distributions vary in catchments in different settings (cf. Maher, 2011). While this problem is certainly fertile ground for future work, the relatively basic assumptions in Equation DR2 should provide a reasonable starting point.

The functional form of Equation DR2 represents a departure from previous similar attempts to parameterize weathering fluxes at the global scale, which have generally assumed either a direct proportionality with runoff (e.g. White and Blum, 1995), or a power law relationship (e.g. West et al., 2005; Riebe et al., 2005). These have been based on the premise that weathering-derived solute fluxes depend inherently on runoff (i.e., because flux = concentration x runoff). A key distinction here is that the intent with Equation DR1 is not to determine the runoff-dependence of weathering flux *per se*, which is defined by Equation DR1 in the main text. Instead the goal is to determine how the *rate of reaction* varies as a function of runoff, with the primary control being the influence on saturation state, reflected in simple form by Equation DR2.

Another simplification is to treat the Arrenhius relationship in Equation DR1 as a general (rather than mineral-specific) term describing the temperature-dependence of weathering rate. In this case, the Arrhenius term is cast to describe temperature variation relative to a reference temperature T_o, using T_o=286K as representative of mean terrestrial temperature (Brady and Carroll, 1994):

$$\mathcal{R} \propto \frac{E_a}{R}\left({}^{1}/_{T} - {}^{1}/_{T_o}\right) \qquad \text{[DR3]}$$

where E_a is the activation energy and R is the gas constant. This treatment follows that used frequently in previous studies of global weathering (e.g. Brady and Carroll, 1994; White and Blum, 1995; West et al., 2005).

Finally, the change in surface area and intrinsic dissolution rate with time ($k_o.A_{min}$ in Equation DR1) can be accounted for based on empirically observed changes of mineral weathering rates with time. This requires accounting for the progressive changes as minerals evolve through the weathering process, such that Equation DR1 becomes, as derived by Yoo and Mudd (2008) and Gabet and Mudd (2009):

$$\varpi = \varepsilon\chi_m\left[1 - exp\left(\frac{-\mathcal{R}(T,Q)\cdot K\cdot(z/\varepsilon)^{\sigma+1}}{\sigma+1}\right)\right] \qquad \text{[DR4]}$$

where σ describes the decrease in weathering rate with time and the constant K defines the intrinsic characteristics of mineral weathering, and its dependence on surface area. This constant is defined as:

$$K = \frac{6abw_m}{D\rho_m} \qquad \text{[DR5]}$$

where a and b are constants reflecting inherent characteristics of mineral weathering, ρ_m is the mineral density, w_m is the mineral molar weight, and D is the grain diameter (Gabet and Mudd, 2009).

Combining Equations DR2, DR3, and DR4 yields the expression in Equation 2 in the text, describing total weathering fluxes, under given erosion rate, runoff, and temperature. This is based on the fundamental rate equation (Equation DR2) but is adapted based on a series of largely empirical simplifications of individual terms. The application in this study is for weathering of predominantly silicate lithologies; the parameterization of reaction rate may be quite different when carbonates or evaporites are dominant, given the very different dissolution kinetics and hydrology expected in these cases.

Part 2. Statistical Approach

This study is partly based on an inverse analysis of the proposed weathering model (Equation 2) with reference to the global weathering dataset compiled by West et al. (2005), with the addition of new data from the Himalaya (specifically from the Marsyandi River and associated tributaries in Nepal; Gabet et al., 2010). Because of the non-linearity in Equation 2, uncertainties in modeled ω are particularly large at high values of ε. To best constrain the relationship between these variables at high denudation rates, all of the individual catchments from Nepal and from New Zealand (the two most rapidly eroding regions with multiple data points from each region) are treated independently in the analysis, rather than using single data points reflecting regional averages. This yields a total dataset of 46 points: the 20 regionally-averaged data points from West et al. (2005), the 10 data points from the Marsyandi in Nepal (Gabet et al., 2010), and the 16 data points from New Zealand (Jacobson and Blum, 2003). All of the data were treated in the manner described in West et al. (2005) in order to calculate the weathering flux of silicate cations (Ca + Mg + Na + K), and this is then the quantity used in the analysis in this study (as representative of ω).

Best-fit parameters were determined by non-linear least squares fitting. The χ^2 sum of misfits for Equation 2, the weathering model equation (relative to observed ω) was calculated for different parameter combinations, based on the known ε, Q, and T for each data point. Calculation of χ^2 followed *Numerical Recipes* approaches (Press et al., 1996); parameters were scaled to unity for fitting, and χ^2 values were weighted by known uncertainties in ε, Q, T, and observed ω. Uncertainties in ε and ω were taken from West et al (2005) and Gabet et al (2010); uncertainties in Q and T were not reported and were estimated as 10% (1σ). This analysis does not account for the possible effect of seasonally variability in temperature on the parameterization (cf. Lasaga et al., 1994). The best-fit parameter combinations, i.e. those that minimize χ^2 misfits, were determined by a simplex search algorithm, using the Matlab routine fminsearch. The thus-calculated best-fit parameter combinations are used to define the solid black lines in Figures 1 and 2, and the best-fit values reported in Table 1.

Uncertainties on the parameter estimates were determined by Monte Carlo analysis, taking two approaches. In the first approach, the propagation of observed uncertainties onto the best-fit parameter values was estimated by generating 10,000 random artificial datasets of ω, ε, Q, and T, each with a normal distribution centered on the mean values for each data point, with a standard

deviation equivalent to the respective known 1σ uncertainties. Best-fit parameter combinations were calculated for each of these datasets, and parameter uncertainties were determined from the standard deviation of the resulting best-fit parameter distributions.

These propagated uncertainties were insignificant when compared to those determined by the second approach, which involved estimating the uncertainty on the best-fit solution itself by determining the full parameter space that yields χ^2 values associated with probability of at least 60% based on the theoretical χ^2 distribution. This range of parameter space was determined using a brute force simulation, calculating χ^2 across a wide range of parameter values ($n > 10^8$) and excluding all parameter combinations with $\chi^2 < \chi^2_{\text{thresh}}$, where χ^2_{thresh} is the threshold defined by 60% probability for the appropriate degrees of freedom. All solutions meeting this criterion are potentially viable parameter combinations. This set of solutions was used to generate the plots in Figures 1 and 2, and the minimum and maximum values define the ranges in Table 1. There are significant correlations between some of the parameters within the distribution of viable solutions, which is likely to contribute substantially to the large inferred uncertainties and may reflect an inherent drawback of this approach when dealing with the somewhat complicated, highly non-linear models that are proposed for describing weathering fluxes, particularly with relatively small datasets.

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