Differential weathering of basaltic and granitic catchments from concentration-discharge relationships

Daniel E. Ibarra^{a*}, Jeremy K. Caves^a, Seulgi Moon^b, Dana L. Thomas^c, Jens Hartmann^d,
C. Page Chamberlain^a and Kate Maher^c

^a *Department of Earth System Science, Stanford University, 473 Via Ortega, Rm. 140, Stanford, CA, 94305-4216 USA*

^b *Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, 595 Charles Young Dr. East, Los Angeles, CA 90095 USA*

^c *Department of Geological Sciences, Stanford University, 450 Serra Mall, Building 320, Stanford, CA, 94305-2115 USA*

^d *Institute for Geology, Center for Earth System Research and Sustainability, Universität Hamburg, Geomatikum, 20146 Hamburg, Germany*

* Corresponding author. Address: Department of Earth System Science, Stanford University, 473 Via Ortega, Rm. 140, Stanford, CA, 94305-4216 USA. Telephone: +1 (650) 714-5097. Fax: +1 (650) 498-5099. E-mail address: danieli@stanford.edu (D.E. Ibarra)

ABSTRACT

A negative feedback between silicate weathering rates and climate is hypothesized to play a central role in moderating atmospheric CO₂ concentrations on geologic timescales. However, uncertainty regarding the processes that regulate the operation of the negative feedback limits our ability to interpret past variations in the ocean-atmosphere carbon cycle. In particular, the mechanisms that determine the flux of weathered material for a given climatic state are still poorly understood. Here, we quantify the processes that determine catchment-scale solute fluxes for two lithologic end-members—basalt and granite—by applying a recently developed solute production model that links weathering fluxes to both specific discharge (runoff) and the reactivity of the weathering material. We evaluate the model against long-term monitoring of concentration-discharge relationships from basaltic and granitic catchments to determine the parameters associated with solute production in each catchment. Higher weathering rates in basaltic catchments relative to granitic catchments are driven by differing responses to increases in runoff, with basaltic catchments showing less dilution with increasing runoff. In addition, results from the solute production model suggest that thermodynamic constraints on weathering reactions could explain higher concentrations in basaltic catchments at lower runoff compared to granitic catchments. To understand how the response to changing discharge controls weathering fluxes under different climatic states, we define basalt/granite weatherability as the ratio of the basalt catchment flux to the granite catchment flux. This weatherability is runoff-dependent and increases with increasing runoff. For HCO₃⁻ and SiO₂(aq) fluxes, for modern global runoff, the derived mean basalt/granite weatherability is 2.2 (1.3–3.7, 2σ) and 1.7 (1.6–2.1, 2σ), respectively. Although we cannot determine the array of individual processes resulting in differences among catchments, the relative differences in certain model

48 parameters that represent catchment-scale weathering fluxes of granitic and basaltic lithologies
49 are robust. Our approach provides a mechanism that links runoff with the distribution of global
50 sub-aerial silicate lithologies to understand how the basalt/granite weatherability of the Earth's
51 surface may have varied on geologic timescales. The relationships between basalt/granite
52 weatherability and runoff derived in this study could be used to parameterize the silicate
53 weathering negative feedback to model past changes in $p\text{CO}_2$.

1. INTRODUCTION

Global silicate weathering rates are thought to be modulated by the geographic distribution and areal extent of rock type, growth and decay of mountain ranges, the nature of biological activity, and the intensity of the hydrologic cycle (Berner, 1991; Kump and Arthur, 1997; Gibbs et al., 1999; Hartmann et al., 2009; Pagani et al., 2009; Banwart et al., 2009; Beerling et al., 2012; Kent and Muttoni, 2013; Maher and Chamberlain, 2014; Froelich and Misra, 2014). Understanding the factors that control global silicate weathering rates is fundamental to constraining the evolution of the Earth's carbon cycle over geologic timescales (Urey, 1952; Sagan and Mullen, 1972; Walker et al., 1981; Berner et al., 1983; Volk, 1987; Berner, 1991; 2006a; Caldeira and Kasting, 1992; Kasting, 1993; Caldeira, 1992; 1995; Berner and Caldeira, 1997; Gibbs et al., 1999; Kump et al., 2000; Berner and Kothavala, 2001).

One challenge for reconstructing past weathering rates is the considerable variability in the reactivity of the Earth's surface. For example, basaltic catchments weather faster than other silicates and account for approximately 20 to 35% of the modern global silicate weathering and CO₂ consumption flux, while occupying less than 5% of sub-aerial continental area (Gíslason et al., 1996; 2009; Louvat and Allègre, 1997; Dessert et al., 2001; 2003; 2009; von Blanckenburg et al., 2004; Rad et al., 2007; Hartmann et al., 2009; Gaillardet et al., 2011a; Schopka et al., 2011; Schopka and Derry, 2012; Moon et al., 2014; Balagizi et al., 2015). The higher weathering fluxes associated with basalt weathering have been explained by the high intrinsic reactivity of basaltic mafic mineral assemblages (Oelkers and Gíslason, 2001; Dessert et al., 2003; Gíslason and Oelkers, 2003), increased porosity in the basalt weathering zone (Navarre-Sitchler et al., 2009; 2011; 2013; 2015; Sak et al., 2010; Gleeson et al., 2011), and the importance of hydrologic fluctuations that moderate the water table depth and total stream discharge (Amiotte-Suchet and

Probst, 1993; Bluth and Kump, 1994; Eiriksdottir et al., 2013; 2015; Balagizi et al, 2015; Dessert et al., 2015; Liu et al., 2015). Given the importance of basaltic weathering to total global solute fluxes, recent modeling studies that reconstruct weathering fluxes over the Cenozoic suggest that the weathering of mafic terrains may have been critically important in controlling past levels of atmospheric CO₂ ($p\text{CO}_2$) (Li and Elderfield, 2013; Kent and Muttoni, 2013; Molnar and Cronin, 2015; Jagoutz et al., 2016). However, scaling modern observations of weathering fluxes from catchments to both large spatial and temporal scales (*e.g.*, Wallmann, 2001; Lefebvre et al., 2013; Li and Elderfield, 2013; Kent and Muttoni, 2008, 2013; Mills et al., 2014a; Li et al., 2016; Jagoutz et al., 2016; Cox et al., 2016) remains a challenge due to the lack of phenomenological modeling frameworks that predict weathering fluxes at both catchment and global scales under different climate states.

To reconstruct changes in the geologic past, weathering fluxes are typically parameterized using modern solute flux data to derive a “weathering rate law.” These empirical laws are derived by fitting modern weathering rates to variables such as lithology, runoff, topographic slope, and temperature (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; White and Blum et al., 1995; Gaillardet et al., 1999; Dessert et al., 2001, 2003; Dupré et al., 2003; Navarre-Sitchler and Thyne, 2007; Hartmann et al., 2010; Hartmann et al., 2014a) and are often assumed to follow the form of either an exponential Arrhenius equation or power law (Velbel, 1993; White et al., 1999a; Gíslason and Oelkers, 2003; Carroll and Knauss, 2005; Gíslason et al., 2009; Eiriksdottir et al., 2013; Li and Long, 2014; Moon et al., 2014; Torres et al., 2015; Li et al., 2016). However, as discharge increases, solute concentrations decrease due to dilution, which results in an apparent plateau in weathering fluxes even as runoff increases (Godsey et al., 2009; Maher, 2011; Eiriksdottir et al., 2013; Maher and Chamberlain, 2014).

Close examination of the catchment-scale weathering data on which these empirical weathering laws are derived (*e.g.*, Bluth and Kump, 1994; Godsey et al., 2009; Gíslason et al., 2009; Clow and Mast, 2010; Maher, 2011; Eiriksdottir et al., 2013) demonstrates that the functional forms of the weathering rate laws (*i.e.*, exponential Arrhenius or power-law) do not accurately reflect the decrease in concentration due to dilution with increasing runoff observed for individual catchments. Thus, existing frameworks do not capture the potential for weathering fluxes to plateau as runoff increases. Furthermore, if different lithologies exhibit variable responses to changes in runoff, global weathering fluxes may show a complex behavior depending on the time-varying areal distribution of rock types.

Maher and Chamberlain (2014) recently developed a process-based solute production framework that links weathering fluxes to both runoff and the reactivity of the weathering zone. Given that this modeling approach contains both thermodynamic and kinetic constraints, as well as physical processes that govern the travel time of water through the subsurface, the solute production model could provide a useful alternative approach for parameterizing weathering fluxes because it allows for fluxes to plateau at sufficiently high runoff. However, this model has only been evaluated against single concentration-discharge pair values (*i.e.*, time-averaged, flux-averaged, or single-samples) for global rivers (Maher and Chamberlain, 2014; von Blanckenburg et al., 2015) and long-term monitoring of $\text{SiO}_2(\text{aq})$ concentration-discharge patterns from a few small silicate bedrock catchments (Maher, 2011), and has not been systematically compared to rivers across gradients in lithology, climate, erosion rate, or basin size. As a consequence, it remains unclear whether such an approach could describe the variability in reactivity and hydrologic processes associated with individual catchments. Here, to isolate lithologic controls, we evaluate the ability of the solute production equations to capture patterns in concentration-

discharge relationships exhibited by long-term monitoring of basaltic and granitic catchments (**Figure 1**). In addition, we consider the extent to which concentration-discharge relationships can elucidate the differences in reactivity and composition that lead to large differences in area-normalized weathering fluxes between basaltic and granitic catchments.

By comparing basaltic and granitic catchments, we quantify patterns in observed concentration-discharge relationships for the two major silicate end-member lithologies responsible for terrestrial silicate weathering (Bluth and Kump, 1994; White and Blum, 1995; Kump and Arthur, 1997; Kump et al., 2000; Dessert et al., 2001; Berner, 2006b; 2008). We focus our analysis on two important parameters: (1) the degree to which solute fluxes from individual catchments resist dilution at high runoff and (2) the maximum solute concentrations. These two parameters determine the efficiency with which a catchment produces solute. We find that weathering fluxes from basaltic catchments are both more resistant to dilution at high runoff and have a greater maximum solute concentration, implying that basaltic catchments are more efficient at producing solute for a given climate. We further use these two parameters to show how the basalt catchment flux normalized to the granite catchment flux —the basalt/granite weatherability ratio—changes with runoff.

Earth surface weatherability is often treated as a tunable parameter in biogeochemical models (*e.g.*, Kump and Arthur, 1997; Gibbs et al., 1999; Berner, 2006a; Berner, 2008; Mills et al., 2014a) because it determines the degree of coupling between climate and weathering. In turn, this coupling is a measure of the strength of the negative feedback between climate/atmospheric $p\text{CO}_2$ and silicate weathering. A weak coupling implies that weathering fluxes change little in response to changes in climate, whereas a strong coupling suggests that weathering responds rapidly to small changes in climate (West, 2012; Maher and Chamberlain, 2014; Goll et al.,

2014; Caves et al., 2015a). Our work demonstrates that weatherability cannot necessarily be treated as a constant, even over the short timescales that characterize rapid climate change in the geologic record. Using these results, we propose a framework for linking basalt/granite weatherability to understand the behavior of the silicate weathering feedback over Earth history.

2. BACKGROUND

Quantifying differences in concentration-discharge relationships among catchments of different lithologies may improve models for how weathering fluxes respond to changes at the Earth surface. We use a modeling framework outlined below that starts with the Damköhler number (Da), a dimensionless number that is the ratio of the fluid travel time (T_f [yr]) to the time required to reach equilibrium (T_{eq} [yr]) (Johnson and DePaolo, 1994; Steefel and Maher, 2009; Maher, 2010; Maher and Chamberlain, 2014; Li et al., 2014):

$$Da = \frac{T_f}{T_{eq}} = \frac{R_n L \phi}{q C_{max}} \quad (1),$$

where q [m/yr] is the flow rate (specific discharge), C_{max} [$\mu\text{mol/L}$] is the maximum solute concentration, R_n [$\mu\text{mol/L/yr}$] is the net mineral dissolution rate, and L [m] is the flowpath length, which is multiplied by ϕ (the effective porosity) to give the reactive flowpath length $L\phi$. A large Damköhler number ($Da > 1$) implies that reaction rates outpace advection such that local equilibrium within the weathering zone controls the solute concentrations (Sverdrup and Warfvinge, 1988; Steefel and Maher, 2009; Maher, 2010, 2011; Siirila and Maxwell, 2012; Maher and Chamberlain, 2014; Maher and Druhan, 2014; Li et al., 2014). Although the Da approach is widely used in reactive transport because it incorporates the balance between physical and chemical processes, the Damköhler number is non-unique when attempting to understand the importance of climatic versus lithologic controls on weathering, because changes

in Da can be driven by changes in travel time (T_f) or equilibrium time (T_{eq}), where the latter is set by the ratio between maximum solute concentrations and net dissolution rates ($T_{eq} = C_{max}/R_n$). For example, two catchments may have the same Da , but very different T_f or T_{eq} , meaning their response to changes in runoff (*i.e.*, flow rate) will be very different (**Figure 2a**). Thus, runoff can be factored out of Da to derive the Damköhler coefficient (Dw [m/yr] = $Da \times q = L\phi / T_{eq}$), which describes the reactivity of the material in the weathering zone over a given length scale, and modifies the relationship between concentration and discharge. The implication for concentration-discharge relationships is that Dw values describe the relative rate of increase in solute concentration for a given flowpath length. Thus, increased Dw values can result from either higher reaction rates or long flow paths (Maher and Chamberlain, 2014). Systems with high Dw values exhibit less dilution with increasing runoff compared to catchments with lower Dw values (**Figure 2a**).

In this study, we focus on lithologic controls on Dw . We do not specifically evaluate the effect of erosion rates or differences in climate on Dw , although we do evaluate for relationships between Dw and temperature. Previous work with this solute production model has demonstrated that rapidly eroding mountain belts tend to have higher Dw values (Maher and Chamberlain, 2014). Accordingly, we expect the intra-lithology Dw distributions to be partially driven by these other factors. Given that the Dw value of a catchment reflects the ratio of the reactive flowpath length ($L\phi$) to the equilibrium time (T_{eq}), both of which may be impacted by erosion or climate, we thus emphasize how further stream measurements and upslope analyses might aid in deconvolving the derived concentration-discharge parameters presented below.

2.1 Solute production framework

Data from individual catchments display a range of solute concentrations (C [$\mu\text{mol/L}$]) as a function of discharge (Q [m^3/yr]) (*i.e.* C - Q relationships). The patterns in C - Q relationships that emerge in response to fluctuations in discharge are thought to indicate the processes that control the weathering flux. Thus, such patterns may inform the response of weathering rates to changes in the local climate (Godsey et al., 2009). Here, specific discharge or runoff (q [m/yr]) is defined as the instantaneous discharge (Q [m^3/yr]) divided by the catchment area (A [m^2]), and C [$\mu\text{mol/L}$] is the solute concentration (**Figure 1b**). Below and for the remainder of the paper, we primarily discuss concentration-runoff (C - q) relationships because area normalization allows for direct comparison between catchments whose areal extents may differ by many orders of magnitude.

Maher and Chamberlain (2014) derived a framework for relating solute (C [$\mu\text{mol/L}$]) production to runoff (q [m/yr]):

$$C = \frac{C_0}{1 + Dw/q} + C_{\max} \frac{Dw/q}{1 + Dw/q} \quad (2),$$

where Dw [m/yr] is the Damköhler coefficient, C_0 is the initial solute concentration, and $C_{\max}$ is the maximum solute concentration, which may be associated with a “thermodynamic limit” imposed by approach to equilibrium with the primary and/or secondary mineral assemblages. Previous work with this solute production model (Maher and Chamberlain, 2014; von Blanckenburg et al., 2015) included a scaling factor (7.39) multiplied by the Dw coefficient that emerged from comparison between 1-dimensional reactive transport simulations and the analytical solution above (*cf.* Maher and Chamberlain, 2014). In the current work, we exclude the scaling factor from the analysis since we make no comparison to reactive transport simulations and account for the scaling factor when comparing to previous results from von Blanckenburg et al. (2015) and Maher and Chamberlain (2014). Here, C_0 is the initial solute

concentration, derived from atmospheric deposition and/or hydrothermal or deep groundwater inputs that mix with water in the weathering zone or the river and are independent of discharge. For most catchments, equation 2 can be simplified if C_0 is assumed to be zero (Maher and Chamberlain, 2014):

$$C = C_{\max} \frac{Dw/q}{1 + Dw/q} \quad (3).$$

Observations of constant concentrations with increasing discharge (*i.e.*, “chemostatic” behavior) have demonstrated that $C_{\max}$ can vary among catchments (Godsey et al., 2009; Maher, 2011). The purpose of the C - q analysis carried out in this study is to derive $C_{\max}$ and Dw values for individual basaltic and granitic catchments, and determine trends between these two sample groups. Dw values derived from concentration-runoff data between catchments of comparable lithology allow for a direct, area-independent comparison of the efficiency of solute generation. At a given runoff, catchments with larger Dw values are more efficient at generating solute and hence more likely to approach the $C_{\max}$ concentration. For example, **Figure 2a** demonstrates schematically how, for a given $C_{\max}$, a higher Dw results in a higher $\text{SiO}_2(\text{aq})$ concentration at a given runoff (yellow point ($Dw = 0.15$) vs. green point ($Dw = 1.5$)). Here, we use $\text{SiO}_2(\text{aq})$ to demonstrate these key concepts because it is a neutral species and closely tracks primary mineral silicate weathering (*e.g.*, feldspar to a secondary clay mineral) although we do consider and analyze other major ions (HCO_3^- , Ca^{2+} , Mg^{2+} and Na^+) and measurements of chemical weathering in this paper (see Methods).

The runoff value where dilution effects are observed varies by element (*e.g.*, $\text{SiO}_2(\text{aq})$ dilution occurs at runoff values higher than for HCO_3^- ; Kump et al., 2000; Godsey et al., 2009; Moon et al., 2014). Dilution curves have been previously derived empirically assuming a power law relationship ($C = aQ^b$, where a and b are constants; Pokrovsky et al., 2005; Godsey et al.,

2009; Moon et al., 2014). Chemostatic behavior has been traditionally defined as occurring when the power law exponent (b) approaches zero (*e.g.*, Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015). Previous work has demonstrated the importance of quantifying and understanding the mechanisms behind chemostatic concentrations of different elements observed in rivers for different lithologies and, most importantly, the extent to which maximum concentrations are associated with a thermodynamic limitation (White et al., 1996; Clow and Mast, 2010; Maher, 2011; Maher and Chamberlain, 2014; Maher and Druhan, 2014).

Finally, the equations presented above assume an idealized exponential transit time distribution of discharge, and thus concentrations represent the flux-weighted average concentration recorded by streams (*cf.* Małoszewski and Zuber, 1982; McGuire et al., 2005; McGuire and McDonnell, 2006; Steefel and Maher, 2009; Maher, 2011; Zapata-Rios et al., 2015), although observations and modeling of transit time distributions are complex and demonstrate fractal behavior (*cf.* Kirchner et al., 2000; Scher et al., 2002; Kollet and Maxwell, 2008; Kirchner and Neal, 2013; Maxwell et al., 2016). In our analysis we derive Dw values, which represent the balance of mean transit time to mean reaction rate to take into account permeability and flowpath heterogeneity (Maher, 2011; Maher and Druhan, 2014; Maher and Chamberlain, 2014; Li et al., 2014; Torres et al., 2015).

2.2 Catchment weathering potential

From Equation 3, the area normalized weathering flux (W [t/km²/yr]) is obtained by multiplying the concentration (C) by the runoff (q):

$$W = qC_{\max} \frac{Dw/q}{1 + Dw/q} \quad (4),$$

and converting to mass using the appropriate atomic or molecular weight (g/mol) of the solute of interest. At higher runoff, solute fluxes from a given catchment or river basin plateau due to increased dilution, defining a maximum weathering flux (W_{max} in **Figure 2b**). Higher Dw and C_{max} values result in a higher W_{max} value (the value as q approaches infinity; i.e., $W_{max}=Dw \times C_{max}$). For a given mean observed solute flux (W_{obs}), we can calculate the possible maximum increase in the weathering flux and the absolute weathering potential (ΔWP [t/km²/yr]) of a catchment, which is the difference between the W_{max} and the W_{obs} :

$$\Delta WP = W_{max} - W_{obs} \quad (5).$$

To compare between catchments of different Dw values, this maximum weathering flux is expressed as the normalized weathering potential (WP_{norm} [%]):

$$WP_{norm} = \left(\frac{\Delta WP}{W_{max}} \right) \cdot 100 \quad (6).$$

As shown schematically in **Figure 2b**, for a given Dw and C_{max} , the weathering potential for a chemostatic catchment (blue point) is higher than for a catchment located on the dilution curve (green and red points). Additionally, for a given runoff and C_{max} , catchments with a higher Dw have a higher weathering potential (green point where $Dw = 1.5$ m/yr and $WP_{norm} = 93.3\%$) than catchments with a lower Dw (yellow point where $Dw = 0.15$ m/yr and $WP_{norm} = 59.6\%$). The utility of this new metric is that it incorporates both Dw and C_{max} . Thus, we account for lithology-dependent variations and distributions in C_{max} values (e.g., Dessert et al., 2003; Dupré et al., 2003) when evaluating catchment weathering efficiency.

For catchments where C_0 is non-zero due to contributions from atmospheric deposition (e.g., soluble dust deposition or sea spray) or hydrothermal or deep groundwater inputs, Equation 2 should be used to determine the catchment Dw . However, to represent only the silicate-

weathering contribution to the solute flux, C_0 is subtracted from the dataset. **Figure 3** demonstrates how, within this solute production framework, there is no W_{max} when C_0 is non-zero because at high runoff the first term in Equation 2 dominates, increasing the total solute flux proportional to increasing runoff. Therefore to calculate Dw and C_{max} values, and the resultant W_{max} values, we correct the flux vs. runoff relationships (as shown schematically in **Figure 3**).

3. METHODS

3.1 Data sources

The concentration-runoff datasets considered in this study were compiled from locations where several years (>2 years) of data, comprising at least 20 solute concentration measurements, have been collected (**Figure 1a**). Riverine solute data were compiled from (1) small ($< 10,000 \text{ km}^2$) basaltic and granitic catchments from the U.S. Geological Survey National Water Information System (USGS NWIS) and used in three previous studies (Bluth and Kump, 1994; Dessert et al., 2003; Godsey et al., 2009); (2) basaltic catchments with sufficient concentration-discharge data from Iceland (Eiriksdottir et al., 2013; 2015), and; (3) additional basaltic and granitic catchments ($>90\%$ single-lithology bedrock) identified from the Global River Chemistry Database (GlorRiCh) using the Global Lithologic Map (GLiM) lithology maps (Hartmann and Moosdorf, 2012; Hartmann et al., 2014b). Our dataset is restricted to sites with the paired runoff and solute data needed to constrain the weathering of primary silicate minerals to secondary minerals and to quantify the resulting solutes, total dissolved solids, and cation-equivalent ($\text{SiO}_2(\text{aq})$, Mg^{2+} , Ca^{2+} , K^+ , Na^+ and HCO_3^-) (*e.g.*, Dessert et al., 2003; Gaillardet et al., 1999; Bouchez and Gaillardet, 2014). As noted by previous workers, it is difficult to fit statistically significant concentration-discharge relationships to datasets displaying minimal

discharge variations (Godsey et al., 2009; Moon et al., 2014). Thus, we exclude catchment data showing minimal variations; of these, most were from catchments without sufficient temporal or seasonally representative coverage. In total, our compilation includes data from 44 basalt catchments, and 27 granite catchments (**Table A1**). In addition, we separate some of the basalt and granite catchments into sub-groups based on region (Iceland, Hawaii, Sierra Nevada, and the Pacific Northwest; **Figure 1, Table A1**).

The analysis presented here utilizes some of the longest time-series available for studying riverine dissolved loads (*e.g.*, Godsey et al., 2009; Maher, 2011; Eiriksdottir et al., 2013; 2015; Torres et al., 2015; Moquet et al., 2015), primarily from the USGS NWIS database. We are still limited by both the lack of spatial coverage of these long time-series datasets and by a lack of sampling at extreme runoff values (*e.g.*, Dessert et al., 2015). However, our datasets allow to examine the influence of high runoff variability—particularly at extreme values and to accurately estimate C_{max} and C_0 values. To assess whether using individual C - q pairs biases the dataset toward rare, extreme runoff values, or temporal sampling biases, we also evaluate our dataset by calculating flux-weighted average concentrations for each catchment and deriving Dw values from single concentration-runoff pairs (*e.g.*, von Blanckenburg et al., 2015), assuming different C_{max} values for each sample group (basalt and granite).

3.2 Quantifying catchment-scale weathering efficiency from concentration-runoff relationship fitting

In order to quantify catchment-scale weathering efficiency, we first separate chemostatic and non-chemostatic catchments. For chemostatic catchments, we mathematically define with a power law b -value indistinguishable from 0 (within 95%, $p > 0.05$) (Godsey et al., 2009). Most

of these catchments still likely fit the modeling framework employed in this study, but lack a sufficient number of concentration-discharge measurements at high runoff necessary to demonstrate dilution. For these catchments, we report C_{max} values as the median (and median absolute deviation) of all observed concentrations and do not quantify Dw values. For non-chemostatic catchments, we quantify catchment-specific Dw values using the paired concentration-runoff data and equations 1 and/or 2. We apply a non-linear least squares fitting to derive Dw and C_{max} values using the Gauss-Newton algorithm ('nls2' R package, Grothendieck, 2013) similar to the Newton methods employed by Godsey et al. (2009) and Moon et al. (2014) for power law fits. Finally, we calculate these fits for a variety of dissolved species, including $\text{SiO}_2(\text{aq})$, HCO_3^- (alkalinity), Mg^{2+} , Ca^{2+} , Na^* (Cl-corrected Na^+ ; $\text{Na}^* = \text{Na}^+ - \text{Cl}$; cf. Moon et al., 2014), for cation-equivalent ($2\text{Mg}^{2+} + 2\text{Ca}^{2+} + \text{K}^+ + \text{Na}^+$ [$\mu\text{eq/L}$]), and for total dissolved solids (TDS; $\text{Mg}^{2+} + \text{Ca}^{2+} + \text{K}^+ + \text{Na}^+ + \text{SiO}_2(\text{aq})$ [mg/L]).

In **Appendix B**, we provide associated example code for fitting concentration-runoff relationships using the Maher and Chamberlain (2014) modeling framework. The Gauss-Newton method minimizes the sum of squares of the errors between the model prediction and input dataset. The advantage of this method is that because C_0 and C_{max} are unknown, we can simultaneously solve for all three required parameters given sufficient sample size (> 20 paired data points). We only report concentration-runoff relationships that are statistically significant at 95% (p-value < 0.05 for all three parameters). If C_0 cannot be assumed to be zero (based on p-value > 0.05 for fitted Equation 1 C_0 value), we correct for atmospheric, spring, and/or hydrothermal inputs by subtracting the calculated C_0 value from the concentration-runoff relationship as shown schematically in **Figure 3**. TDS [mg/L] derived from the weathering of silicate rocks, which is a measure of total silicate chemical denudation, is calculated by

weighting the concentrations by the molar mass of each major cation and SiO_2 (e.g., Bouchez and Gaillardet, 2014) and correcting the concentration-runoff relationship for C_0 . We also similarly calculate and correct concentration-runoff relationships for cation-equivalent (e.g., Gaillardet et al., 2011b), which is the charge-weighted concentration of positively charged cations (Mg^{2+} , Ca^{2+} , K^+ , and Na^+) and compare them to the HCO_3^- results (in units of $\mu\text{mol/L}$).

We calculate the absolute weathering potential (ΔWP) and normalized weathering potential (WP_{norm}) using Equations 5 and 6. The observed weathering flux, W_{obs} , is determined using Equation 4 where q is the median of the runoff distribution, with the range of weathering fluxes calculated for each catchment using the maximum and minimum observed runoff values that are paired to solute concentrations. The maximum weathering flux, W_{max} , is determined as the product of C_{max} and Dw (see Background).

In addition to deriving Dw values from fitting concentration-runoff relationships from all available data, we also derive Dw values using single concentration-runoff pairs for each catchment. Maher and Chamberlain (2014) noted the lack of long-term monitoring available to fully constrain mechanisms driving the distribution of weathering efficiency (Dw values) in modern systems. Previous work using this solute production framework took the approach of assuming C_{max} values for global river datasets to derive flux-weighted Dw values from single concentration-runoff pairs (von Blanckenburg et al., 2015), assuming that time-averaging of discharge and concentrations in existing global river datasets were accurate (e.g., Gaillardet et al., 1999; Moon et al., 2014; Goldsmith et al., 2015). The advantage of using the single flux-averaged concentration-runoff pair for this analysis is that hysteresis (on storm event or seasonal timescales; e.g., Chanut et al., 2002; Moquet et al., 2015) is accounted for, rather than resulting in greater uncertainty around the solute production parameters derived from the concentration-

runoff relationship fit (see below for fitting methods). However, recent work has shown, using an inverse modeling and bootstrapping approaches, that estimates of fluxes using these datasets result in overestimation of global weathering fluxes (Moon et al., 2014, see their Figure 8). Thus, we pair flux-weighted concentrations using all available data with average runoff values from each catchment. For each sample group, we calculate C_{max} as the 95th percentile (e.g., Dixon and von Blanckenburg, 2012; Maher and Chamberlain, 2014; von Blanckenburg et al., 2015). Assuming C_0 is zero, equation 3 is solved for flux-weighted Dw values. The results from the single concentration-runoff pairs are compared to those derived by fitting concentration-runoff relationships.

3.3 Statistics of sample groups

We report and illustrate the variability of C_{max} , C_0 -corrected C_{max} , Dw , and W_{max} values for each sample group of basalt and granitic catchments in Table and Figures. We use box and whisker plots with mean, median, interquartile range (IQR) and 95% confidence intervals. Summary statistics are necessary because (1) distributions in Dw and C_{max} are not normally distributed (typically positively skewed) within sample groups (Maher and Chamberlain, 2014), and the distribution in q observed within each catchment also tends to be non-normal; and (2) the rational forms of Equations 1 and 2 result in asymmetric propagated errors (*cf.* discussion in von Blanckenburg et al., 2015) when calculating W_{max} from derived values of C_{max} and Dw . It is notable that although we only include catchment fits with statistically significant Dw , C_{max} , and C_0 parameters (95%, $p > 0.05$), the estimated uncertainty for each parameter can vary by an order of magnitude or more depending on the goodness of fit and absolute values. Uncertainty in C_0 is

propagated in quadrature when correcting the C_{max} values of concentration-runoff relationships for individual catchments.

Linear regressions between mean weathering temperature and the derived parameters (C_{max} and Dw) are illustrated for significant (p-value < 0.05) relationships only. We report coefficients of correlation, and slopes between C_{max} and temperature. The mean water temperature of the collected samples used to derive the concentration-runoff fits was selected to represent the mean weathering temperature of each catchment.

3.4 Saturation indices

To evaluate thermodynamic controls on C_{max} , we calculate the saturation index according to the ion activity product (IAP) and the equilibrium constant K (*i.e.*, $\log(IAP/K)$) for calcium and sodium feldspar end-members and key secondary minerals. When $\log(IAP/K) = 0$, the fluid is in equilibrium with the mineral. When $\log(IAP/K) < 0$, the fluid is undersaturated relative to the mineral, and when $\log(IAP/K) > 0$, the fluid is supersaturated relative to the mineral. Saturation index calculations were performed in Geochemist's Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015) at the temperature of sample collection. Approximately 25% of the data considered in this study includes aluminum concentration data required for the speciation and saturation index calculations. Potassium feldspar saturation index calculations were not included due to a lack of potassium solute data (<8 % of data). We include all available samples with pH and aluminum concentrations (n=1,952) from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic basaltic catchments (Eiriksdottir et al., 2013; 2015).

4. RESULTS

4.1 Concentration-discharge relationships

Concentration-runoff (C - q) fits for all catchments in our compilation are illustrated in **Figure 4** and reported in **Tables A2-8**. Many statistically significant C - q relationships for HCO_3^- (51%, $n = 24$), Ca^{2+} (50%, $n = 24$), and Mg^{2+} (40%, $n = 18$) (and by extension TDS and cation-equivalent) required C_0 corrections (**Tables A3-A8**). In contrast, proportionally fewer $\text{SiO}_2(\text{aq})$ (28%, $n = 12$) and Na^* (20%, $n=8$) statistically significant relationships required a C_0 correction (**Table A2**). For the $\text{SiO}_2(\text{aq})$ C - q relationships, this likely reflects the fact that $\text{SiO}_2(\text{aq})$ is a primary recorder of silicate weathering (White and Blum, 1995; Waldbauer and Chamberlain, 2005; Maher and Chamberlain, 2014) with minimal C_0 contributions (Maher, 2011). Statistically significant C_0 values ($C_0 > 0$) for $\text{SiO}_2(\text{aq})$ and Na^* (**Tables A2 and A5**) proportionally account for less of the uncorrected $C_{\max}$ values relative to Ca^{2+} , Mg^{2+} and HCO_3^- (**Tables A3, A4 and A6; see also Figure 4**). Because we are interested in analyzing the weathering zone component of the solute load, in particular apparent controls on $W_{\max}$ (e.g., Dixon and von Blanckenburg, 2012; Maher and Chamberlain, 2014), we focus below on the C_0 -corrected C - q fits illustrated in **Figure 5**. In addition, **Figure 6** illustrates the derivation of the flux-weighted Dw values reported in **Table A9** for single C - q pairs for each catchment, assuming sample group $C_{\max}$ values (95th percentiles) derived by calculating flux-weighted average concentrations for each catchment.

4.2 Chemostatic concentrations ($C_{\max}$)

The distribution of $C_{\max}$ values demonstrates that the net weathering stoichiometry of the primary lithology plays a first order control on setting $C_{\max}$ (**Figure 5**). To the right of each panel

in **Figure 5** shows distribution of the C_{max} summary statistics for each group (**Table 1**). Also annotated for each dissolved species is the ratio of the mean basalt C_{max} to the mean granite C_{max} .

Based on a comparison of Dessert et al. (2003) and Gaillardet et al. (1999) datasets, Maher and Chamberlain (2014) estimated that basaltic C_{max} values are approximately 1.5 times greater than C_{max} values of large rivers, assuming similar Dw distributions (discussed below). The results presented in **Figure 5** (and **Table 1**) suggest that this estimate was of the correct magnitude and varies depending on the dissolved species considered. The mean C_{max} value for basaltic catchment $\text{SiO}_2(\text{aq})$ is 1.6 times higher than that of granite (324 vs. 209 $\mu\text{mol/L}$; **Table 1**), similar to the values derived for Na^+ (1.6), HCO_3^- (1.3), TDS (1.8), and cation-equivalent (1.8). The difference in C_{max} suggested by the $\text{SiO}_2(\text{aq})$ values is bracketed by Ca^{2+} (1.2) and Mg^{2+} (2.1), reflecting the mafic (*i.e.*, Mg-rich) nature of basaltic bedrock and the net stoichiometry of the weathering reactions (discussed in detail below), or the secondary mineral assemblage (e.g., Bouchez and Gaillardet, 2014).

The $\text{SiO}_2(\text{aq})$ C_{max} values for both basalt (324 $\mu\text{mol/L}$) and granite (209 $\mu\text{mol/L}$) catchments are lower than the C_{max} value originally suggested by Maher and Chamberlain (2014), who used the 95th percentile of annually averaged datasets (Gaillardet et al., 1999) to infer a large river $\text{SiO}_2(\text{aq})$ C_{max} of 375 $\mu\text{mol/L}$. A population of annually averaged concentration data biases the apparent C_{max} values towards higher values because observations of lower concentrations at high runoff are sparse (*cf.* Godsey et al., 2009; Moon et al., 2014; von Blanckenburg et al., 2015; Dessert et al., 2015). Similarly, by calculating flux-weighted average concentrations for all catchments and deriving C_{max} values (using the 95th percentile; **Table A9**; **Figure 6**) for each sample group, we find C_{max} values that are higher than those derived using the concentration-discharge relationships. However, based upon the flux-weighted concentrations,

the apparent $\text{SiO}_2(\text{aq})$ C_{max} value for basalt is 1.3 times that of granite (455 $\mu\text{mol/L}$ vs. 353 $\mu\text{mol/L}$; **Table 1**), which is of a similar magnitude to the mean C_{max} difference derived using the individual river concentration-discharge relationships. Importantly, this suggests that both methods produce comparable weatherability estimates at low runoff (discussed further below). Differences in C_{max} values between basalt and granite catchments of approximately a 1.3 to 1.9 factor remain for HCO_3^- (1.7), TDS (1.4), and cation-equivalent (1.7) using the flux-weighted concentrations (**Table 1**). The spread observed in basalt and granite catchments (**Figure 5**) C_{max} values may be due to variations in soil $p\text{CO}_2$, bedrock age, temperature, effects of subsurface structure on flow regime, and additional geomorphic properties (Godsey et al., 2009; Clow and Mast, 2010; Maher, 2011; Moon et al., 2014; Torres et al., 2015).

The effect of temperature (**Table A1**) on C_{max} is assessed in **Figure 7**. We find that only C_{max} values for $\text{SiO}_2(\text{aq})$ and Na^* (granite only) have statistically significant ($p\text{-values} < 0.05$) positive relationships with average water (i.e., weathering) temperature, with low coefficients of determination ($r^2 < 0.4$). The positive slopes of the temperature– C_{max} (C_o -corrected C_{max}) relationship are reported in **Figure 7** and suggest a weak, but statistically significant temperature control for $\text{SiO}_2(\text{aq})$ and Na^* only. These trends are consistent with observations that dissolution rates increase with increasing temperature following Arrhenius-type relationships (e.g., Oelkers and Gislason, 2001; Gislason and Oelkers, 2003; Eiriksdottir et al., 2013; Li et al., 2016). Since solute fluxes are driven by runoff (Eiriksdottir et al., 2013), these results emphasize the importance of evaluating and considering concentration-discharge behavior in weathering flux datasets and compilations (e.g., Moon et al., 2014). Runoff and temperature are inherently positively correlated in most datasets covering large ranges in latitudinal settings, such as those used to derive Arrhenius-type weathering relationships (e.g., Dessert et al., 2003; Li et al., 2016).

Lastly, we acknowledge that the C_{max} values from this analysis may not be directly applied to heterogeneous (non-monolithologic) catchments or global rivers (e.g., Gaillardet et al., 1999; Maher and Chamberlain, 2014; Moon et al., 2014) due to the same factors listed above and different proportions of silicate weathering. Further work with databases combining the areal extent of silicate bedrock with large river solute data including water temperature data (e.g., Moon et al., 2007; 2009; Jansen et al., 2010; Moosdorf et al., 2011; Hartmann and Moosdorf, 2011, 2012; Hartmann et al., 2014b) will allow for direct comparison between the apparent contribution (via inverse methods) to the dissolved load chemistry by the silicate lithologies and bedrock-based lithologic distributions within catchments.

4.3 Saturation Indices of Primary and Secondary Minerals

The trends between granitic and basaltic catchments in the C_{max} distributions (**Figure 5**) may be controlled by the thermodynamics and the net stoichiometry of the primary silicate minerals (*i.e.*, feldspars, olivine, and pyroxene) weathering to secondary minerals and generating solute (e.g., Schott et al., 2009; Navarre-Sitchler et al., 2013; Bouchez and Gaillardet, 2014). We propose that the dissolution of primary minerals and the approach to chemical equilibrium with secondary mineral assemblages formed in the weathering zone (e.g., Maher et al., 2009; Maher, 2010; 2011; Clow and Mast, 2010; Maher and Chamberlain, 2014; Li et al., 2014; Maher and Druhan, 2014) controls solute concentration and C_{max} values for specific catchments. At present, few aluminum concentration data and/or bed-load x-ray diffraction data exist to determine the specific secondary minerals driving variations in C_{max} between lithologic groups and under different climatic conditions.

Here, we use aluminum concentration data as available for the catchments analyzed in this study to derive saturation indices of primary and secondary minerals. C_{max} values should reflect concentrations during base flow (*i.e.*, low runoff), and the assumption that equilibrium with secondary phases is achieved given long flow paths (see Background; Maher, 2010, 2011). We also consider idealized end-member compositions whereas primary mineral compositions and assemblages can be highly variable, especially in catchments with hydrothermally altered bedrock. In addition, these speciation and saturation index calculations may be impacted by CO_2 evasion in the stream channel (*e.g.*, Wallin et al., 2011; Lauerwald et al., 2015), emphasizing the need for upslope monitoring of soil and groundwater solute chemistry (*e.g.*, Kim et al., 2014) to determine controls on C_{max} values for individual catchments.

In **Figure 8**, we compare histograms of basalt and granite saturation indices for feldspar end-members, typical secondary weathering aluminosilicate minerals (halloysite, gibbsite, imogolite, smectites (Ca, Na and Mg end-members) and kaolinite), amorphous silica, and calcite (see Methods for details). We separately show the chemostatic catchments as solid bars in **Figure 8**. The histograms indicate that most samples are undersaturated with respect to end-member feldspars (albite and anorthite), amorphous silica and calcite, as well as for olivine and pyroxene minerals (not shown), in agreement with previous work (*e.g.*, Bluth and Kump, 1994; Gíslason et al., 1996; Stefánsson and Gíslason, 2001; Stefánsson et al., 2001; Oelkers and Gíslason, 2001; Jacobson et al., 2003; 2015; Eiríksdóttir et al., 2013). Chemostatic basalt catchments are most undersaturated with respect to feldspars compared to granitic catchments (discussed further below). This apparent higher degree of undersaturation observed for primary minerals (see feldspars in **Figure 8**) in chemostatic catchments may suggest hydrologic thresholds on C_{max} concentrations (Chanet et al., 2002; Eiríksdóttir et al., 2013) as saturation

state with respect to primary minerals tends to decrease with increasing discharge. Given this undersaturation with respect to primary minerals, the departure from equilibrium with respect to primary phases (feldspars (**Figure 8**), as well as olivine and pyroxenes (not shown)), could be a factor in determining C_{max} concentrations, especially in granitic catchments. Despite this, as shown below, incorporation of elements into and equilibrium with secondary phases likely plays a controlling role on C_{max} concentrations.

Importantly, all samples are oversaturated with respect to the clay minerals (halloysite, imogolite, smectites, and kaolinite) and gibbsite. This saturation with respect to metastable alluminosilicate secondary clays is expected and has been observed in both stream/river waters (*e.g.*, Gislason and Eugster, 1987; Bluth and Kump, 1994; Stefánsson and Gíslason, 2001; Eiríksdóttir et al., 2013) and soils (Maher et al., 2009; White et al., 2009; Kim et al., 2014). Of the clay minerals, samples from both chemostatic and non-chemostatic catchments are closer to saturation ($\log(IAP/K_e) = 0$) with halloysite (and imogolite), and highly supersaturated with respect to kaolinite and the smectite end-members. Since halloysite and imogolite are thought to be metastable precursors (Stefánsson and Gíslason, 2001; Maher et al., 2009; White et al., 2009; Kim et al., 2014) and are closer to equilibrium compared to kaolinite or smectite (**Figure 8**), this may justify the use of halloysite (or imogolite) in reaction path reactive transport modeling instead of kaolinite or smectite (*e.g.*, Maher, 2011). Field observations demonstrate that multiple different secondary clay minerals co-exist in typical weathering profiles (*e.g.*, White et al., 2009; Maher et al., 2009). In **Figure 9**, we illustrate activity diagrams of the Ca-Na and Ca-Mg systems with kaolinite and smectite stability fields (for different assumed $\text{SiO}_2(\text{aq})$ activities and the appropriate smectite end-members). We plot all of the basalt and granite data with available pH and sufficient solute data (anions, cations and $\text{SiO}_2(\text{aq})$) for speciation. The data for basalts and

granites plot between the phase boundaries (**Figure 9**), confirming previous work suggesting possible equilibrium between the more stable secondary phases of kaolinite and smectite (e.g., Bluth and Kump, 1994; Kump et al., 2000).

For feldspars, amorphous silica, and calcite, chemostatic basalt catchments are further from saturation compared to non-chemostatic catchments (filled red bars in histograms of **Figure 8**). Whereas primary feldspars are not expected to be stable at surface temperatures, undersaturation of amorphous silica, and calcite is surprising given the high reactive surface areas of basaltic systems (Eiriksdottir et al., 2013). This may result from several factors, including the possibility that rapid weathering of basaltic catchments has reduced the amount of primary mineral (the reactant) in the weathering zone. In addition, some samples, mostly chemostatic granitic catchments, are near saturation with respect to calcite. This is not unexpected because trace calcite in granitic bedrock is commonly observed, as is new calcite precipitation in many seasonally arid/semi-arid granitic weathering systems (e.g., Wang et al., 1996; Amundson et al., 1996; Blum et al., 1998; White et al., 1999b; Kim et al., 2014; Hartmann and Moosdorf, 2011; Jacobson et al., 2015).

Cumulatively, these observations corroborate observations of the mineral assemblages in weathering profiles from silicate dominated systems (e.g., Eberl, 1984; Steefel and Van Cappellen, 1990; White et al., 1999a; 2009; Maher et al., 2009) and suggest that solute concentrations are influenced by the thermodynamic potential for primary mineral dissolution and secondary mineral precipitation – the stoichiometry of which consequently may determine the catchment C_{max} values for various solutes (Maher, 2011; Maher and Chamberlain, 2014). The nature of this analysis is preliminary given limited available datasets. Future acquisition of accurate aluminum concentration and pH data (e.g., Eiriksdottir et al., 2013; 2015) is vital for

speciation calculations of solute chemistry measurements in this manner and for informing further reaction path modeling of soil zone weathering (*e.g.*, Maher, 2011).

4.4 Comparison of Damköhler coefficients (D_w)

The Damköhler coefficient (D_w) provides a metric to extract the resistance to dilution from the concentration-discharge relationship (Maher, 2011; Maher and Chamberlain, 2014). Higher D_w values would correspond to catchments that start to show dilution at higher discharge values, similar to more negative b -values in power-law C - Q relationships (*e.g.*, Godsey et al., 2009; Moon et al., 2014; Torres et al., 2015) (**Figure 2a**). Due to different thermodynamic (*i.e.*, dissolution/precipitation) processes and stoichiometric constraints associated with C_{max} , along with kinetic effects at increasing runoff, D_w values should differ among elements. D_w values capture both the physical length scale setting fluid residence times and the reactivity of the weathering reactions. Thus, D_w values have been linked to erosion rates, which determine the abundance of fresh minerals at the surface and hence the reactivity (Maher and Chamberlain, 2014). Increased erosion rates remove highly weathered material from the weathering zone, exposing new material at the surface and increasing reactive surface areas (*e.g.*, Waldbauer and Chamberlain, 2005; West, 2012). Erosion may further alter the topography and drainage structure, resulting in different porosity and permeability distributions. Thus, the observed intra-lithology spread in D_w distributions may be driven by these variations in flow path porosity/permeability (*e.g.*, White et al., 1996; 1999a; 2001; 2005; 2009; Jacobson et al., 2002; Maher et al., 2009; Navarre-Sitchler et al., 2009; 2011; 2013; 2015; Sak et al., 2010; Ryu et al., 2013; Parry et al., 2015) and/or erosion rates (*e.g.*, Chamberlain et al., 2005; Waldbauer and Chamberlain, 2005; Hren et al., 2007; Porder et al., 2007; Eiriksdottir et al., 2008; Moon et al.,

2011; West, 2012; Torres et al., 2015; Lee et al., 2015). Finally, on seasonal timescales ion-exchange on clay minerals or organic matter surfaces can serve as a temporary reservoir (Sverdrup and Warfvinge, 1988; White and Blum, 1995; Chorover and Sposito, 1995; Clow and Mast, 2010; Chorover et al., 2007; Andrews et al., 2016) and decouple the fluid residence times from the solute residence times, although for this study, we limit our dataset to sites with sufficient temporal coverage to negate seasonal biases.

In **Figure 10**, we show cross-plots of D_w values for different solutes of individual catchments (for statistically significant C - q relationships only). Plotted above and to the right are D_w distributions for each sample group as derived in **Figure 5**. These results demonstrate that among all solutes the distribution of D_w values is positively skewed. Observation of skewed distributions using the annually averaged Gaillardet et al. (1999) $\text{SiO}_2(\text{aq})$ data is consistent with previous work by Maher and Chamberlain (2014) and von Blanckenburg et al. (2015). However, because these studies used a $C_{\max}$ value of 375 $\mu\text{mol/L}$ for all catchments and used annually averaged datasets (see above), these studies underestimate absolute D_w values. Consequently, we find for basalt and granite catchments mean $\text{SiO}_2(\text{aq})$ D_w values of 3.47 m/yr and 1.49 m/yr, respectively (**Table 1**), compared to 0.21 m/yr for large rivers (*cf.* von Blanckenburg et al., 2015, their Table S6 corrected for the scaling factor). An additional, possible reason for this discrepancy may be that large rivers may not be merely a representation of mixing (and dilution) from small catchments for $\text{SiO}_2(\text{aq})$. Instead, processes in flood plains and modern dams/lakes may provide temporary storage (*i.e.*, buffering the concentration) and/or sequestration (through biological sedimentation) of $\text{SiO}_2(\text{aq})$ (Admiraal et al., 1990; Dürr et al., 2011; Hartmann et al., 2011; Lupker et al., 2012; Lauerwald et al., 2013; Bouchez et al., 2012; 2014; Maavara et al., 2014). Further, changes in anthropogenic nutrient inputs (Hartmann et al., 2007) can cause

SiO₂(aq) levels to vary with time when considering longer term as well as seasonal trends (Hartmann et al., 2011). Future longitudinal sampling campaigns along major rivers that integrate smaller silicate catchments may help explain this potential discrepancy (see Amazon River compilations by Bouchez et al., 2014; Torres et al., 2015; Moquet et al., 2015).

The cross-plots in **Figure 10** demonstrate that resistance to dilution is not uniform among solutes for a given catchment or within sample groups. The *C-q* relationships for SiO₂(aq) for both basalts and granites are characterized by higher *D_w* values for some catchments compared to the base cations (Mg²⁺, Ca²⁺, and Na⁺) and HCO₃⁻ (**Figure 5, Figure 10a-d**). This potential bias appears to be greatest among basaltic catchments (red basalt catchments in the lower right of **Figure 10a-d**). However, a majority of catchments are within a factor of two of each other when comparing SiO₂(aq)-derived *D_w* values to other solutes (diagonal dashed lines in **Figure 10**). The result that some catchments demonstrate higher SiO₂(aq) *D_w* values is consistent with power-law *b*-values from Moon et al. (2014) for large rivers, which had a median SiO₂(aq) value of -0.06, compared to median values of -0.12 to -0.24 for other solute species (cations and HCO₃⁻). Godsey et al. (2009) and Torres et al. (2015) also observed SiO₂(aq) relationships typically closer to chemostatic values (*b*-values approaching ~0).

Across all concentration-discharge fits, basaltic catchments typically have greater *D_w* values. Mean *D_w* values of basaltic catchments are two to five times higher than granitic catchments (**Table 1**). However, observed *D_w* values for Mg²⁺ and Ca²⁺ are similar, despite large differences in the Mg²⁺ and Ca²⁺ *C_{max}* values between basalts and granites (shown above) (**Figure 10g**), suggesting similar behavior of these cations during primary mineral dissolution and secondary mineral precipitation, and dilution processes, despite differences in absolute values of *C_{max}* driven by the net stoichiometry of the weathering reactions. In addition, cation-

equivalent and HCO_3^- , which may be influenced differently by ion exchange processes, have consistently similar Dw values, with only 8 of 37 catchments having Dw values that differ by more than a factor of two (**Figure 10f**). Finally, we also analyzed the relationship between Dw and temperature. We find no statistically significant ($p < 0.05$) correlations for any solutes between Dw and the average weathering temperature, shown as scatterplots in **Figure 11**.

4.5 Weathering potential (WP)

The results above demonstrate that basalt catchments, with higher Dw and C_{max} values than granite catchments, have a greater absolute capacity to increase weathering rates with increased runoff (*i.e.*, larger ΔWP). This implies that increases in runoff result in much larger absolute increases in weathering fluxes in basaltic catchments (**Figure 2b**). The absolute departure of catchment weathering fluxes from a theoretical maximum (*i.e.*, $\Delta WP = W_{max} - W_{obs}$) is dependent on the derived Dw and C_{max} values, which combine to set W_{max} (see Background), and on the runoff distribution, which sets W_{obs} . Using $\text{SiO}_2(\text{aq})$ and HCO_3^- catchment fits, we show in **Figure 12** that basaltic catchments have a higher ΔWP relative to granitic catchments (y -axis). Basalts have higher and more positively skewed Dw and higher C_{max} distributions, resulting in higher W_{max} values (**Figure 12; Table 1**), implying that both stoichiometric and thermodynamic effects and resistance to dilution result in a greater weathering potential for basalts. At equivalent runoff distributions, this results in basaltic catchments having a higher normalized weathering potential (WP_{norm}) due to higher W_{max} values than those in granitic catchments. Monitored basalt catchments included in this dataset are typically associated with higher Dw values, but also higher runoff distributions (**Figure 1**) due to their proximity to coastal environments and potential for orographic effects (Bluth and Kump, 1994; Dessert et al., 2001;

2003; Hartmann et al., 2009; Gaillardet et al., 2011b; Maher and Chamberlain, 2014). Despite these effects, the fact that basaltic WP_{norm} values remain high at higher runoff illustrates the high reactivity of basalt catchments (**Figure 12**).

These results imply that resistance to dilution at increasing runoff (higher Dw) and stoichiometric considerations (higher C_{max}) are lithology-dependent. Given that C_{max} values between basalts and granites vary by <2 orders of magnitude and Dw values vary by 4-5 orders of magnitude (**Figures 5 and 10**), the differences in observed (W_{obs}) and maximum weathering (W_{max}) fluxes from basalt catchments are primarily driven by differences in Dw . Although this dataset includes substantial variations in runoff, bedrock age, temperatures, and vegetation types within basalt and granite catchments, systematic testing of these two silicate lithology end-members under identical conditions is not yet possible (*cf.* Navarre-Sitchler and Brantley, 2007; Berner, 2008; Maher and Chamberlain, 2014). In **Figure 13a and 13b**, we show the distribution of W_{max} values derived from the C - q fits (**Figure 5**) for $\text{SiO}_2(\text{aq})$ and HCO_3^- . The mean basalt $\text{SiO}_2(\text{aq})$ W_{max} is 3.6 times higher than for granites, whereas the mean basalt HCO_3^- W_{max} is 8.5 times higher than for granites (**Table 1**). These large differences in the SiO_2 and HCO_3^- W_{max} values are driven by differences in Dw values, which are 2.3 and 6.7 times greater, respectively, rather than C_{max} concentrations, which are only 1.6 and 1.3 times greater, respectively (**Table 1**). Saturation state histograms shown in **Figure 8** demonstrate that basaltic catchments are closer to equilibrium (more oversaturated) with some secondary minerals such as the smectite end-members and kaolinite. Since $\text{SiO}_2(\text{aq})$ is involved in the dissolution of primary minerals and the precipitation and dissolution of secondary minerals (*i.e.*, secondary phase buffering), this may result in more $\text{SiO}_2(\text{aq})$ removal relative to HCO_3^- in basaltic catchments compared to granitic catchments, driving the lower $\text{SiO}_2(\text{aq})$ Dw differences between catchment types.

If the W_{max} value is set by both thermodynamic and dilution effects at high runoff, this may provide a mechanism to explain lithologic differences in “maximum” fluxes or weathering speed-limits observed across silicate catchments (Dixon and von Blanckenburg, 2012) (**Figure 13**). However, for catchments that display near-chemostatic behavior, thermodynamic constraints (C_{max}) will control the chemical fluxes. Furthermore, there are very few datasets with concentration measurements at very high runoff, resulting in a large degree of uncertainty in the averaged W_{max} values for both sample groups presented in **Figure 13**. Acquisition of new datasets that include storm event concentration-discharge pairs, such as recently published dataset by Dessert et al. (2015) from Guadeloupe, will provide further constraints on extrapolated W_{max} values.

5. DISCUSSION

5.1 Runoff dependence of weatherability

The utility of the analysis presented in this paper is to derive the distribution of Dw and C_{max} values of the silicate end-member lithologies. Unlike previous parameterizations of weathering laws (*e.g.*, Dessert et al., 2003), we use paired discharge and solute concentration measurements for individual catchments—rather than annually averaged datasets—to parameterize lithology-specific Dw and C_{max} values. Although we did not analyze a globally comprehensive dataset of basaltic and granitic catchments, the first-order lithological trends are robust. Our results demonstrate that higher weathering rates in basaltic catchments relative to granites are driven by differing responses to increases in runoff, with basaltic catchments showing less dilution with increasing runoff (higher average Dw). Further, the results suggest that thermodynamic constraints on weathering reactions, reflected in chemostatic concentrations

(C_{max}) could explain higher concentrations in basaltic catchments at lower runoff compared to granitic catchments. For the remainder of the discussion, we primarily discuss the mean values derived from the analysis of $\text{SiO}_2(\text{aq})$ and HCO_3^- concentration-runoff fits, and the 2σ uncertainty of these estimates is also reported.

We illustrate the annual modern global and regional runoff distributions in **Figure 14** by area-weighting the Dai and Trenberth (2002) global river discharge dataset. Comparison of basalt and granite datasets within our solute production framework directly quantifies the relative weatherability between the two major end-member silicate lithologies responsible for terrestrial silicate weathering (Bluth and Kump, 1994; White and Blum, 1995; Kump and Arthur, 1997; Horton et al., 1999; Kump et al., 2000; Dessert et al., 2001; Berner, 2006b; 2008; Navarre-Sitchler et al., 2015). We demonstrate how the relative weatherability, the ratio between the basalt and granite fluxes, varies spatially along the latitudes based on global runoff distribution (**Figure 14d**). These results suggest that the relative weatherability is runoff-dependent, which likely varies through geologic time depending on the area and location of granite vs. more reactive basalt, continental configuration, and spatial changes in the runoff distribution (see Section 5.2).

Modern weathering observations have defined the range of expected basalt/granite weatherability values, in some cases attempting to control for climate and other influences (*i.e.*, bedrock age, slope etc.; Horton et al. 1999; Hartmann, 2009; Hartmann et al., 2010; Hartmann and Moosdorf, 2011). Flux-runoff relationships derived by Bluth and Kump (1994), also plotted in **Figure 13**, suggest basalt/granite weatherability of ~ 1.5 (*cf.* Bluth and Kump, 1994, see Table 4; Kump et al., 2000), with slight variations with changing runoff. Similarly, synthesis of weathering fluxes from Japan suggests that the average basalt/granite weatherability is 1.67,

ranging from ~1 to ~6, corresponding to steep and flat slopes respectively (*cf.* Hartmann, 2009; Hartmann et al., 2010; Hartmann and Moosdorf, 2011). By investigating proximal catchments with the same runoff distributions, Horton et al. (1999) suggested an andesite/granite weatherability of ~1.5 to 5.

In contrast, carbon cycle models have generally assumed invariant basalt/granite weatherability through time. For example, using data from Dessert et al. (2001), Berner (2006b) estimated that volcanic (basaltic) silicate weathering is ~5 times that of plutonic (granitic), with bounds of 2 to 10, as included into GEOCARBSULF (*e.g.*, Royer et al., 2014). Subsequent sensitivity analysis of GEOCARBSULF indicated that the lower bound of ~2 is likely more realistic considering requirements for seawater composition and reconstructions of $p\text{CO}_2$ during the Mesozoic (Berner, 2008). Notably, the average flux-runoff curves from this analysis (solid red and blue lines in **Figure 13a,b**) diverge from the Bluth and Kump (1994) relationships (dashed lines) at high runoff due to the mathematical formulation of the relationships (power-law vs. rational). Given that at an individual catchment scale, plateaus in weathering fluxes do occur at high runoff (*e.g.*, Maher, 2011; Torres et al., 2015), the mathematical formulation of the solute production model employed here appears to capture both chemostatic and dilution processes adequately. As shown in **Figure 14a** for HCO_3^- fluxes, because the modern global runoff distribution primarily lies between the end-members set by W_{max} and C_{max} , the derived weatherability is 2.2 at global mean runoff.

Higher area-normalized weathering rates and maximum limits on weathering fluxes for basaltic catchments, relative to granites (**Figure 13a,b**), are primarily driven by higher Dw values and also higher C_{max} (see Results). Thus, depending on the underlying runoff distribution, weatherability is set by both C_{max} and W_{max} (**Figure 14a**). For example, at modern global mean

runoff values of 0.344 m/yr (0.117–0.409, 2σ), basalt/granite weatherability is 2.2 (1.3–3.7, 2σ) for HCO_3^- fluxes and 1.7 (1.6–2.1, 2σ) for $\text{SiO}_2(\text{aq})$ fluxes (see red horizontal line in **Figure 9d**). This difference is driven by a higher extrapolated weatherability (from derived W_{max} values) using HCO_3^- fluxes at high runoff. Notably, these calculations agree with basalt/granite weatherability calculated using the flux-weighted Dw values derived using the single C-q pairs (**Figure 6**). That method suggests a global mean runoff basalt/granite weatherability is 2.3 (1.7–3.6, 2σ) for HCO_3^- fluxes and 1.7 (1.3–2.4, 2σ) for $\text{SiO}_2(\text{aq})$ fluxes (**Table 1**).

Under this framework end-member plateaus occur at both runoff extremes. At low runoff, weatherability is only set by the difference in chemostatic concentrations (C_{max}) shown in **Figure 5**. The mean $\text{SiO}_2(\text{aq})$ and HCO_3^- basalt/granite weatherability at low runoff (approximately $q < 10^{-2}$ m/yr) is 1.6 and 1.3, respectively (**Table 1, Figures 5 and 14a**). In contrast, apparent mean W_{max} values suggest basalt/granite weatherability of 8.5 for HCO_3^- and 3.6 for $\text{SiO}_2(\text{aq})$ at very high runoff (approximately > 30 m/yr; **Table 1, Figure 14a**). The higher basalt/granite weatherability at high runoff for HCO_3^- is primarily driven by the 6.7-fold difference between average basalt vs. granite Dw values, compared to a lesser 2.3-fold difference derived from $\text{SiO}_2(\text{aq})$ fluxes (**Table 1**; see also Section 4.5). This inference of runoff-dependent basalt/granite weatherability presented in **Figure 14** implies that future carbon cycle modeling, in addition to influences of temperature (Li et al., 2016), should not necessarily assume invariant basalt/granite weatherability through time.

5.2 Dw , weatherability, and a variable silicate weathering feedback

Above, we demonstrate that the weatherability of the surface of the Earth is runoff-dependent under our modeling framework, with modern mean runoff primarily spanning the

785 transition in weatherability between thermodynamic and kinetic limitations. To describe the
 786 functional form of the silicate weathering negative feedback, previous work has parameterized
 787 global terrestrial weatherability (Kump and Arthur, 1997) with adjustable parameters that relate
 788 the silicate weathering flux to climate, usually $p\text{CO}_2$ and runoff (*e.g.*, Berner, 2006a; Berner,
 789 2008; Zeebe, 2012; Royer et al., 2014; Mills et al. 2014b). These adjustable parameters
 790 determine the total weathering flux according to the strength of the silicate weathering negative
 791 feedback and the dependence on atmospheric $p\text{CO}_2$ and/or climate. Often, in 0-D models, global
 792 weathering fluxes (F_{sil}) are parameterized as proportional to climate through $p\text{CO}_2$; for example:
 793 $F_{\text{sil}} = k \times [p\text{CO}_2]^n$ (Uchikawa and Zeebe, 2008; Zeebe, 2012; Mills et al., 2014b), where k is the
 794 weathering time constant and n encapsulates a non-linear response to climate. Together, k and n
 795 modify the strength of the weathering feedback (Schwartzmann and Volk, 1989; Mills et al.,
 796 2014a; Caves et al., 2015a). Globally, although weathering fluxes are determined by runoff
 797 because weatherability is modified by the overlying runoff distribution (**Figure 14**), the strength
 798 of the feedback (the k and n terms) is also dependent on runoff. To relate the weatherability
 799 framework developed here to global feedback parameters (calibrated values of k and n) requires
 800 knowledge of both the time-varying spatial distribution of silicate lithologies and changes in
 801 runoff patterns set by changes in atmospheric circulation and continental configuration.
 802 Assuming that increases in global runoff are positively correlated with increasing $p\text{CO}_2$ (Otto-
 803 Bliesner, 1995; Gibbs et al., 1999; Pierrehumbert, 2002; Manabe et al., 2004), our solute
 804 production framework provides a quantitative method to parameterize formulations of the
 805 negative feedback in both 0-D carbon cycle models and spatially explicit weathering models.
 806 Thus, the strength of the negative feedback is set by the interaction between the D_w values of
 807 silicate bedrock catchments and the spatial runoff distribution.

Given changes in continental configuration, eruptions of large igneous provinces, and changes in tectonic uplift, global D_w distributions must be non-stationary through geologic time. We propose here that a variable silicate weathering feedback may be driven by shifts in the D_w distribution of silicate catchments globally. Further, atmospheric circulation drives large variations in runoff across the Earth's surface today (**Figure 14c**); thus, changes in climate that affect this circulation will vary the spatial pattern of runoff, further altering the strength of the negative feedback.

To demonstrate how the spatial distribution of lithology and runoff interact to determine basalt/granite weatherability, we plot in **Figure 14c,d** the modern weatherability as a function of latitude. We calculate this for modern basalt catchments using the modern latitudinal runoff distribution from Dai and Trenberth (2002) (see **Figure 14** caption for details). In this figure, because runoff substantially varies latitudinally (**Figure 14c**), weatherability also varies latitudinally and displays large, ~50% variability. Over geologic timescales, if the proportion of basalt relative to granite changes (black lines **Figure 14d**), weatherability must also change, with the largest changes occurring in the tropics due to high runoff. Thus, for example, the eruption of a large igneous province in the tropics should have a much larger effect on global weathering than a similarly sized eruption in subsiding portions of Hadley cells (Kent and Muttoni, 2008; 2013). Similarly, changes in climate that alter the distribution of runoff (such as Hadley cell expansion, shifting mid-latitude westerlies, etc.) would also produce changes in weatherability without necessarily a change in the areal distribution of lithologies. This view of weatherability contrasts with that presented in **Figure 14b**. Here, we derive weatherability for global average runoff, which—due to energetic constraints (Pierrehumbert 2002)—cannot change dramatically. Thus, 0-D models of weathering are potentially limited in their ability to capture large changes in

weatherability due to changes in the spatial distribution of runoff and/or lithology, even if global averages remain constant.

Changes in global basalt/granite weatherability due to variations in runoff and in the distribution of bedrock silicate lithologies indicate that weatherability can change on both short and very long timescales (**Figure 14d**). For example, basalt/granite weatherability increases at higher runoff; therefore, rapid climate change during greenhouse climates, such as in the early Eocene or Cretaceous, may cause pronounced changes in weatherability as runoff intensity and distribution changes (**Figure 14a**). Thus, across a carbon-cycle perturbation such as the PETM—which witnessed large-scale changes in hydrology and runoff (Bolle and Adatte, 2001; Bowen et al., 2004; Pagani et al., 2006; Foreman et al., 2012) against a background greenhouse climate state—weatherability cannot be assumed constant. An increase in weatherability would tend to shorten the duration of the carbon cycle perturbation. Across such perturbations, globally averaged runoff may change, though likely not substantially (*cf.* Manabe et al., 2004; Pierrehumbert 2002). However, if the spatial distribution of runoff changes dramatically (*e.g.*, Pagani et al., 2006; Tipple et al., 2011; Foreman et al., 2012), this would drive larger changes in the basalt/granite weatherability relative to changes expected based solely on globally-averaged runoff.

Similarly, on longer timescales, as continental configuration and climate change, the spatial interactions between these two effects will affect weatherability and, hence, the strength of the negative feedback. These effects are likely to be greater than those caused by changes in the global average runoff given that spatially runoff varies substantially. Indeed, previous studies have suggested that changes in global silicate weathering fluxes could be driven by the interaction of continental configuration and sea level with the overlying runoff distribution, as

determined by atmospheric circulation, over both short (10^3 to 10^5 yr) and long ($>10^6$ yr) timescales (*e.g.*, Gibbs and Kump, 1994; Gibbs et al., 1999; Ludwig et al., 1999; Munhoven, 2002; Donnadieu et al., 2004; Goddris et al., 2008; Kent and Muttoni, 2008; 2013; Le Hir et al., 2009; Mills et al., 2011; Jagoutz et al., 2016).

The spatial sensitivity of the weathering feedback points to the importance of further development of spatially explicit weathering models coupled to or driven by global climate models (*e.g.*, Munhoven, 2002; Goddris et al., 2008; Lefebvre et al., 2013; Goll et al., 2014; von Blanckenburg et al., 2015) that will allow us to better quantify how the interaction between lithologic exposure, tectonic processes, configuration of continents, and climate sets the strength of the silicate weathering feedback through time. Though we have focused here on the role of lithology in determining the efficiency of silicate weathering, exposure of more rapidly eroding areas (*e.g.*, higher D_w values) due to tectonic uplift (*e.g.*, Waldbauer and Chamberlain, 2005; von Blanckenburg, 2005; West et al., 2005; Hilley et al., 2010; Norton and von Blanckenburg, 2010; West, 2012) may also provide a mechanism for varying the strength of the silicate weathering feedback (Maher and Chamberlain, 2014; Caves et al., 2015a).

Because the weatherability of the Earth's surface can vary through geologic time, paleogeographic and paleotopographic reconstructions are intrinsically important for placing bounds on the strength of the silicate weathering feedback. Constraining the strength of the silicate weathering feedback through time will require the use of paleoclimate model simulations to determine past runoff distributions under changing continental configurations (*e.g.* Gibbs et al., 1999; Munhoven, 2002; Goddris et al., 2008; von Blanckenburg et al., 2015), in combination with: (1) reconstructing the interaction of large orogenic belts with climate (*e.g.*, Montgomery et al., 2001; Rowley and Currie, 2006; Mulch and Chamberlain, 2006; DeCelles et

al., 2007; Garzione et al., 2008; Mix et al., 2011; 2016; Caves et al., 2014; 2015b), (2) the inferred erosion rates of orogenic belts (*e.g.*, Drever and Zobrist, 1992; Willett, 1999; Kirchner et al., 2001; Hilley et al., 2010; Willenbring and von Blanckenburg, 2010; Moon et al., 2011; Moore et al., 2013; Willett et al., 2014; Lee et al., 2015), (3) the spatial distribution and evolution of shielding soils (*e.g.*, Taylor and Blum, 1995; Chamberlain et al., 2005; Porder et al., 2007; Goddris et al., 2008, Kent and Muttoni, 2013; Hartmann et al., 2014a; Minasny et al., 2015; St. Clair et al., 2015), (4) the interaction of climate and erosional processes on basin evolution to determine reactive flow path length and subsurface permeability (*e.g.*, Rempe and Dietrich, 2014; St. Clair et al., 2015), and (5) the areal extent and spatial configuration of rapidly eroding areas (*e.g.*, Bluth and Kump, 1991; Gibbs et al., 1999; Kent and Muttoni, 2008; 2013; Molnar and Cronin, 2015; Jagoutz et al., 2016; Cox et al., 2016) through geologic time.

6. CONCLUSIONS

We have shown using modern concentration-runoff relationships how hydrologic and lithologic controls combine to set weathering fluxes from catchments by applying the process-based model of Maher and Chamberlain (2014) to assess the weathering efficiency of individual catchments of the two silicate end-member lithologies, granites and basalts. Although our analysis is limited to the Northern Hemisphere and primarily mid-latitude North America, the dataset shows first-order trends in weathering efficiency and lithological controls. We find that the relative weatherability of basalt compared to granites is runoff dependent due to both the plateaus in weathering fluxes caused by dilution of solutes at high runoff and the thermodynamic controls at lower runoff. As a consequence, the weatherability of basalt relative to granites has likely not been constant over geologic time—as runoff and lithologic exposure changes

spatially—and is perhaps not constant even on shorter timescales. In addition, when more directly comparable modern data becomes available, weatherability can be assessed under constant climate, soil age, and vegetation parameters using the framework presented in this paper. Finally, if the differences in bedrock weatherability can be extrapolated to the geologic past as presented here, then determining the global distribution and geographic configuration of lithologies, in addition to the interaction of topography with atmospheric circulation changes, will be essential in constraining the variable strength of the silicate weathering negative feedback and its role in controlling past atmospheric $p\text{CO}_2$.

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APPENDIX A. SUPPLEMENTARY TABLES

923 The following is a list of the supplementary tables related to this article.

- 924 - Table A1. Summary of Compiled Datasets
- 925 - Table A2. $\text{SiO}_2(\text{aq})$ Concentration-Runoff Results
- 926 - Table A3. Mg^{2+} Concentration-Runoff Results
- 927 - Table A4. Ca^{2+} Concentration-Runoff Results
- 928 - Table A5. Na^+ Concentration-Runoff Results
- 929 - Table A6. HCO_3^- Concentration-Runoff Results
- 930 - Table A7. Cation-equivalent Concentration-Runoff Results
- 931 - Table A8. Total Dissolved Solid (TDS) Concentration-Runoff Results
- 932 - Table A9. Flux Weighted Concentrations and D_w Values

933

934 **APPENDIX B. SUPPLEMENTARY CODE**

935 The following is the supplementary code related to this article.

- 936 - B1. Example Concentration-Runoff Gauss-Newton Fit

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Tables

Table 1. Summary Statistics for Concentration-Runoff Fits and Flux-Weighted Data

Figure Captions

Figure 1. Location of datasets and conceptual model for concentration-runoff processes. (a)

Map of catchments included in this analysis. For overlapping sites the numbers are listed by group (e.g., 10x) (see **Table A1**). PNW - Pacific Northwest, SN - Sierra Nevada. (b) Catchment-scale conceptual model used to illustrate fluxes shown in Equations 2 and 3, and the framework presented in **Figure 2**. In this study we only analyze concentration-runoff relationships of end-member silicate catchments. Analysis of concentration-runoff relationships of large rivers by Maher and Chamberlain (2014) and von Blanckenburg et al. (2015) was carried out on datasets from heterogeneous, mix-lithology datasets (e.g., Gaillardet et al., 1999; Moon et al., 2014).

Figure 2. Framework for evaluating catchment solute production. (a) $\text{SiO}_2(\text{aq})$ concentration

as a function of runoff (Equation 3). Illustrated catchments types are from Maher (2011).

Constant Damköhler numbers (Da) are denoted as horizontal dashed lines of constant concentration. Note log-scale runoff axis. (b) $\text{SiO}_2(\text{aq})$ fluxes as a function of runoff and illustration of weathering potential (WP) (Equations 4-6). Weathering potential is expressed in percent ($\text{WP}_{\text{norm}}[\%]$). Note that both axes are on log-scales.

Figure 3. Illustrative correction of concentration-runoff relationship for non-zero C_0 within

the solute production framework; solid lines are a hypothetical observed concentration-runoff relationship and the dashed lines are the silicate weathering component only. Log-scale axes are

as in Figure 2. **(a)** $\text{SiO}_2(\text{aq})$ concentration as a function of runoff (Equations 2 and 3). Values of $C_{\max}$ and C_0 are annotated. **(b)** $\text{SiO}_2(\text{aq})$ fluxes as a function of runoff showing that the correction for C_0 contributions results in a plateau of the weathering flux ($W_{\max}$). Chemostatic portions of the curve are annotated.

Figure 4. Concentration-runoff fits for catchments; plotted as concentration as a function of runoff (Equations 1 and 2) for **(a)** $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), **(b)** Mg^{2+} ($\mu\text{mol/L}$), **(c)** Ca^{2+} ($\mu\text{mol/L}$), **(d)** Na^* ($\mu\text{mol/L}$), **(e)** HCO_3^- ($\mu\text{mol/L}$), **(f)** cation-equivalent ($\mu\text{eq/L}$), and **(g)** total dissolved solids (mg/L). The median sampled runoff is denoted by dots (diamonds for chemostatic catchments and circles for catchments demonstrating dilution) and lines are plotted for the full range of paired runoff and solute observations from each catchment. Note that both axes are log-scaled.

Figure 5. C_0 -corrected concentration-runoff fits and $C_{\max}$ distributions. Concentration-runoff fits are displayed as in **Figure 4**, corrected for C_0 (as demonstrated in Figure 2) for **(a)** $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), **(b)** Mg^{2+} ($\mu\text{mol/L}$), **(c)** Ca^{2+} ($\mu\text{mol/L}$), **(d)** Na^* ($\mu\text{mol/L}$), **(e)** HCO_3^- ($\mu\text{mol/L}$), **(f)** cation-equivalent ($\mu\text{eq/L}$), and **(g)** total dissolved solid (mg/L). $C_{\max}$ distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Also shown (*e.g.*, 1.50X) is a comparison of the mean basalt $C_{\max}$ to the mean granite $C_{\max}$ value.

Figure 6. Flux-weighted concentration pairs. Fluxed weighted concentration-runoff relationships. Each point represents a single catchment. $C_{\max}$ values, denoted in square brackets, are determined from the 95th percentile of concentrations for each catchment type (granite or

basalt) following Maher and Chamberlain (2014) (see their Figure S3 and Table S1). D_w values contoured here, and reported in **Table A9**, assume the 95th percentile C_{max} value.

Figure 7. Concentration-runoff derived maximum concentration (C_{max}) vs. water temperature. Scatter plots of average water temperature vs. concentration-runoff derived C_{max} values (C_0 -corrected C_{max} values) for **(a)** $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), **(b)** Mg^{2+} ($\mu\text{mol/L}$), **(c)** Ca^{2+} ($\mu\text{mol/L}$), **(d)** Na^+ ($\mu\text{mol/L}$), **(e)** HCO_3^- ($\mu\text{mol/L}$), **(f)** cation-equivalent ($\mu\text{eq/L}$), and **(g)** total dissolved solid (mg/L). Temperature is the average of the water temperature during sample collection, not the air temperature. C_{max} errors (reported in **Tables A2 to A8**) are 1σ . For clarity temperature errors are not included, but are reported in **Table A1**. Linear regressions are individually calculated for each sample group (basalts and granites), using the C_{max} and temperature population statistics (mean and errors). Only statistically significant regressions are illustrated and reported ($p\text{-value} < 0.05$). The temperature-concentration relationships (dC/dT) are reported for the statistically significant regressions and 95% confidence intervals are shaded.

Figure 8. Histograms of saturation indices (i.e., $\log(IAP/K)$) for select primary and secondary minerals. Saturation index calculations carried out in Geochemist's Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015). Here we include all available samples with aluminum concentrations ($n=1952$) from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic catchments (Eiriksdottir et al., 2013; 2015). Data from chemostatic catchments are highlighted as solid bars. For smectite we use the end-member half reactions for Na, Ca and Mg (Smectite-Na = $\text{Na}_{0.34}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$; Smectite-Ca = $\text{Ca}_{0.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$; Smectite-

Mg = $\text{Mg}_{0.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$). The “Albite (High)” histogram uses thermodynamic data for the highly disordered albite end-member more typically found in basalts (*cf.* Stefánsson et al., 2001).

Figure 9. Activity diagrams of the smectite-kaolinite system for Ca-Mg and Ca-Na.

Following Bluth and Kump (1994) activity diagrams were constructed assuming that $\log [\text{SiO}_2(\text{aq})] = 10^{-3}$ to $10^{-3.7}$ and temperature = 15°C. Brackets denote activity. All available data from the USGS NWIS database from basaltic and granitic catchments as well as from the Icelandic catchments (Eiriksdottir et al., 2013; 2015) were speciated using Geochemist’s Workbench (Bethke and Yeakel, 2015) using the Thermoddem database (version: llvl2; Blanc et al., 2012; Marty et al., 2015) to calculate $\log [\text{Ca}^{2+}]/[\text{H}^+]^2$ (n=7853), $\log [\text{Na}^+]/[\text{H}^+]$ (n=8031), and $\log [\text{Mg}^{2+}]/[\text{H}^+]^2$ (n=7835).

Figure 10. Concentration-runoff derived Damköhler coefficient (D_w) cross-plots.

Comparison of concentration-runoff derived D_w values for basalts (red) and granites (blue) derived using different solutes. Diagonal solid lines are the 1:1 line, and the parallel dashed lines are a factor of two envelope ($2\times$ and $0.5\times$ the 1:1 line). Note both axis scales are equivalent and are log-scaled. D_w distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Plots compare (a) $\text{SiO}_2(\text{aq})$ vs. Mg^{2+} , (b) $\text{SiO}_2(\text{aq})$ vs. Ca^{2+} , (c) $\text{SiO}_2(\text{aq})$ vs. TDS, (d) $\text{SiO}_2(\text{aq})$ vs. HCO_3^- , (e) Mg^{2+} vs. Ca^{2+} , and (f) cation-equivalent vs. HCO_3^- .

Figure 11. Concentration-runoff derived Damköhler coefficients (D_w) vs. water temperature. Scatter plots of average water temperature vs. concentration-runoff derived D_w values for (a) $\text{SiO}_2(\text{aq})$ ($\mu\text{mol/L}$), (b) Mg^{2+} ($\mu\text{mol/L}$), (c) Ca^{2+} ($\mu\text{mol/L}$), (d) Na^+ ($\mu\text{mol/L}$), (e) HCO_3^- ($\mu\text{mol/L}$), (f) cation-equivalent ($\mu\text{eq/L}$), and (g) total dissolved solid (mg/L). As in **Figure 9**, temperature errors are not included but are reported in **Table A1**. No statistically significant regressions ($p\text{-value} < 0.05$) exist between D_w and temperature in this dataset.

Figure 12. Weathering potential. Maximum weathering potential (ΔWP) vs. the median normalized weathering potential (WP_{norm}) for basalts (red) and granites (blue) derived for (a) $\text{SiO}_2(\text{aq})$ and (b) HCO_3^- . Note the log-scale for ΔWP (y-axis). Error bars for ΔWP are the minimum and maximum range of observations. Error on WP_{norm} are not shown for clarity but can be calculated using the minimum and maximum runoff values given in **Tables A2 and A6**. Linear regressions with confidence intervals are individually illustrated for each sample group (basalts and granites).

Figure 13. $\text{SiO}_2(\text{aq})$ and HCO_3^- fluxes. (a) $\text{SiO}_2(\text{aq})$ fluxes ($\text{t/km}^2/\text{yr}$) and (b) HCO_3^- fluxes ($\text{t/km}^2/\text{yr}$). Note both axes are log-scales. Heavy plotted lines are the mean fluxes (granite–blue; basalt–red) based on the C_{max} and D_w distributions (**Figure 5, Table 1**) derived from the granite (thin lighter blue) and basalt (thin lighter red) catchments (see text). W_{max} distributions are displayed with summary statistics (mean (diamonds), median, interquartile range (IQR) and 95% range) color coded by catchment type (granite or basalt). Previously derived flux-runoff relationships by Bluth and Kump (1994) are also plotted for reference.

Figure 14. Weatherability of basalt vs. granite catchments. (a) Basalt/granite weatherability, calculated from the average area-normalized basalt/granitic fluxes derived from the average C_{max} and D_w values (**Table 1, Figure 9a,b**) for $\text{SiO}_2(\text{aq})$ (thick black line), and HCO_3^- (thick grey line) as a function of runoff. Errors associated with the parameters used to calculate the weatherability curves are reported in **Table 1**. Global average runoff (thick red horizontal line) is calculated from Dai and Trenberth (2002) (panel c) with an uncertainty band assuming a 10% increase/decrease in runoff for a doubling of global $p\text{CO}_2$ (based on Manabe et al., 2004) up to a five times doubling. (b) Range of weatherability from previous studies (Horton et al., 1999; Berner, 2006b; 2008; Hartmann, 2009; Hartmann et al., 2010; Hartmann and Moosdorf, 2011). (c) Area-weighted global river runoff distribution (mean and 95% range) binned by latitude (3° bins) derived from the volumetric discharge and variance of observations from the 200 largest rivers reported by Dai and Trenberth (2002). Calculated by area-weighting and combining the binned northern and southern hemisphere runoff averages. (d) Mean basalt/granite $\text{SiO}_2(\text{aq})$ weatherability (mean and 95% range) vs. latitude (binned at 3° latitude bands) based on the modern runoff distribution. Calculated by area-weighting the binned northern and southern hemisphere runoff averages (panel c) and multiplying by the $\text{SiO}_2(\text{aq})$ runoff-dependent weatherability relationship (panel b) assuming 100% basalt proportion relative to granites.

Table 1

Table 1. Summary Statistics for Concentration-Runoff Fits and Flux Averaged Data

	C _{max} ^a							Dw (m/yr) ^b							Basalt vs. Granite Dw values	Basalt vs. Granite Weatherability End- Members ^b		Global Runoff Distribution Weatherability		
	Mean	Median	Q1 (25%)	Q3 (75%)	2σ Range	Skewness		Mean	Median	Q1 (25%)	Q3 (75%)	2σ Range	Skewness	Basalt/Granite	C _{max} End-Member	W _{max} End-Member	Mean	2σ Range		
SiO ₂ (aq) (μmol/L)																				
Basalt Catchments	323.6	293.9	185.0	430.1	605.8	89.4	1.99	3.47	1.93	0.78	5.99	10.28	0.14	0.98	2.32	1.55	3.61	1.74	1.56	2.09
Granite Catchments	208.5	209.6	95.4	301.6	356.3	70.2	-0.07	1.49	0.73	0.30	1.58	5.55	0.06	1.78						
Mg ²⁺ (μmol/L)																				
Basalt Catchments	210.6	137.3	64.4	272.0	537.8	32.5	1.83	2.34	0.67	0.08	2.68	7.00	0.06	3.73	3.55	2.10	7.45	2.79	2.12	3.96
Granite Catchments	100.2	75.7	55.7	112.0	205.3	29.9	2.93	0.66	0.49	0.22	1.17	1.48	0.03	0.42						
Ca ²⁺ (μmol/L)																				
Basalt Catchments	267.2	196.1	129.7	329.2	621.9	58.6	3.03	3.12	1.46	0.40	4.16	9.28	0.05	2.81	6.74	1.17	7.86	1.83	1.18	3.08
Granite Catchments	229.1	176.2	150.0	238.4	446.4	63.3	3.20	0.46	0.27	0.10	0.52	1.28	0.03	3.28						
Na ⁺ (μmol/L)																				
Basalt Catchments	321.7	157.0	78.9	305.4	731.5	43.2	3.41	3.05	0.74	0.14	3.82	10.59	0.03	2.86	4.55	1.57	7.16	2.14	1.59	3.19
Granite Catchments	204.3	98.9	52.3	285.1	556.3	18.5	1.29	0.67	0.33	0.18	0.76	1.96	0.03	1.14						
HCO ₃ ⁻ (μmol/L)																				
Basalt Catchments	1080.8	812.0	481.3	1357.3	2391.7	233.7	3.32	2.47	0.41	0.13	1.49	11.02	0.05	3.00	6.66	1.28	8.52	2.17	1.30	3.71
Granite Catchments	844.7	613.4	500.2	787.1	1967.5	390.0	3.26	0.37	0.23	0.09	0.54	1.12	0.02	1.19						
Cation-Equivalent Alkalinity (μeq/L)																				
Basalt Catchments	1504.9	1085.5	540.2	1558.8	4063.1	268.6	3.45	2.26	0.44	0.17	1.58	7.81	0.05	3.84	2.95	1.76	5.20	2.22	1.77	2.99
Granite Catchments	853.4	728.2	493.9	1192.2	1614.6	243.5	0.65	0.76	0.33	0.21	0.71	2.18	0.06	2.87						
Total Dissolved Solid (mg/L)																				
Basalt Catchments	46.3	39.8	19.1	51.9	114.3	11.0	2.99	2.97	0.62	0.21	4.81	10.31	0.04	2.25	2.26	1.82	4.12	2.06	1.83	2.50
Granite Catchments	25.4	17.3	14.6	34.0	43.3	5.7	1.87	1.31	0.34	0.12	0.93	5.04	0.02	2.51						
	Flux Weighted Data ^c							Dw (m/yr)							Basalt vs. Granite Dw values	Basalt vs. Granite Weatherability End- Members ^b		Global Runoff Distribution Weatherability		
	C _{max}							Mean	Median	Q1 (25%)	Q3 (75%)	2σ Range	Skewness	Basalt/Granite	C _{max} End-Member	W _{max} End-Member	Mean	2σ Range		
SiO ₂ (aq) (μmol/L)																				
Basalt Catchments	455.1				605.8	2.27	1.06	0.52	2.75	8.25	0.20	1.48	3.45	1.29	4.45	1.71	1.30	2.41		
Granite Catchments	352.8				356.3	0.66	0.38	0.16	0.66	2.03	0.08	3.45								
Mg ²⁺ (μmol/L)																				
Basalt Catchments	220.2				537.8	5.61	0.58	0.33	1.03	37.22	0.13	4.59	12.89	1.72	22.21	2.91	1.75	5.44		
Granite Catchments	127.8				205.3	0.44	0.23	0.12	0.54	1.01	0.04	3.43								
Ca ²⁺ (μmol/L)																				
Basalt Catchments	350.0				621.9	1.43	0.45	0.32	0.97	6.51	0.11	3.34	1.84	1.32	2.43	1.53	1.32	1.83		
Granite Catchments	265.6				446.4	0.77	0.36	0.20	0.84	2.22	0.09	3.03								
Na ⁺ (μmol/L)																				
Basalt Catchments	218.6				731.5	0.83	0.53	0.25	0.99	2.41	0.08	2.71	1.51	1.06	1.61	1.22	1.07	1.39		
Granite Catchments	205.6				556.3	0.55	0.22	0.13	0.44	1.84	0.04	3.36								
HCO ₃ ⁻ (μmol/L)																				
Basalt Catchments	1257.2				2391.7	7.71	0.49	0.30	1.15	10.63	0.08	6.10	8.95	1.71	15.27	2.29	1.72	3.59		
Granite Catchments	736.8				1967.5	0.86	0.39	0.25	1.04	3.36	0.14	2.53								
Cation-Equivalent Alkalinity (μeq/L)																				
Basalt Catchments	1573.2				4063.1	1.87	0.54	0.38	1.14	8.34	0.15	4.20	3.06	1.71	5.24	2.26	1.73	3.12		
Granite Catchments	918.2				1614.6	0.61	0.57	0.18	0.81	1.55	0.09	1.14								
Total Dissolved Solid (mg/L)																				
Basalt Catchments	54.9				114.3	2.50	0.91	0.34	1.79	15.00	0.23	2.98	2.72	1.44	3.91	1.74	1.45	2.26		
Granite Catchments	38.2				43.3	0.92	0.49	0.33	0.94	4.02	0.19	2.88								

^a Summary Statistics of Tables A2-8

^b Calculated using the mean C_{max} and Dw values

^c Table A9 (Notes: C_{max} is derived as the 95th maximum of the discharge weighted concentrations of each sample group following Maher and Chamberlain (2014)

Figure 1

B

Figure 2

Figure 3

Figure 4

Figure 5

Figure 7

Figure 9

Figure 10

C-q derived Dw values vs. mean water temperature

Granite Catchments (1σ)

Basalt Catchments (1σ)

Figure 12

Figure 13

$W_{\max}$ Distributions

Figure 14

0-D Models

Spatially Explicit Models