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

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Abstract

A negative feedback between silicate weathering rates and climate is hypothesized to play a central role in moderating atmospheric CO_2 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 discharge 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 HCO_3^- and $SiO_2(aq)$ 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 parameters that represent catchment-scale weathering fluxes of granitic and basaltic lithologies are robust. Our approach provides a mechanism that links runoff with the distribution of global sub-aerial silicate lithologies to understand how the basalt/granite weatherability of the Earth's surface may have varied on geologic timescales. The relationships between basalt/granite weatherability and runoff derived in this study could be used to parameterize the silicate weathering negative feedback to model past changes in pCO_2.

Keywords: Silicate weathering; Solute fluxes; Geologic carbon cycle; Feedbacks

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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; Caldeira, 1992, 1995; Kasting, 1993; 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 20–35% of the modern global silicate weathering and CO_2 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; Schopka et al., 2011; Gaillardet et al., 2011a; 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, 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 CO_2 (pCO_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, 1995; Gaillardet et al., 1999; Dessert et al., 2001, 2003; Dupré et al., 2003; Navarre-Sitchler and Thyne, 2007; Hartmann et al., 2010, 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 $SiO_2(aq)$ 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 (Fig. 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