1 **Title: Cenozoic carbon cycle imbalances and a variable weathering feedback**

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Abstract

The long-term stability of Earth's climate and the recovery of the ocean-atmosphere system after carbon cycle perturbations are often attributed to a stabilizing negative feedback between silicate weathering and climate. However, evidence for the operation of this feedback over million-year timescales and in response to tectonic and long-term climatic change remains scarce. For example, the past 50 million years of the Cenozoic Era are characterized by long-term cooling and declining atmospheric CO₂ ($p\text{CO}_2$). During this interval, constant or decreasing carbon fluxes from the solid Earth to the atmosphere suggest that stable or decreasing weathering fluxes are needed to balance the carbon cycle. In contrast, marine isotopic proxies of weathering (*i.e.*, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$, and $^{187}\text{Os}/^{188}\text{Os}$) are interpreted to reflect increasing weathering fluxes. Here, we evaluate the existence of a negative feedback by reconstructing the imbalance in the carbon cycle during the Cenozoic using the surface inventories of carbon and alkalinity. Only a sustained 0.25–0.5% increase in silicate weathering is necessary to explain the long-term decline in $p\text{CO}_2$ over the Cenozoic. We propose that the long-term decrease in $p\text{CO}_2$ is due to an increase in the strength of the silicate weathering feedback (*i.e.*, the constant of proportionality between the silicate weathering flux and climate), rather than an increase in the weathering flux. This increase in the feedback strength, which mirrors the marine isotope proxies, occurs as transient, <1 million year increases in the weathering flux, which remove CO₂. As runoff and temperature decline in response, the integrated weathering flux over >1 million year timescales remains invariant to match the long-term inputs of carbon. Over the Cenozoic, this results in stable long-term weathering fluxes even as $p\text{CO}_2$ decreases. We attribute increasing feedback strength to a change in the type and reactivity of rock in the weathering zone, which collectively has increased the reactivity of the surface of the Earth. Increasing feedback strength through the Cenozoic

47 reconciles mass balance in the carbon cycle with the marine isotopic proxies of weathering and
48 may explain why there are periods when the Earth system is more sensitive to carbon cycle
49 perturbations.

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51 **Keywords:** Cenozoic; Carbon Cycle; Weathering; Negative Feedback; Marine Isotopes

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1. Introduction

The Earth has experienced several profound long-term climate transitions. The most recent transition, occurring over the last 50 million years, consists of a long-term cooling and $p\text{CO}_2$ decrease that culminated in the onset of ice ages (Figure 1) (Beerling and Royer, 2011; Lear et al., 2000; Zachos et al., 2001). Over these transitions, $p\text{CO}_2$ is governed by four primary fluxes of carbon between the surface (ocean-atmosphere) and solid Earth reservoirs. Solid Earth degassing and organic carbon oxidation are the primary sources of CO_2 to the ocean-atmosphere system, whereas organic carbon burial and silicate rock weathering, coupled with burial of carbonate sediments, are the main processes that return CO_2 to the solid Earth reservoir (Berner, 2006a; Zeebe and Caldeira, 2008). Because the surface carbon reservoir is small relative to the fluxes to and from the solid Earth, a negative feedback between silicate weathering and climate is thought to be a requirement for a stable climate system (Berner and Caldeira, 1997; Maher and Chamberlain, 2014; Walker et al., 1981). On short timescales, this negative feedback is also hypothesized to modulate the recovery from transient carbon cycle perturbations (Archer, 2005; Colbourn et al., 2015; Panchuk et al., 2008; Uchikawa and Zeebe, 2008; Zeebe et al., 2009). However, direct evidence for this negative feedback over long timescales remains elusive.

Present-day estimates of silicate weathering fluxes are more closely linked with tectonic activity than with $p\text{CO}_2$ or climate (Edmond and Huh, 1997; Gaillardet et al., 1999; Millot et al., 2002; West et al., 2005), suggesting a weak or non-existent coupling between $p\text{CO}_2$ and silicate weathering and presenting a challenge to the negative feedback model (Edmond and Huh, 1997; McCauley and DePaolo, 1997). Estimates of silicate weathering fluxes in the geologic past also result in contradictory conclusions regarding the relationship between weathering and climate. For example, the long-term decrease in $p\text{CO}_2$ over the Cenozoic coupled with invariant or

declining carbon fluxes from solid Earth degassing (Rowley, 2002; van der Meer et al., 2014) suggest that silicate weathering fluxes must have also been stable or decreasing to balance the surface carbon cycle. However, marine isotopic proxies of silicate weathering—such as $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$, and $^{187}\text{Os}/^{188}\text{Os}$ —are often interpreted as reflecting increased silicate weathering fluxes over the same interval (McCauley and DePaolo, 1997; Misra and Froelich, 2012; Raymo and Ruddiman, 1992; Torres et al., 2014).

A number of hypotheses have been proposed to reconcile this inconsistency, many of which focus on varying the input and removal fluxes of carbon. For example, coupled inversion of a larger set of marine isotopic weathering proxies suggests that the increase in weathering derived from continental silicates over the Cenozoic has been balanced by an equivalent decrease in island arc basalt weathering (Li and Elderfield, 2013), a result supported by some forward models (Berner, 2006b; Mills et al., 2014). Most recently, Torres et al. (2014) demonstrated that sulfide weathering—combined with the long residence time of sulfur in the ocean—could contribute a geologically relevant source of carbon to the ocean-atmosphere system, balancing an increase in silicate weathering. Alternatively, at sufficiently low $p\text{CO}_2$, plant productivity may decrease non-linearly, reducing silicate weathering fluxes and stabilizing $p\text{CO}_2$ at the low values estimated for the Neogene (Pagani et al., 2009).

In contrast, Kump and Arthur (1997) proposed that total silicate weathering fluxes may not have varied over the Cenozoic; rather, $p\text{CO}_2$ may have declined simply as a consequence of increasing “weatherability”. In their hypothesis, increased weathering fluxes from active orogens (*i.e.*, the Himalayas) are balanced by declining fluxes elsewhere due to Cenozoic cooling. Collectively, these hypotheses predict different behaviors for the weathering feedback over the Cenozoic. For example, an increase in weatherability (Kump and Arthur, 1997) implies that the

surface of the Earth today is more efficient at weathering material than in the past, whereas reduced weathering fluxes due to decreasing plant productivity (Pagani et al., 2009) implies the opposite—that the Earth’s surface today is less efficient at generating weathering fluxes.

Thus, as a consequence of the inconsistencies between theory and geologic observations, the existence and precise behavior of the silicate weathering negative feedback remains uncertain. We define the strength of the negative feedback as the constant of proportionality (k) that relates the silicate weathering flux to climate (*i.e.*, $[p\text{CO}_2]^n$, where n allows for a non-linear response to climate). At a given $p\text{CO}_2$, a larger k results in a higher weathering flux; thus, k determines the efficiency by which CO_2 is converted to alkalinity. During transient or long-term carbon cycle perturbations, the value of k also determines the duration and magnitude of variations in $p\text{CO}_2$ by controlling the rate at which excess carbon is removed from the surface reservoir (Archer, 2005; Uchikawa and Zeebe, 2008). Thus, a negative feedback should result in a balanced carbon cycle over geologic timescales.

To test for the existence of a negative feedback, we first use carbon cycle data spanning the last 65 million years to reconstruct the inventories of carbon and alkalinity in the surface reservoir and calculate the resulting imbalances in the carbon cycle. This approach is independent of interpretations of marine isotopic weathering proxies (Zeebe and Caldeira, 2008). Second, we combine this result with carbon isotope data to apportion the fluxes of carbon from carbonate and silicate weathering. We find that (1) there has been minimal imbalance in the carbon cycle over the Cenozoic, which requires a strong negative feedback, and (2) silicate weathering fluxes have remained stable or slightly decreased over the same interval.

We use these two results to reconstruct the strength of the negative feedback over the Cenozoic. Given a combination of stable or slightly decreasing silicate weathering fluxes and a

much larger, long-term decrease in $p\text{CO}_2$, mass balance constraints require an increase in the strength of the negative feedback. In short, the coupling between silicate weathering and climate has become stronger, permitting stable silicate weathering fluxes through time, but at a lower $p\text{CO}_2$. We propose that the long-term decrease in $p\text{CO}_2$ over the Cenozoic can be explained entirely by changes in the strength of the feedback, without the need to invoke long-term changes in the removal or input fluxes of carbon (*e.g.*, silicate weathering or solid Earth degassing). An increase in the feedback strength may result from greater physical denudation in the late Cenozoic that results in a stronger coupling between weathering fluxes and climate (Maher and Chamberlain, 2014; West, 2012). Increasing feedback strength could also explain the observed modern-day correlation between physical denudation and weathering fluxes, the increases in marine isotopic weathering proxies during the Cenozoic, and the preponderance of carbon cycle perturbations in the Paleogene.

2. Approach and Carbon Cycle Model and Fluxes

The existence of a negative feedback between climate and silicate weathering should result in a small to negligible imbalance between the input and output fluxes (Berner and Caldeira, 1997; Zeebe and Caldeira, 2008). To test for the existence of a negative feedback that operates on less than 1 million year timescales, we use equations that relate the inventories of carbon and alkalinity to their respective fluxes in the ocean-atmosphere system. The advantage of this approach is that the inventories can be used to directly evaluate the imbalance in the carbon cycle without knowledge of the individual fluxes. To calculate the inventories, we use a model of the ocean-atmosphere carbon cycle, combined with estimates of Cenozoic $p\text{CO}_2$, calcite compensation depth (CCD), and seawater Mg/Ca and $[\text{Ca}^{2+}]$. After evaluating these

inventories, we then estimate the silicate weathering flux over the Cenozoic using carbon isotopes as recorded in organic matter and bulk carbonate and estimates of the solid Earth degassing and carbonate burial fluxes. Finally, we parameterize silicate weathering as a function of $p\text{CO}_2$ (*i.e.*, climate) and use the estimated silicate weathering flux to evaluate the strength of the coupling between silicate weathering fluxes and $p\text{CO}_2$ over the Cenozoic (see Section 4). Below, we present the equations, model, data compilation, and methodology upon which we rely to evaluate the strength of the negative feedback through time.

2.1. Carbon Cycle Imbalances

We first use equations that relate the mass balance of the surface inventories of carbon (M_C) and alkalinity (M_A) to the major fluxes of carbon to and from the solid Earth (Zeebe and Caldeira, 2008). Here, equation 1 tracks the mass balance of carbon in the ocean-atmosphere, whereas equation 2 balances the associated charges through the concept of alkalinity (Zeebe and Wolf-Gladrow, 2001):

$$\frac{dM_C}{dt} = F_{carb\omega} - F_{carb\beta} + F_{volc} + F_{org\omega} - F_{org\beta} \quad (1),$$

and

$$\frac{dM_A}{dt} = 2F_{carb\omega} - 2F_{carb\beta} + 2F_{sil\omega} \quad (2),$$

where $F_{carb\omega}$ and $F_{carb\beta}$ are carbonate weathering and burial, $F_{org\omega}$ and $F_{org\beta}$ are organic weathering and burial, F_{volc} is solid Earth degassing, and $F_{sil\omega}$ is the silicate weathering flux.

By subtracting equation 2 from equation 1, the total imbalance (I) can be calculated as:

$$I = \frac{dM_C}{dt} - 0.5 \frac{dM_A}{dt} = F_{volc} + F_{org\omega} - F_{org\beta} - F_{sil\omega} \quad (3).$$

Thus, the imbalance can be evaluated without knowledge of the individual fluxes if changes in M_C and M_A are constrained. Equation 3 also illustrates how I is unaffected by carbonate weathering and burial and reflects the balance between the net input flux of carbon from the solid Earth (F_{volc} and F_{orgw}) and the net removal flux to the solid Earth (F_{silw} and F_{orgb}) (McCauley and DePaolo, 1997; Zeebe and Caldeira, 2008).

2.1.1. Ocean-Atmosphere Carbon Cycle Model

To calculate the inventories of carbon (M_C) and alkalinity (M_A) through time, we use a three-box model of the ocean-atmosphere (Supplementary Figure S1). First, we speciate the surface ocean carbonate system by combining a compilation of proxy-estimated $p\text{CO}_2$ (Figure 1a and Table S1) with the assumption that the globally averaged surface ocean calcite saturation state (Ω) has remained constant over the Cenozoic ($\Omega = 4.5 \pm 1$ (1σ)) (Key et al., 2004; Tyrrell and Zeebe, 2004). Here, $\Omega = [\text{CO}_3^{2-}]/[\text{Ca}^{2+}]/K_{sp}$, where K_{sp} is the solubility product of calcite. We constrain $[\text{Ca}^{2+}]$ using fluid inclusion data from evaporites (Figure 1d and Table S1). Because K_{sp} is sensitive to Mg/Ca, we correct for changing Cenozoic seawater Mg/Ca (Figure 1c and Table S1) by using a linear relationship that relates K_{sp} to seawater Mg/Ca (Tyrrell and Zeebe, 2004). To speciate the deep ocean carbonate system, we treat the calculated surface ocean alkalinity as a conservative quantity (Key et al., 2004; Zeebe and Wolf-Gladrow, 2001) and assume the difference between deep and surface ocean alkalinity is 0 ± 200 $\mu\text{mol/kg}$ (Foster et al., 2012). To obtain a second deep ocean carbonate parameter, we calculate deep ocean $[\text{CO}_3^{2-}]$ by assuming that the CCD (Figure 1b) is equivalent to the calcite saturation horizon (CSH), where $\Omega = 1$.

Because we are concerned only with ocean-atmosphere equilibria, we calculate M_C and M_A every 1 million years. The above calculations are performed with a version of the “*seacarb*” R package (Lavigne and Gattuso, 2011) that has been modified to account for the effect of changing $[\text{Mg}^{2+}]$ on the carbonate system constants (K_1 and K_2) (Ben-Yaakov and Goldhaber, 1973). We also correct for deep ocean Cenozoic temperature change (Lear et al., 2000) (Figure 1e) and assume that the average surface ocean temperature is 11 °C warmer than the deep ocean (Key et al., 2004). We also assume constant ocean and atmosphere mass. The exact value of many of these parameters (Table 1) are drawn from the GLODAP database (Key et al., 2004). For calculating differences between the surface and deep ocean, we treat the upper 100 m of the water column as the surface ocean. The model is relatively insensitive to several of the primary assumptions, including the relationship between the CCD and CSH, the value and evolution of surface ocean Ω , and the precise reconstruction of seawater $[\text{Ca}^{2+}]$ and Mg/Ca (see Sensitivity Tests in Supplementary Material S2).

To account for the uncertainties in both the model parameters and in the input data, we use a Monte Carlo routine and calculate M_A and M_C 500 times over the Cenozoic (Table S2). To encapsulate the wide range of $p\text{CO}_2$ estimates, we evaluate two different CO_2 scenarios: Scenario 1 includes 82% of the proxy $p\text{CO}_2$ data and excludes values above ~2000 ppm (dark gray, Figure 1a), whereas scenario 2 includes nearly all $p\text{CO}_2$ data, including high (up to ~4500 ppm) $p\text{CO}_2$ estimates in the Eocene (light blue, Figure 1a). To further account for possibly large changes in $p\text{CO}_2$ over less than 1 million years, we assume any $p\text{CO}_2$ value within the minimum and maximum bounds set by these CO_2 scenarios is equally likely (*i.e.*, uniform distribution). This approach likely gives maximum bounds on the uncertainty associated with our results as this

implicitly assumes that $p\text{CO}_2$ throughout the Paleogene could have changed by more than 1000 ppm every 1 million years, which—outside of documented hyperthermal events—is unlikely.

2.1.2. Data-Model Comparison

As a test of this model, we compare our results to the modern ocean as well as reconstructions of the past ocean-atmosphere system using proxies and other model-based approaches. First, our calculations replicate approximate modern-day average surface ocean pH and alkalinity concentrations as well as total pre-industrial surface carbon (M_C) (Zeebe and Caldeira, 2008) (Figures 2 and 4a; Table S2). Second, our calculated pH estimates show similar trends to estimates from B/Ca and $\delta^{11}\text{B}$ -based estimates of surface ocean pH through time (Figure 2a and Table S1). Much of the uncertainty in these data is also captured by our Monte Carlo routine. Other model-based estimates of surface ocean pH further support our calculations. For instance, using a carbon cycle model embedded in a general ocean circulation model, Heinze and Ilyina (2015) found a globally averaged surface ocean pH of 7.9 in the late Paleocene (blue circle, Figure 2a). Using an Earth system model of intermediate complexity (GENIE), Ridgwell and Schmidt (2010) estimated a similar surface ocean pH and alkalinity concentration as our estimate for the late Paleocene (blue circle, Figure 2).

2.2. Estimating Cenozoic Silicate Weathering Fluxes

The degree of coupling between F_{silw} and $p\text{CO}_2$ (*i.e.*, strength of the feedback) can only be evaluated given knowledge of F_{silw} ; therefore, we use records of bulk carbonate (Katz et al., 2005; Kump, 1991) and organic (Falkowski et al., 2005) carbon isotopes (Figure 3a) to partition the fluxes of carbon to and from the ocean-atmosphere (Zeebe and Caldeira, 2008):

$$\frac{d(\delta_C M_C)}{dt} = F_{carbw} \delta_{carbw} - F_{carbb} \delta_{carbb} + F_{volc} \delta_{volc} + F_{orgw} \delta_{orgw} - F_{orgb} \delta_{orgb} \quad (4),$$

where δ_C is the $\delta^{13}\text{C}$ of M_C and δ_x is the $\delta^{13}\text{C}$ of the corresponding flux. In short, we combine equation 4 with equations 1 and 2 and reduce the number of unknowns in these equations to three (F_{silw} , F_{carbw} , and F_{orgw}), allowing us to fully constrain the fluxes of carbon using these three equations. The full range of parameter space and uncertainties in these calculations are captured through an additional Monte Carlo routine. Below, we describe the values for the known δ parameters and fluxes through time.

First, we directly calculate M_C and M_A , and associated dM_C/dt , and dM_A/dt , using our three-box model of the ocean-atmosphere system (Section 2.1). For δ_{carbb} , we use the carbonate $\delta^{13}\text{C}$ record of Katz et al. (2005), and, for δ_{orgb} , we use the organic $\delta^{13}\text{C}$ record of Falkowski et al. (2005) (Figure 3a). The $\delta^{13}\text{C}$ of ocean-atmosphere carbon (δ_C) is offset from carbonate $\delta^{13}\text{C}$ by approximately 2‰ (Hayes et al., 1999; Zeebe and Caldeira, 2008). For the remaining $\delta^{13}\text{C}$ values (δ_{volc} , δ_{orgw} , and δ_{carbw}), we use representative values that have been widely used in past work on geologic carbon cycling (Hayes et al., 1999; Kump and Arthur, 1999; Zeebe and Caldeira, 2008). For these δ values, we account for uncertainty in these values through time by assuming a uniform distribution of possible values; thus, for δ_{volc} , we use -6 to -1 ‰; for δ_{carbw} , we use 1.5 to 2 ‰, and; for δ_{orgw} , we use -30 to -20 ‰.

To estimate F_{carbb} , we rely primarily on the reconstruction of carbonate burial fluxes from Opdyke and Wilkinson (1988); however, we note that there is disagreement concerning carbonate burial fluxes in the past. For example, Earth system models of intermediate complexity configured for late Paleocene boundary conditions predict a total weathering flux of 35×10^{18} mol C/Myr in order to match the observed distribution of carbonate sediments (Panchuk et al.,

2008)—much higher than the original estimates of Opdyke and Wilkinson (1988) (Supplementary Figure S3a). In contrast, the LOSCAR model configured for the late Paleocene prescribes a total weathering flux of only 16×10^{18} mol C/Myr (Zeebe et al., 2009) (see error bars in Figure 3b). To incorporate this wide range of uncertainty into our calculations, we assume that any value within this range is equally likely (*i.e.*, uniform distribution) (Figure 3b) (see also discussion in Supplementary Material S1). Conceptually, this implies that the carbonate burial flux could vary by a factor of two every one million years. Though we view such large, rapid variations as unlikely, we do not reject them *a priori* given that there are documented large and rapid variations in CCD depth that may be associated with changes in carbonate burial (Pälike et al., 2012).

To estimate F_{volc} , we use a compilation of degassing estimates and seafloor spreading reconstructions (Table S1). For the seafloor spreading reconstructions, we normalize the estimated spreading half-rate to the modern and consider this normalized value to be equivalent to a degassing parameter (Bernier, 2006a; van der Meer et al., 2014). We then scale these reconstructions to the estimated modern-day degassing flux (Burton et al., 2013; Wallmann, 2001) (see Figure S3b for the individual degassing and seafloor spreading reconstructions). However, the modern-day degassing flux is uncertain, so we adopt minimum and maximum values for this flux ($8\text{--}14 \times 10^{18}$ mol C/Myr). These minimum and maximum values are then scaled with the degassing compilation to produce a large range of possible degassing histories through the Cenozoic (Figure 3c). Similar to F_{carbb} , we incorporate this wide range of uncertainty by assuming any value within this range is equally likely (*i.e.*, uniform distribution). Thus, our reconstructed degassing flux encompasses both a 40% decrease in degassing, as recently

estimated by van der Meer et al. (2014), and a null change in degassing over the Cenozoic, as estimated by some seafloor spreading reconstructions (Rowley, 2002).

Finally, to estimate F_{orgb} , we note that the fraction of carbon buried as organic matter (f_{orgb}) can be estimated using only carbon isotopes according to equation 5 (Hayes et al., 1999; Kump and Arthur, 1999):

$$f_{orgb} = \frac{\delta_{carb} - \delta_i}{\delta_{carb} - \delta_{orgb}} \quad (5),$$

where δ_i is the $\delta^{13}\text{C}$ of the total inputs of carbon to the ocean, which represents a weighted average of δ_{volc} , δ_{carb} , and δ_{org} . Though δ_i is a function of these δ values, we treat it as an independent variable. Typically, δ_i is assumed to be -5‰ , which is thought to be the long-term volcanic carbon $\delta^{13}\text{C}$ (Hayes et al., 1999; Kump and Arthur, 1999), though we assume δ_i can range uniformly from -8 to -3‰ , which should encompass any expected variation in the weighted-average $\delta^{13}\text{C}$ value of the input fluxes. With values of F_{carb} specified, we calculate F_{orgb} , incorporating the uncertainties in δ_i and in F_{carb} .

Using these parameters and input variables, we simultaneously solve for F_{carb} , F_{silw} , and F_{orgw} using equations 1, 2, and 4. We then use an additional Monte Carlo routine to calculate these values over the Cenozoic 10,000 times. The uniform uncertainties used in this Monte Carlo routine assumes that F_{volc} , F_{carb} , and the δ parameters could vary every one million years by the full range of our estimates. Consequently, the uncertainty on our estimates of F_{carb} , F_{silw} , and F_{orgw} are likely to be maximum bounds. If any calculation produces a negative flux, the entire set of calculations for the Cenozoic is discarded. Conceptually, this suggests that certain combinations of parameters are physically unrealistic. A total of approximately 2,500 of our 10,000 iterations are discarded as a result of this requirement. We then calculate associated mean

and standard deviations of F_{carbw} , F_{silw} , and F_{orgw} (Figure 3d; F_{orgw} presented in Supplementary Figure S5). Implicitly included in our calculation of F_{silw} is the portion of the silicate weathering flux derived from seafloor basalt weathering (F_{sfbw}). To test the sensitivity of our results to variations in F_{sfbw} , we explicitly partition these two silicate weathering fluxes in Supplementary Material S1 (Figure S7). Explicit treatment of the seafloor basalt weathering flux does not change our conclusions, but it does reduce and slightly smooth our estimate of terrestrial F_{silw} over the Cenozoic.

3. Results

3.1. Ocean-atmosphere inventories of carbon and alkalinity

We find that the total inventory of carbon (M_C) in the ocean-atmosphere was likely lowest in the Paleocene and Miocene and highest in the Eocene, though the precise magnitude of change depends upon the assumed CO_2 scenario (Figure 4a). The long-term decrease in $p\text{CO}_2$ during the mid-Cenozoic, from 40 to 20 Ma, resulted from the removal of $1.7\text{--}3.4 \times 10^{18}$ mol C from the ocean-atmosphere. Relative to the modern, this represents the removal of approximately 50–100% of the modern ocean-atmosphere M_C ($\sim 3.2 \times 10^{18}$ mol C). Calculated total ocean alkalinity (M_A) largely mirrors calculated M_C (not shown; Table S2). Unfortunately, there are few data-based constraints with which to compare these results. Using the LOSCAR model, Zeebe et al. (2009) estimated a baseline ocean carbon content of 2.83×10^{18} moles in the late Paleocene, which, when combined with their estimate of atmospheric $p\text{CO}_2$ (1000 ppm), yields a total ocean-atmosphere M_C strikingly similar to our estimated M_C (CO_2 scenario 2) in the late Paleocene (gray circle, Figure 4a).

3.2. Carbon Cycle Imbalances

For the entire Cenozoic, the imbalance (I) is always less than 10^{18} mol C, except for individual iterations with large (>1000 ppm), rapid (<1 Myr), and unrealistic $p\text{CO}_2$ changes (Figure 4b). Across the mid-Cenozoic decrease in $p\text{CO}_2$ (from 40 to 20 Ma), the cumulative imbalance is $1\text{--}2 \times 10^{18}$ mol C, a remarkably small number compared to cumulative inputs of $\sim 10^{20}$ mol C over that same interval (Berner and Caldeira, 1997; Berner, 2006a; Wallmann, 2001). Distributed over approximately 20 Myr, this decrease in $p\text{CO}_2$ requires only a sustained $\sim 0.25\text{--}0.5\%$ increase in the output fluxes (F_{silw} and/or F_{orgb}) relative to the input fluxes (F_{volc} and F_{orgw}). Normalized to the approximate modern day carbon input flux ($\sim 20 \times 10^{18}$ mol/Myr) (Wallmann, 2001), the removal flux has likely not differed from the input flux by more than 5% on 1 Myr timescales.

3.3. Silicate Weathering Fluxes

Our calculations reproduce the estimated modern F_{silw} from independent studies of the riverine flux of silicate-derived solutes (Gaillardet et al., 1999; Moon et al., 2014) ($\sim 10 \times 10^{18}$ mol C/Myr), though our calculated modern F_{carbw} ($16 \pm 4.9 \times 10^{18}$ (1σ) mol C/Myr) is on the lower end of the estimated modern F_{carbw} (Gaillardet et al., 1999; Meybeck, 1987) (Table S3). This low estimate is due primarily to the wide-range in the estimated Quaternary carbonate burial flux—ranging from $18\text{--}35 \times 10^{18}$ mol C/Myr (Hay, 1994; Iglesias-Rodriguez et al., 2002; Milliman and Droxler, 1996; Opdyke and Walker, 1992; Suchéras-Marx and Henderiks, 2014; Wallmann, 2001). Over the Cenozoic, we estimate an approximate 20% decrease in F_{silw} (dark, green line in Figure 3d), though our estimated uncertainty encompasses both no change and larger decreases (green shading in Figure 3d). This result is robust even given different

assumptions concerning F_{volc} , seafloor basalt weathering, and the δ_{orgb} record (see Supplementary Material S1). Similarly, F_{carbw} has also likely been relatively constant or slightly increasing over the Cenozoic, although the uncertainty on this flux is much larger than for F_{silw} .

4. Discussion

4.1. Parameterizing the Silicate Weathering Feedback

Given an approximately 3-fold decline in CO_2 , but only a 20% decline in F_{silw} , the relationship between the silicate weathering flux and CO_2 must have changed. In particular, the coupling between climate and silicate weathering must have increased, producing approximately the same weathering flux through time, but at a much lower $p\text{CO}_2$. Further, that the imbalance has been approximately zero through time provides further support for the presence of a negative feedback. To understand how variable feedback strength could explain the Cenozoic $p\text{CO}_2$ record, we use our results to develop and evaluate a new formulation for the negative feedback.

Because silicate weathering fluxes must be sensitive to climate, we approximate this relationship as a function of the well-constrained logarithmic sensitivity of climate to $p\text{CO}_2$ (Knutti and Hegerl, 2008):

$$F_{silw} = k [\log_2(R_{\text{CO}_2}) + 1] \quad (6).$$

Here, R_{CO_2} is the ratio between $p\text{CO}_2$ at time t and the modern, $\log_2$ accounts for the logarithmic response of climate to changes in $p\text{CO}_2$, and k is a constant of proportionality that links climate and the silicate weathering flux. This constant of proportionality is a measure of the collective reactivity at the Earth's surface and is modified by a variety of factors, including the geographic distribution of lithology and topography (Gibbs et al., 1999; Lee et al., 2015; Maher and Chamberlain, 2014), plant physiochemical responses (Doughty et al., 2014; Pagani et al., 2009;

Quirk et al., 2014), and total continental area (Gibbs et al., 1999; Munhoven, 2002). Other functional relationships between F_{silw} and $p\text{CO}_2$ have been proposed (Berner, 2006a; Gibbs et al., 1999; Uchikawa and Zeebe, 2008; Walker et al., 1981), but our results are largely insensitive to the exact form of this relationship (see Section 4.4).

4.2. Evaluating Feedback Strength

We combine our estimate of F_{silw} with the $p\text{CO}_2$ compilation to calculate the strength of the silicate weathering feedback (*i.e.*, k) through time. To do so, we normalize F_{silw} to the modern flux ($R_{F_{silw}}$) and calculate the strength of the silicate weathering feedback relative to modern (R_k):

$$R_k = \frac{R_{F_{silw}}}{\log_2(R_{\text{CO}_2}) + 1} \quad (7).$$

Given stable or slightly decreasing F_{silw} (Figure 3d) and decreasing $p\text{CO}_2$ (Figure 5a), the strength of the silicate weathering feedback must have reached a minimum in the Eocene and increased substantially to a high in the Neogene (Figure 5b). This increase in k implies that silicate weathering has become more efficient, producing the same weathering flux at lower $p\text{CO}_2$. The increase in feedback strength is robust despite the large uncertainties in F_{carb} and F_{volc} (see also Figure S2) and largely insensitive to our assumed F_{volc} record (Figure S4). Indeed, k over the Cenozoic resembles the inverse of the $p\text{CO}_2$ record, due to the relative invariance of F_{silw} compared to $p\text{CO}_2$.

Alternatively, if the feedback strength (k) has been constant through time, high $p\text{CO}_2$ in the Eocene results in F_{silw} two- to four-fold higher than today (Figure 6a). There are no estimates of Paleogene F_{silw} of this magnitude. Furthermore, such a high alkalinity flux would manifest as high F_{carb} . Although estimates of Paleogene F_{carb} are uncertain (see Section 2.2), there is currently no evidence that F_{carb} was sufficiently elevated to accommodate such high F_{silw} . Even

if F_{carb} was higher in the Paleogene, a constant feedback strength would require that carbonate weathering (F_{carbw}) supplied little to no alkalinity to the ocean and that silicate weathering was the dominant or sole source of alkalinity in the Paleogene (Figure 6b). Although we consider such a scenario unlikely, there is little data concerning past variations in F_{carbw} with which to evaluate this alternative. Although sea level was likely higher in the Paleogene (Gasson et al., 2012), which may have reduced carbonate weathering on continental shelves, higher $p\text{CO}_2$ —and consequently higher temperature and runoff—would have promoted greater carbonate weathering elsewhere (Gibbs et al., 1999). Thus, it appears unlikely that F_{silw} was two- to four-fold higher in the Paleogene and, as a consequence, k must have increased through time.

Remarkably, marine isotopic proxies of weathering—including $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$, and $^{187}\text{Os}/^{188}\text{Os}$ —mirror the increase in k (Figure 5c), suggesting that these proxies record changes in feedback strength rather than changes in the weathering flux. Our results support previous work from both river-catchment and single-site studies, as well as carbon cycle arguments that marine isotopic records may not directly record the weathering flux (Berner and Caldeira, 1997; Myrow et al., 2015; Quade et al., 1997; Willenbring and von Blanckenburg, 2010). An increase in the efficiency of weathering, for example due to higher erosion rates and enhanced supply of fresh mineral to the weathering zone, does not necessarily generate an increase in weathering fluxes (Maher and Chamberlain, 2014), but could shift the isotopic composition of those weathering fluxes, particularly for $\delta^7\text{Li}$ (Bouchez et al., 2013), but also for Sr isotopes (Clow et al., 1997; Taylor et al., 2000). The possibility that the marine isotope records reflect the strength of the feedback may allow for the quantitative use of isotopes in deconvolving the various factors that influence k , such as regolith formation rates, uplift, the distribution of exposed lithologies, and plant physiochemical responses.

4.3 Variable Feedback Strength and $p\text{CO}_2$

How does changing feedback strength alter $p\text{CO}_2$ levels? On long timescales, the mass balance of atmospheric CO_2 is set by:

$$\frac{d\text{CO}_2}{dt} = P - k[\log_2(R_{\text{CO}_2}) + 1] \quad (8)$$

where P is the net carbon release in equation 3 (*i.e.*, $P = F_{\text{volc}} + F_{\text{orgw}} - F_{\text{orgb}}$). Because I is approximately zero through time and, given ocean-atmosphere equilibrium, is proportional to changes in $p\text{CO}_2$ on long timescales, we solve equation 9 at steady-state:

$$R_{\text{CO}_2} = 2^{\left(\frac{P}{k} - 1\right)} \quad (9)$$

According to equation 9, changes in $p\text{CO}_2$ are caused by changes in P or in k (Figures 7 and 9a). In these figures, the steady-state $p\text{CO}_2$ is denoted by the intersection of the solid and dashed lines, and long-term $p\text{CO}_2$ is set by a combination of P and the feedback strength k . Thus, long-term changes in $p\text{CO}_2$ are accomplished by transient imbalances that last less than 1 Myr, with the precise magnitude and timescale of the transient imbalance modulated by the value of k (Uchikawa and Zeebe, 2008). These transient increases in the weathering flux are the physical manifestation of a strengthening weathering feedback. Alternatively, decreases in solid Earth degassing (*i.e.*, decreases in P) of up to ~40% over the Cenozoic (van der Meer et al., 2014) can explain a portion of the decline in $p\text{CO}_2$; however, because $p\text{CO}_2$ has declined 3-fold requires an additional change in k . If, instead, degassing has been constant (Rowley, 2002), then the required change in k is even greater (see R_k uncertainty bounds in Figure 5b).

4.4. Comparison among different formulations of the feedback

The precise mathematical form of the feedback is an important consideration for understanding the weathering response to changes in climate and for modeling both long- and short-term carbon cycle perturbations. Although our calculations cannot precisely determine the mathematical form of the feedback, the logarithmic formulation presented in equation 6 (Section 4.1) has two advantages over previous formulations of the feedback. First, it effectively removes the climatic sensitivity of the feedback [$\text{Log}_2(R_{CO_2})$] from the aspects which are not likely to be driven primarily by climate (*i.e.*, k), such as paleogeography, uplift rates, distribution of exposed lithologies, etc. Although there are certainly connections between these effects and climate, this distinction provides a useful method to separate the drivers of changes in weathering. Second, this formulation is based firmly within an actual mechanism to translate climate to silicate weathering fluxes—through the well-constrained logarithmic sensitivity of climate to $p\text{CO}_2$. Nevertheless, we discuss how alternative formulations affect our results.

Different formulations of the feedback strength alter the precise change in k needed to explain the Cenozoic $p\text{CO}_2$ record and maintain carbon mass balance. Here, we compare our results with a more general form of the weathering feedback that has been used extensively in carbon cycle models (Archer, 2005; Gibbs et al., 1999; Schwartzman and Volk, 1989; Uchikawa and Zeebe, 2008; Zeebe, 2012):

$$F_{silw} = k[CO_2]^n \quad (10),$$

where k is the weathering time constant [units: Myr^{-1} if $n = 1$] and n is a reaction order term. In equation 10, n acts similarly to the logarithmic dependence in equation 6; however, the value of n is poorly constrained. Previous studies have specified values of n that range from 0.2 to 1 (Berner, 2006a; Gibbs et al., 1999; Kump et al., 2000; Uchikawa and Zeebe, 2008; Walker et al., 1981; Zeebe et al., 2009). To better compare equation 10 with the logarithmic formulation

(equation 6), we first normalize $p\text{CO}_2$ (R_{CO_2}) and F_{silw} (R_{Fsilw}) to solve for the relative strength of the feedback (R_k), such that:

$$R_{\text{Fsilw}} = R_k (R_{\text{CO}_2})^n \quad (11).$$

In Figures 7 and 8, we compare the logarithmic formulation of the feedback (equation 6) with the more general form (equation 11) solved for $n = 0.6$ and $n = 0.2$, similar to the range of values used in the GEOCARB and LOSCAR models (Berner and Kothavala, 2001; Uchikawa and Zeebe, 2008; Zeebe, 2012), though we note that in the GEOCARB model, the effective n changes over the Phanerozoic. The lower the value of n , the smaller the required change in R_k over the Cenozoic relative to the logarithmic formulation (Figure 8).

Unfortunately, there are few constraints on the value of n with which to evaluate the precise sensitivity of the weathering feedback. Many parameterizations of silicate weathering are sourced from the original weathering feedback model of Walker et al. (1981), which uses an $n = 0.3$ derived from feldspar dissolution experiments that were performed with exceptionally high $p\text{CO}_2$ (1 to 10 bars). However, $p\text{CO}_2$ has never been that high during the Cenozoic and weathering in catchments is far more complex than in a laboratory (Maher and Chamberlain, 2014; White and Brantley, 2003). Walker et al. (1981) also included a temperature and runoff dependence in their model, implying a weathering sensitivity equivalent to $n \approx 0.5$, rather than simply $n = 0.3$ (Figure 7). Further, the rise of land plants and the spread of angiosperms is thought to have made silicate weathering more sensitive (*i.e.*, higher n), particularly in the Phanerozoic (Berner, 1992).

Further, the lower the value of n , the greater the increase in steady-state $p\text{CO}_2$ given an increase in carbon inputs. A negative feedback characterized by a very low n (*i.e.*, $n = 0.2$) is exceptionally insensitive and permits large changes in CO_2 given changes in carbon inputs. We

conceptualize this in Figure 7 by plotting different formulations of the feedback at steady-state with a modern k . For example, changes in P of 50-100%—as estimated for the Mesozoic (Berner, 2006a; van der Meer et al., 2014)—coupled with a feedback characterized by $n = 0.2$, would produce exceptionally large changes in $p\text{CO}_2$ (Figure 7; from P_1 to P_2). Thus, we view such an insensitive feedback as unlikely given that large, long-term changes in P could not be matched by silicate weathering fluxes. Alternatively, although we argue that k has varied over the Cenozoic, we cannot exclude simultaneous changes in the formulation (*i.e.*, changing n or variable logarithmic sensitivity) through time (Berner and Kothavala, 2001). Such variations would also cause changes in the strength of the weathering feedback that would be difficult to distinguish from changes in only k . High-resolution carbon isotope records across carbon cycle perturbations (*i.e.*, Cui et al., 2011) may be a promising method to resolve the precise formulation of the weathering feedback and changes through time.

5. Implications and Conclusions

Because feedback strength partially sets the steady-state $p\text{CO}_2$ level and determines both the magnitude and timescale of transience in the geologic carbon cycle, changing feedback strength over the Cenozoic impacts both short-term carbon cycle perturbations and long-term climatic change. For instance, a weaker negative feedback permits a greater accumulation of CO_2 in the ocean-atmosphere reservoir and a more pronounced climatic response. Thus, an increase in P would produce a greater $p\text{CO}_2$ response (point 2 to 4, Figure 9a) than would an equivalent P increase coupled with a strong feedback (point 1 to 3, Figure 9a). Further, a weaker silicate weathering feedback removes CO_2 more slowly from the ocean-atmosphere reservoir following a carbon cycle perturbation (Figure 9a, inset). This prolongs the effects of such a perturbation, and

may explain the prevalence of numerous carbon cycle perturbations (“hyperthermals”) in the Paleogene (lower R_k) relative to the Neogene (higher R_k). Although several hypotheses have been proposed to explain the high frequency of Paleogene hyperthermals (DeConto et al., 2012; Kirtland Turner et al., 2014; Lunt et al., 2011), we propose a weaker silicate weathering feedback may have pre-conditioned the Earth system to be more susceptible to sudden carbon release by permitting excess carbon to remain in the surface reservoir for a longer interval. Thus, at constant P , hyperthermals and high $p\text{CO}_2$ are emergent properties of the same phenomenon—a weakened negative feedback.

Cenozoic increases in seawater $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$, and $\delta^7\text{Li}$ (Figure 5c) have been attributed to elevated global silicate weathering fluxes in response to uplift of mountain ranges (McCauley and DePaolo, 1997; Misra and Froelich, 2012; Raymo and Ruddiman, 1992). In contrast, stable or decreasing solid Earth degassing (Rowley, 2002; van der Meer et al., 2014) combined with minimal carbon imbalance (*i.e.*, $I = 0$) are inconsistent with elevated global weathering fluxes (Kump and Arthur, 1997). Our calculations reconcile this long-standing debate. The long-term decline of CO_2 over the Cenozoic may not have been driven by long-term (>1 Myr) changes in silicate weathering fluxes or changes in carbon inputs. Instead, the climate system could have been entirely forced by changes in the weathering feedback strength, although to determine the precise magnitude of the change in feedback strength will require more robust carbon cycle reconstructions. The feedback strength, which is fundamentally a measure of the collective reactivity at the Earth’s surface, closely mirrors the marine isotope proxies, suggesting that these proxies are recording a marked change in the nature of weathering over the course of the Cenozoic.

That the efficiency of weathering has increased over the Cenozoic is in contrast to the hypothesis of Pagani et al. (2009) that weathering fluxes are inhibited at low $p\text{CO}_2$ by plants, which would be manifest as decreased weathering efficiency and, hence, a weaker feedback. Indeed, our hypothesized increase in the strength of the weathering feedback may actually be an underestimate if weathering fluxes have increased in the Cenozoic as a result of additional CO_2 supply from sulfide weathering (Torres et al., 2014). Because our analysis only provides constraints on the magnitude of the total fluxes permitted by current carbon cycle reconstructions, we cannot pinpoint the precise lithological source or geographic area that has driven constant, global weathering fluxes. Thus, we cannot evaluate more specific hypotheses that suggest decreasing island-arc basalt weathering has balanced increased continental silicate weathering fluxes (Li and Elderfield, 2013) or that increased Himalayan weathering has been balanced by decreased weathering elsewhere (Kump and Arthur, 1997).

Instead, we propose that the mechanism that sets the feedback strength is the interplay between tectonics, exposed lithologies and climate (Berner, 2006a; Maher and Chamberlain, 2014; West, 2012). Uplift and glaciation in the late Cenozoic (Herman et al., 2013) would increase the supply of reactive lithologies at the Earth's surface, elevating silicate weathering and removing CO_2 over less than 1 Myr timescales. This drives cooling and reduces runoff (Gibbs et al., 1999; Manabe et al., 2004), which, in turn, reduces silicate weathering (point 2 to 1, Figure 9b). Thus, over 1 Myr timescales, this mechanism maintains invariant F_{silw} , while simultaneously strengthening the weathering feedback, resulting in the modern-day observed correlation between tectonics and weathering fluxes. As a consequence, the Quaternary Earth has a greater capacity to increase weathering fluxes in response to large carbon cycle perturbations than in the geologic past. Future work to identify the functional form of the weathering feedback, and its

relationship to marine isotope proxies, will greatly improve our ability to model past and future Earth systems.

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Tables

Table 1: Parameters and uncertainties used in speciating the inorganic carbonate system in our three-box model of the deep ocean, surface ocean, and atmosphere. Uncertainties are accounted for using a Monte Carlo routine.

Parameter	Value	Uncertainty (abs)	Units	Uncertainty Distribution ⁸
Salinity	35 ¹	± 0.6 ¹	psu	Gaussian
Deep Ocean T	0.8-13.6 ²	± 2 ³	°C	Gaussian
Surface-Deep Temperature Difference	11 ¹	--	°C	--
Surface Ocean Ω	4.5 ^{1,4}	± 1 ^{1,4}	--	Gaussian
Surface-Deep [Alkalinity] Difference	0 ^{1,5}	± 200 ^{1,5}	μmol/kg	Uniform
Deep Ocean Mass	1.37 ⁶	--	10 ²¹ kg	--
Surface Ocean Mass	2.8 ⁶	--	10 ¹⁹ kg	--
CCD	3-4.7 ⁷	±0.6	km	Gaussian
Atmospheric Volume	1.8	--	10 ²⁰ mol	--

¹Key et al. (2004)

²Lear et al. (2000)

³We use a truncated Gaussian distribution, with 0 °C as the lower limit.

⁴Tyrrell and Zeebe (2004)

⁵Foster et al. (2012)

⁶Zeebe and Caldeira (2008)

⁷Pälike et al. (2012); Van Andel (1975)

⁸These distributions are used in the Monte Carlo routine.

Figure Captions

Figure 1: Carbon cycle data used in reconstructing the Cenozoic carbon cycle. (a) $p\text{CO}_2$ proxy data. (b) Reconstructed calcite compensation depth (CCD) (Pälike et al., 2012; van Andel, 1975); (c) Seawater Mg/Ca; (d) Seawater $[\text{Ca}^{2+}]$, and; (e) Deep ocean temperature (Lear et al., 2000). In c and d, gray points are estimates from cited studies, and black line is the estimate used in reconstructing the carbon cycle. In d, error bars are full range of estimated $[\text{Ca}^{2+}]$ from the cited references. Shaded areas in a, b, and e indicate the uncertainty used in the Monte Carlo routine, and black line indicates the mean value. Full references to data are listed in Supplementary Table S1. [size: full page width]

Figure 2: Model output from the three-box model of the ocean-atmosphere carbon cycle and comparison with data and additional carbon cycle models. (a) Surface ocean pH, compiled from proxy estimates using $\delta^{11}\text{B}$ and B/Ca. Error bars are absolute 1σ from the cited studies. Blue circle at 56 Ma is a globally averaged estimate of surface ocean pH from a carbon cycle model embedded in an ocean general circulation model (Heinze and Ilyina, 2015). (b) Surface ocean alkalinity concentrations. Red circles in (a) and (b) are estimates from an Earth system model of intermediate complexity (GENIE) (Ridgwell and Schmidt, 2010). Shading indicates individual iterations from Monte Carlo routine for CO_2 scenarios 1 and 2. Surface ocean dissolved inorganic carbon (DIC) mirrors the alkalinity record (not shown). Full references to data are listed in Supplementary Table S1. [size: full page width]

Figure 3: $\delta^{13}\text{C}$ records and estimated weathering fluxes. (a) Carbonate (Katz et al., 2005) (black line; gray points) and organic carbon (Falkowski et al., 2005) (green line and points) $\delta^{13}\text{C}$ records. (b) Range of $F_{\text{carb}}^{\text{bb}}$ used to calculate F_{silw} . Black line is the lower estimate of $F_{\text{carb}}^{\text{bb}}$ from Opdyke and Wilkinson (1988), and upper, dashed line indicates the lack of data to constrain the maximum $F_{\text{carb}}^{\text{bb}}$ flux. Error bars at 0 Ma and 56 Ma are estimated total weathering fluxes (Gaillardet et al., 1999; Moon et al., 2014; Panchuk et al., 2008; Zeebe et al., 2009). (c) Range of F_{volc} . (d) Calculated F_{silw} (solid and green shading) and $F_{\text{carb}}^{\text{bw}}$ (dashed and gray shading). Shading in (d) indicates 1σ from Monte Carlo routine. [size: full page width]

Figure 4: Calculated total ocean-atmosphere carbon (M_C) and carbon cycle imbalance. (a) Calculated M_C . Gray point at ~ 56 Ma is estimated M_C from Zeebe et al. (2009). (b) Absolute imbalance (I) and imbalance normalized to modern carbon input fluxes ($\sim 20 \times 10^{18}$ mol C/Myr). Shading indicates individual iterations from Monte Carlo routine for the 2 CO_2 scenarios. [size: full page width]

Figure 5: Strength of the weathering feedback and marine isotope records. (a) Proxy $p\text{CO}_2$ estimates plotted on log-axis (same data as in Figure 1a). (b) Relative strength of the weathering feedback, normalized to the modern (R_k). Shading indicates estimated range of R_k given mean values of $p\text{CO}_2$ and incorporating 1σ uncertainty in F_{silw} . (c) Marine carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ (McCauley and DePaolo, 1997), $^{187}\text{Os}/^{188}\text{Os}$ (Klemm et al., 2005; Torres et al., 2014), and $\delta^7\text{Li}$ (Misra and Froelich, 2012) records (smoothed). [size: full page width]

Figure 6: Implications of a constant weathering feedback strength (*i.e.*, constant k) through time. (a) The predicted absolute silicate weathering flux (F_{silw}) if k is constant. (b) The percentage of

the carbonate burial flux (from Figure 3b) supplied by the silicate weathering flux (from a). Note that the maximum allowable percentage is 100%, which requires that all of the alkalinity buried in carbonate sediments be supplied by silicate weathering. Such a condition would imply that carbonate weathering supplies no alkalinity. [size: full page width]

Figure 7: A comparison of the effect of the mathematical formulation of the feedback on steady-state $p\text{CO}_2$. Blue lines are negative feedback curves utilizing the logarithmic sensitivity [*i.e.*, $\text{Log}_2(R_{\text{CO}_2})$] (this study; equation 6) and a modern R_k (1) and an Eocene R_k value (0.34). Green line is based upon the Walker et al. (1981) formulation of the weathering feedback. Black lines use the more general formulation of the feedback, using a modern k , and solved at different values of n (equation 11) (Uchikawa and Zeebe, 2008). R_p is the carbon input flux (P) normalized to the modern P . R_{CO_2} is the normalized $p\text{CO}_2$ relative to modern. P_1 and P_2 indicate different levels of carbon inputs. Note that, depending upon the value of n and on the mathematical form, increases in P produce different levels of steady-state $p\text{CO}_2$, as indicated by the intersections between the feedback lines (solid) and P (dashed lines). [size: one-and-a-half page width]

Figure 8: Comparison of R_k over the Cenozoic with different mathematical formulations of the silicate weathering feedback. (a) Assumes the feedback is characterized by a logarithmic expression (equation 6) (same as in Figure 5b). (b) and (c) Assumes the feedback is characterized by both a weathering time constant (k) and a reaction order term (n) (equation 11). In (b) and (c), n is specified, and we solve for k , and then normalize to the modern k , yielding R_k . (b) $n = 0.6$. (c) $n = 0.2$. All figures are plotted on the same y-axis scale. [size: full page width]

Figure 9: Conceptual model for steady-state $p\text{CO}_2$, invariant weathering fluxes, and weathering feedback strength. (a) Steady-state $p\text{CO}_2$ (intersection of dashed (P) and solid lines (F_{silw})) for different silicate weathering feedback strengths (variable k) and carbon inputs (P_1 and P_2) (Equation 9). A long-term increase in carbon inputs (P_1 to P_2) produces a smaller steady-state $p\text{CO}_2$ increase given a strong feedback (point 1 to 3) versus a weak feedback (point 2 to 4). Increasing feedback strength can also decrease $p\text{CO}_2$ without changing F_{silw} (arrow). Inset shows the transient response to an equivalent $p\text{CO}_2$ increase given either a strong (gray) or weak (blue) weathering feedback. (b) Translation of feedback strength into a conceptual model for weathering fluxes per continental area adapted from Maher and Chamberlain (2014), demonstrating an increase in the strength of the weathering feedback (point 2 to 1) due to uplift and/or an increase in reactive lithologies. After an initial, transient (<1 Myr) increase in weathering fluxes (path denoted by arrows), the reduction in $p\text{CO}_2$ decreases global temperatures and runoff, in turn reducing weathering fluxes, and resulting in invariant weathering fluxes and an increase in the strength of the weathering feedback over >1 Myr timescales. [size: half page width]

Figure 1

Figure 2

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Figure 9