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5 GEOLOGIC CARBON CYCLE CONSTRAINTS ON THE
6 TERRESTRIAL HYDROLOGICAL RESPONSE TO HIGHER
7 ATMOSPHERIC CO₂

8
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16 **Key Points:**

- 17 1. The silicate weathering negative feedback depends upon runoff to drive recovery
18 from carbon cycle perturbations.
19 2. Decreases in runoff with warming would lead to runaway greenhouse states.
20 3. The sensitivity of runoff to warming has a lower-bound of 0%/K as dictated by
21 carbon cycle constraints.
22

23 **Abstract**

24 How runoff will change as atmospheric CO₂ rises depends upon several difficult to project
25 factors, including CO₂ fertilization, lengthened growing seasons, and vegetation greening.
26 However, geologic records of the hydrological response to past carbon cycle perturbations
27 indicate large increases in runoff with higher CO₂. We demonstrate that the fact that the Earth
28 has remained habitable since life emerged sets a lower-bound on the sensitivity of runoff to
29 CO₂ changes. The recovery of the Earth system from perturbations is attributed to silicate
30 weathering, which transfers CO₂ to the oceans as alkalinity via runoff. Though many factors
31 mediate weathering rates, runoff determines the total flux of silicate-derived cations and hence
32 the removal flux of excess CO₂. Using a carbon cycle model that parameterizes weathering as
33 a function of rock reactivity, runoff, temperature, and soil CO₂, we show that recovery from a
34 perturbation is only possible if the lower-bound for the sensitivity of runoff to atmospheric CO₂
35 is 0%/K. Using proxy data for the Paleocene-Eocene Thermal Maximum, we find that to match
36 the marine $\delta^{13}\text{C}$ record requires a runoff sensitivity greater than 0%/K and similar to estimates
37 of the modern runoff sensitivity derived from an ensemble of Earth system models. These
38 results suggest that the processes that enhance global runoff are likely to prevail over processes
39 that tend to dampen runoff. In turn, that the Earth has always recovered from perturbations
40 suggests that, though the runoff response is spatially complex, global discharge has never
41 declined in response to warming, despite quite varied paleogeographies.

42

43 **Plain Language Summary**

44 Runoff—the quantity of water delivered by rivers to the ocean—is likely to change as the
45 climate warms. However, because generation of runoff involves many small-scale processes,
46 it is difficult to forecast how global patterns of runoff will change as atmospheric CO₂ rises.
47 We take advantage of the fact that runoff is the primary mechanism that transfers excess CO₂
48 from the atmosphere to the ocean for eventual burial as carbonate rock. It is this process that
49 permits the Earth to recover from major perturbations. We find that runoff must increase in a
50 warmer world; if it did not, then atmospheric CO₂ would continually increase in the
51 atmosphere, leading to a runaway greenhouse. This hard constraint places a lower-bound on
52 how runoff must change in response to rising atmospheric CO₂.

53

54 1. Introduction

55 Runoff—the transfer of water from the continents to the oceans and to closed basins—
56 is a critical component of the Earth system. Runoff (q) determines the amount of freshwater
57 available for societal use, transports nutrients from upland landscapes to lowland and marine
58 ecosystems and provides the water necessary to weather rocks that sequester atmospheric CO₂.
59 Despite its importance for the functioning of the Earth system and for societies, how q will
60 change as atmospheric CO₂ rises remains highly uncertain. Part of this uncertainty arises
61 because the hydrological cycle is comprised of a number of different and interacting
62 components—including precipitation (P), bare-soil and vegetation-controlled evaporation
63 (ET), and q —which may respond differently to rising atmospheric CO₂ and temperature (Milly
64 & Dunne, 2016). For some components, there are well grounded theoretical expectations for
65 how they should change. Precipitation globally is thought to increase by approximately 2%/K
66 given constraints on how much energy is available for evaporation (Held & Soden, 2006;
67 Pendergrass & Hartmann, 2014). Potential evapotranspiration (PET) over land should also
68 increase, as rising temperatures drive increases in the saturation vapor deficit. This increase in
69 PET is robustly predicted to be larger than the increase in P (Scheff & Frierson, 2014).

70 Collectively, these expectations—combined with observations that support them—
71 suggest that much of the land surface will become more arid with warming (Cook et al., 2014;
72 Ficklin & Novick, 2017; Mankin et al., 2019; Milly & Dunne, 2020; Novick et al., 2016;
73 Overpeck & Udall, 2020). However, there remain two critical, linked components of the
74 hydrological cycle for which theoretical expectations and observational constraints are of low-
75 confidence and poor—actual ET and q (Douville et al., 2021). ET determines how much P is
76 returned to the atmosphere and how much is partitioned to q ; as a consequence, ET and P
77 determine surface water availability. Vegetation water use (*i.e.*, transpiration) is thought to be
78 the predominant component of ET (~ 60%) (Good et al., 2015; Schlesinger & Jasechko, 2014;
79 Wei et al., 2017); vegetation additionally impacts another 10-15% of ET due to intercepted P
80 that evaporates directly from the leaf or woody surface (Wang-Erlandsson et al., 2014). Thus,
81 in addition to the physical response to CO₂ increase (P and PET), the global vegetation
82 response to rising CO₂ will further determine the trajectory of surface water availability.

83 However, projecting how global vegetation will change and its impact on q remains
84 difficult. Though leaf-level transpiration is expected to decrease as CO₂ rises, total leaf area is
85 expected to increase; the competition of these two processes globally will partially determine
86 the total change in q . Satellite observations indicate that the world is overwhelmingly greening
87 and that this greening is leading to greater ET (Forzieri et al., 2020; Winkler et al., 2021; Zhu

88 et al., 2016). In semi-arid regions, observations indicate this greening and associated increase
89 in ET has led to declining q (Ukkola et al., 2016), and many land-surface models—which are
90 designed to encapsulate a number of specific plant physiological process—find that increases
91 in leaf area have been substantial enough to reduce q globally (Forzieri et al., 2020; Piao et al.,
92 2007). In contrast, coupled land-atmosphere models find that, while the Earth’s surface greens
93 substantially, the resulting increase in ET fluxes is less than the increase in P (Lemordant et
94 al., 2018; Swann et al., 2016). Though this prediction is spatially heterogeneous (Mankin et al.,
95 2019) and of low-confidence, the mean global average change in q with temperature is
96 predicted to be $\sim 2.9 \pm 1$ %/K across the CMIP5 ensemble using the RCP8.5 scenario (Zhang
97 et al., 2014). Much of this increase is driven by widespread model agreement of increasing q
98 in the northern high latitudes (Scheff et al., 2017). However, there remain serious questions
99 about how leaf-level processes and slower vegetation responses (*i.e.*, species compositional
100 changes) are parameterized within these coupled models. As a consequence, there is no firm
101 theoretical expectation nor well-constrained observations to indicate whether global ET will
102 increase or decrease relative to P and, therefore, how globally averaged q will change as
103 atmospheric CO_2 rises.

104 This disagreement and uncertainty regarding the direction and magnitude of the global
105 q change as CO_2 rises stands in sharp contrast to both geologic observations of the hydrological
106 response to increasing CO_2 and theory regarding how the Earth system has recovered from
107 large carbon cycle perturbations in the geologic past. These recoveries are mediated by the
108 weathering of silicate rocks, which converts atmospheric CO_2 to alkalinity and permanently
109 buries carbon in marine sediments (R. A. Berner & Kothavala, 2001; Penman et al., 2020).
110 Critically, the weathering of rocks and transport of alkalinity to the ocean is thought to be
111 mediated primarily by q (Kump et al., 2000; Li et al., 2022; Maher & Chamberlain, 2014; Otto-
112 Bliesner, 1995; Park et al., 2020), both to supply water to the weathering zone and to transport
113 the products of weathering to the ocean. The fact that life has persisted on Earth for more than
114 3 Ga indicates that this feedback must be particularly robust, capable of regulating Earth’s
115 climate largely independent of the precise position of the continents, extant flora and fauna,
116 and magnitude and nature of the various climatic perturbations that have befallen Earth over
117 its history (Sagan & Mullen, 1972; Walker et al., 1981). Similarly, a growing body of literature
118 suggests that these past perturbations caused dramatic reorganizations of the terrestrial
119 hydrological cycle, recorded as thick packages of coarse-grained fluvial sediments during peak
120 warming (Chen et al., 2018; Foreman et al., 2012) and enhanced fluxes of nutrients and silica

121 to the ocean as reflected in widespread marine anoxia and chert deposits during many of these
122 carbon cycle perturbations (Penman, 2016; Them et al., 2017).

123 Here, we exploit this fundamental negative feedback in the Earth system and its
124 relationship with q to provide a lower bound on how globally q must respond to changes in
125 atmospheric CO₂. To constrain how q must respond to changes in atmospheric CO₂, we employ
126 a version of a geological carbon cycle model that has been modified to represent the explicit
127 role of q in modulating weathered solute concentrations and fluxes. We demonstrate that the
128 operation of this weathering feedback requires that q does not decrease with rising atmospheric
129 CO₂ and, most likely, is positively sensitive to changes in CO₂, such that the flux of weathered
130 material always increases if CO₂ rapidly increases in the atmosphere. We further test this model
131 against geological data from the Paleocene-Eocene Thermal Maximum (PETM), and
132 demonstrate that, to match geological proxy data from the PETM requires that globally
133 averaged q increase with atmospheric CO₂. We conclude by discussing how these constraints
134 on the sensitivity of the hydrological cycle carries profound implications for our understanding
135 of biogeochemical cycles in Earth's past and for Earth's future as CO₂ rises.

136

137 **2. Background**

138 *2.1 Silicate Weathering and Runoff*

139 Silicate weathering is thought to be the primary process that removes CO₂ from the
140 coupled atmosphere-ocean system on geological timescales, neutralizing the input of CO₂ from
141 volcanoes (R. A. Berner & Kothavala, 2001). Silicate weathering is also thought to be sensitive
142 to climate, such that increases in the input flux of CO₂ and the resulting rise in atmospheric
143 CO₂ causes increased silicate weathering fluxes, which removes this excess CO₂ from the
144 Earth's surface (Robert A. Berner & Caldeira, 1997; Zeebe & Caldeira, 2008). Though other
145 Earth surface processes are important for the geological carbon cycle, including the weathering
146 and burial of organic carbon and oxidation/reduction of sulfur (Hilton & West, 2020; Torres et
147 al., 2014), the evidence for these processes being sensitive to climate—and therefore capable
148 of providing a negative feedback on atmospheric CO₂—is less extensive. Further, the reaction
149 of silicate rocks with CO₂ dissolved in water (*i.e.*, carbonic acid) is likely to have been
150 applicable for the entirety of Earth history. Critically, both data and models suggest that Earth
151 system recovery once a perturbation ceases typically occurs within 1 Myr or less (Bowen,
152 2013; Colbourn et al., 2015; Lenton & Britton, 2006; Uchikawa & Zeebe, 2008).

153 Equation 1 describes the long-term relationship between total carbon in the ocean-
154 atmosphere system (M ; mol C) and the input and output fluxes of CO₂ (Caves et al., 2016;
155 Kump & Arthur, 1999):

$$157 \frac{dM}{dt} = I - F_{silw} \quad (\text{Eq. 1})$$

158
159 where F_{silw} is the silicate weathering flux [mol C/yr] and I is the sum of the primary remaining
160 input and output fluxes of CO₂ [mol C/yr], including CO₂ from volcanism and solid Earth
161 degassing and organic carbon weathering and burial. On timescales longer than ocean
162 overturning, changes in the atmospheric partial pressure of CO₂ ($p\text{CO}_2$) are proportional to
163 changes in M . The global silicate weathering flux is defined as (White & Blum, 1995):

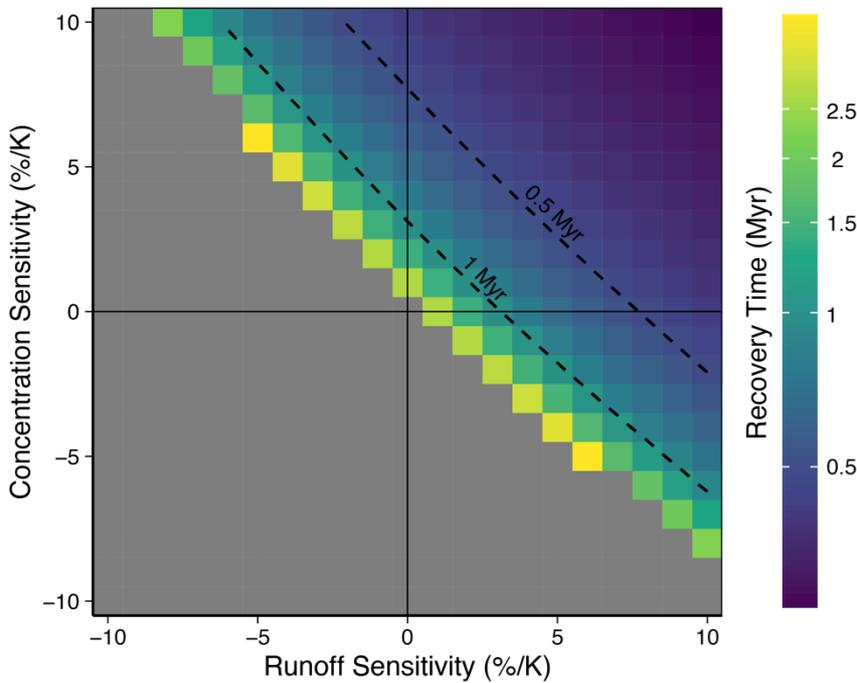
$$164 \quad 165 F_{silw} = Q \times [C]_{sil} \quad (\text{Eq. 2})$$

166
167 where Q is global discharge [L/yr] and $[C]_{sil}$ is the global average concentration of bicarbonate
168 (HCO_3^-) derived from the weathering of silicate rocks [mol C/L]. Q is related to q via the global
169 land area [m^2] ($Q = q \times \text{area}$), which, for the purposes of our simulations, we assume to be
170 constant. Consequently, for silicate weathering to act as a negative feedback on atmospheric
171 CO₂, either q , $[C]_{sil}$, or both must be sensitive to climate.

172 To demonstrate this, we use CH2O-CHOO (the Carbon-H₂O Coupled HydroOlogical
173 model), a modified version of CLiBeSO-W, which is a geological carbon cycle model that
174 calculates the mass balance of carbon and alkalinity in the ocean-atmosphere system (Caves
175 Rugenstein et al., 2019), and uses equation 2 to calculate F_{silw} . We first treat q and $[C]_{sil}$ as
176 being independently sensitivity to CO₂-induced global warming (*i.e.*, Δq and $\Delta[C]_{sil}$ have units
177 of %/K) and assume a climate sensitivity of 4K/CO₂ doubling (Knutti et al., 2017). In these
178 simulations, we inject 1000 Pg C into the atmosphere over 100 years and calculate the amount
179 of time required for atmospheric CO₂ to return to its initial value—termed the recovery time
180 [yr].

181 As shown in Figure 1, a negative sensitivity in either q or $[C]_{sil}$ with temperature
182 requires a correspondingly larger sensitivity in the other parameter. Recovery from
183 perturbations is fastest when both parameters have a positive sensitivity, but small, positive
184 sensitivities still result in recovery times greater than 1 Ma. Thus, to place constraints on the
185 sensitivity of q to CO₂ requires knowledge of how $[C]_{sil}$ will respond to atmospheric CO₂.

186 Recent advances in biogeochemistry, however, have resulted in improved constraints on how
 187 $[C]_{\text{sil}}$ is likely to change with climate (Godsey et al., 2009, 2019; Li et al., 2022; Maher &
 188 Chamberlain, 2014; West, 2012; Winnick & Maher, 2018). Following previous work, we
 189 consider here three parameters that are likely to have the greatest impact on $[C]_{\text{sil}}$ and which
 190 are also sensitive to climate: temperature (T), runoff (q), and soil $p\text{CO}_2$.



191
 192 *Figure 1:* The time required for atmospheric CO_2 to recover to pre-perturbation values (shading
 193 in 10^6 yr) as a function of the q -sensitivity (%/K) and $[C]_{\text{sil}}$ -sensitivity (%/K). Gray shading
 194 indicates that atmospheric CO_2 does not return to pre-perturbation values within 4 Ma post-
 195 perturbation. Solid lines denote the 0% q - and $[C]_{\text{sil}}$ -sensitivities; dashed lines denote the 0.5
 196 and 1 Myr recovery time contours.

197
 198 To encapsulate these three terms, we use a recently developed reactive-transport model
 199 of solute generation from Maher and Chamberlain (2014) to predict $[C]_{\text{sil}}$ (also termed the
 200 MAC model (Baum et al., 2022; Graham & Pierrehumbert, 2020). Critically, this model also
 201 permits us to explicitly treat the reactivity of the land surface—set by erosion and by the type
 202 of exposed lithologies on Earth’s surface (Caves Rügenstein et al., 2019; Ibarra et al., 2016;
 203 West, 2012)—and which determines the rate at which silicate weathering occurs. These
 204 equations are summarized in the Supporting Information, but are briefly described here.
 205 Temperature affects $[C]_{\text{sil}}$ through its impact on net reaction rates, as parameterized by an
 206 Arrhenius equation. Runoff affects $[C]_{\text{sil}}$ via dilution, though only in weathering systems that
 207 are kinetically limited; whether $[C]_{\text{sil}}$ is kinetically-limited depends upon the reactivity of the

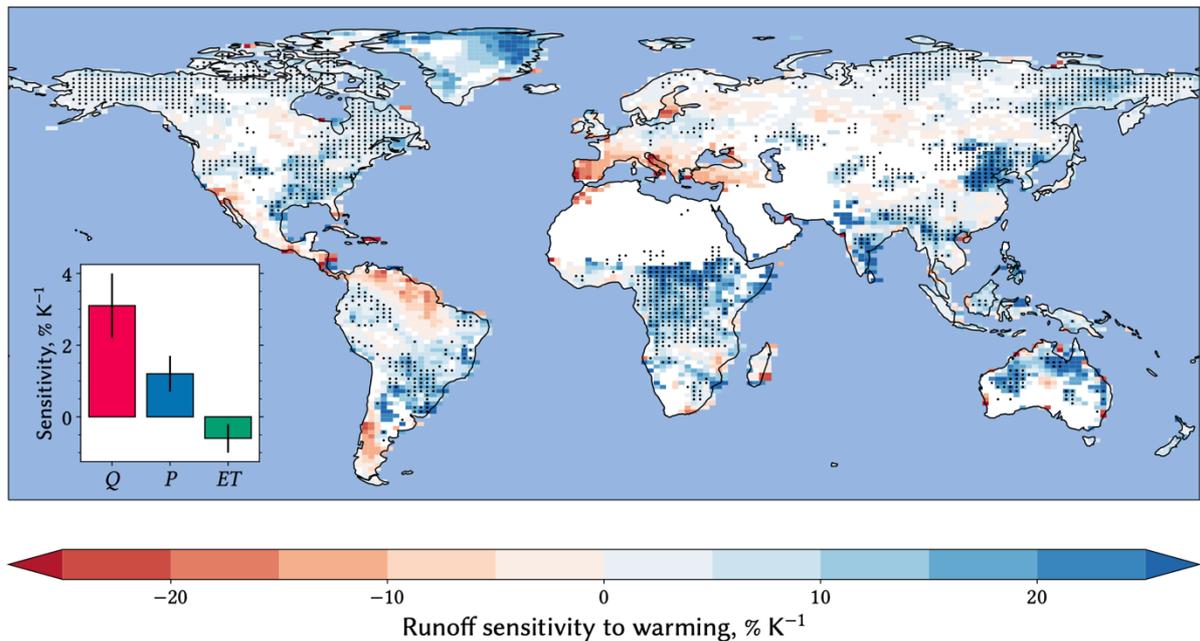
208 weathering material, which is parameterized as a function of the age of the weathering zone
209 (T_s [yr]). Low weathering zone ages, for instance, are indicative of fast supply of fresh
210 minerals, resulting in higher reaction rates, and consequently reduced kinetic limitation. Many
211 catchments today have concentrations that are invariant to changes in runoff (*i.e.*, chemostatic;
212 Godsey et al., 2009), suggesting that kinetic-limitation may not be widespread. Lastly, soil
213 $p\text{CO}_2$ modifies the maximum equilibrium $[\text{C}]_{\text{sil}}$ ($[\text{C}]_{\text{sil,eq}}$), and we assume an open weathering
214 zone CO_2 system (Winnick & Maher, 2018), which is a reasonable assumption given that plants
215 and microbes continually supply CO_2 to the weathering zone via root and soil respiration. We
216 assume that soil $p\text{CO}_2$ scales—via a Michaelis-Menton relationship—to changes in
217 atmospheric $p\text{CO}_2$ that increase aboveground gross primary productivity (Volk, 1987).
218 Assuming a linear scaling between soil CO_2 and atmospheric CO_2 does not substantially alter
219 the conclusions presented here. This set of equations permits us to constrain $[\text{C}]_{\text{sil}}$ as a function
220 of several climatic parameters (*i.e.*, temperature (T), CO_2 , and q) and the weathering zone
221 reactivity and, therefore, treat q -sensitivity as the main unknown parameter.

222

223 2.2 Projected changes in runoff

224 To compare our CH_2O - CHOO model results with state-of-the-art Earth system model
225 projections of global q change, we interrogate those models that participated in the C4MIP
226 experiments (Table S2) (Arora et al., 2013, 2020). These model versions account for a more
227 elaborate representation of land processes, such as the response of evapotranspiration to
228 warming and rising CO_2 . We calculate the ensemble mean runoff sensitivity to warming (%/K)
229 in the 1pct CO_2 experiments (1% annual increase in atmospheric CO_2) across CMIP5 and
230 CMIP6 models. For each model, we estimate the relative q -sensitivity by linearly regressing
231 the change in q against the change in temperature. We find that, while the spatial distribution
232 of q change is patchy and there is poor model agreement across much of the land surface, the
233 ensemble average global q -sensitivity is $3.1 \pm 0.9\%$, driven by an increase in P and a slight
234 decrease in ET (Figure 2).

235



236

237 *Figure 2: The q -sensitivity ($\%/K$) averaged across the C4MIP models (combined CMIP5 and*
 238 *CMIP6). Stippling indicates where at least 75% of the models (6 of 8) agree on the sign of the*
 239 *runoff sensitivity. Inset shows the globally-averaged q -, P -, and ET -sensitivity ($\%/K$)*

240

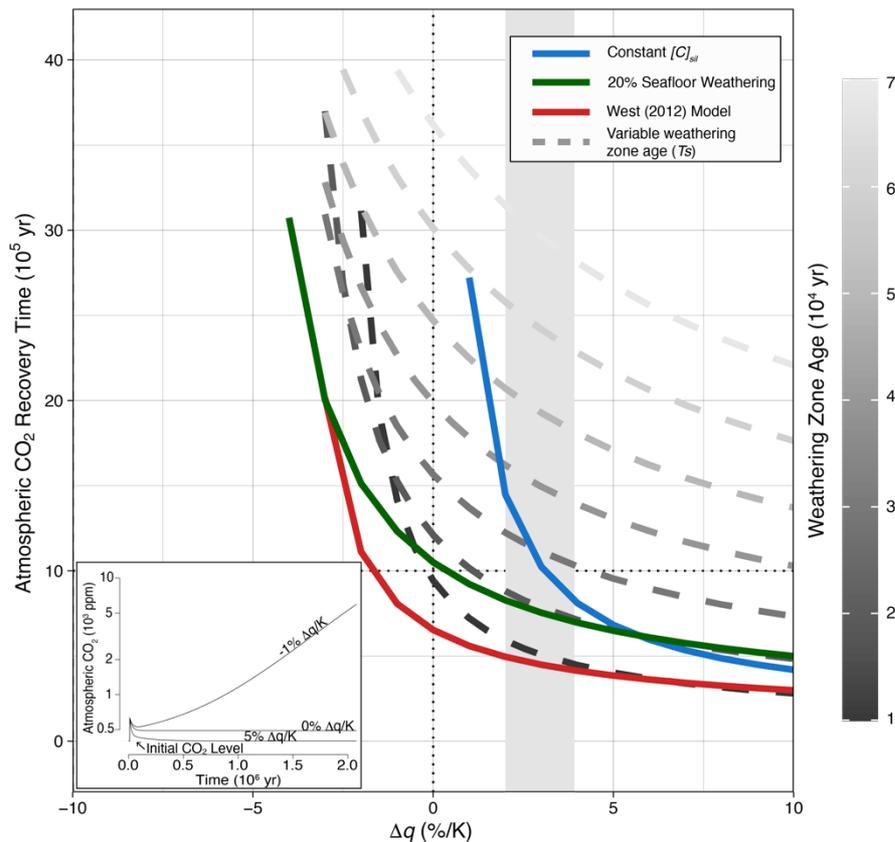
241 **3. Carbon Cycle Constraints on Runoff Changes with Warming**

242 To estimate how differences in the sensitivity of runoff with warming (*i.e.*, the q -
 243 sensitivity) affect the long-term carbon cycle, we again use CH2O-CHOO and inject 1000 Pg
 244 of carbon into the ocean-atmosphere over the span of 100 years and permit long-term carbon
 245 cycle processes to restore atmospheric CO_2 to pre-perturbation conditions. Here, we treat the
 246 q -sensitivity as an independent variable; however, unlike in the example above, $[C]_{sil}$ is now
 247 constrained via its relationship to atmospheric CO_2 through T , q , and soil pCO_2 (Maher &
 248 Chamberlain, 2014; Volk, 1987; Winnick & Maher, 2018). We test cases where (1) we vary
 249 T_s between 10,000 and 100,000 years (the average weathering zone age today is 20,000; Larsen
 250 et al., 2014); (2) $[C]_{sil}$ is constant, following indications that many catchments on short
 251 timescales are chemostatic (Godsey et al., 2009; Ibarra et al., 2016); (3) seafloor weathering—
 252 which is dependent only upon bottom-water temperatures and not upon q (Brady & Gíslason,
 253 1997; Coogan & Gillis, 2018)—represents 20% of the pre-perturbation weathering flux (Hilton
 254 & West, 2020), and; (4) silicate weathering rates are predicted using a different model, from
 255 West (2012), which also contains terms for q , T , and land surface reactivity.

256 Though the precise recovery time [yr] for CO_2 at a given q -sensitivity varies depending
 257 upon the value of the weathering parameters, in all cases, the timescale for atmospheric CO_2

258 to return to pre-perturbation values decreases as the q -sensitivity increases. This is perhaps
259 most easily shown by the case of constant concentrations (blue line, Figure 3). In this case,
260 $[C]_{\text{sil}}$ remains constant as CO_2 changes and is unaffected by changes in q , T , or $p\text{CO}_2$;
261 consequently, recovery from a perturbation is impossible once the q -sensitivity falls below
262 $0\%/K$, given the relationship in Eq. 1. Indeed, even where $[C]_{\text{sil}}$ is constant, recovery timescales
263 surpass 1 Ma for q -sensitivities below $\sim 2.5\%/K$. In all other cases, both q and $[C]_{\text{sil}}$ are
264 permitted to vary as atmospheric CO_2 changes; yet, even in these other experiments, recovery
265 times surpass 1 Ma at or near a q -sensitivity of $0\%/K$. This result arises because, though both
266 q and $[C]_{\text{sil}}$ are linearly related to F_{silw} (Eq. 2), changes in $[C]_{\text{sil}}$ are typically smaller than
267 changes in q as atmospheric CO_2 changes (Figure S1), resulting in a greater influence of q on
268 the ultimate recovery from a C-cycle perturbation. While this supposition is based upon our
269 model of weathering, decreases in $[C]_{\text{sil}}$ do not follow perfect dilution trajectories as q
270 increases, as seen in datasets that reflect short-term (Godsey et al., 2009) and long-term
271 processes (Godsey et al., 2019; Li et al., 2022), further supporting the idea that variations in
272 q —and not in $[C]_{\text{sil}}$ —are the dominant control on F_{silw} .

273 The critical influence of q can be seen in how different parameterizations affect the
274 recovery time. As weathering zone age increases, the recovery time increases for a given q -
275 sensitivity because $[C]_{\text{sil}}$ becomes insensitive to changes in q , due to the relative decrease in
276 weathering zone reactivity. Similarly, if 20% of the initial, global F_{silw} occurs due to seafloor
277 basalt weathering (green line), recovery times are slightly shorter for a given q -sensitivity,
278 because a portion of $[C]_{\text{sil}}$ —that generated by seafloor weathering—is insensitive to changes
279 in q and only sensitive to changes in T . Below a q -sensitivity of $0\%/K$, seafloor weathering
280 begins to substantially reduce recovery times because T rises far more in response to the carbon
281 cycle perturbation due to the reduction in weathering on land, causing seafloor weathering to
282 become a greater proportion of total F_{silw} . The West (2012) formulation (red line) posits a faster
283 recovery time for most q -sensitivities, largely because F_{silw} is formulated not as a linear
284 combination of q and $[C]_{\text{sil}}$ but rather as linearly dependent upon erosion rate, which is
285 presumed to be independent of climate. This linear sensitivity to erosion rate yields a strong
286 dependence upon land surface reactivity that helps to decouple F_{silw} from changes in q .
287 Nevertheless, as in the model of Maher and Chamberlain, if erosion rate decreases (equivalent
288 to an increase in the weathering zone age), the West (2012) model predicts longer recovery
289 times for equivalent q -sensitivities (Figure S2).



290

291 *Figure 3:* Recovery time [10^5 yr] for atmospheric CO_2 as a function of the q -sensitivity ($\%/K$)
 292 given a 1000 Pg C-cycle perturbation over 100 years. Dashed, gray lines use the standard
 293 parameters in Table S1 and variable T_s ; blue line assumes globally chemostatic catchments
 294 (*i.e.*, $[C]_{\text{sil}}$ is invariant with changes in CO_2); green line assumes that seafloor weathering
 295 accounts for 20% of the total alkalinity flux to the ocean (with all other parameters derived
 296 from Table S1); red line uses the silicate weathering model of West (2012) using values from
 297 Table S1. Vertical gray bar is the range of q -sensitivity from the C4MIP models considered
 298 herein. Inset shows atmospheric CO_2 (log-scale) of three representative experiments from the
 299 case of invariant $[C]_{\text{sil}}$ (blue line). Given a -1% q -sensitivity, atmospheric CO_2 increases in
 300 perpetuity. With 0% q -sensitivity, atmospheric CO_2 stabilizes but does not recover to pre-
 301 perturbation conditions. A q -sensitivity of 5% results in recovery to pre-perturbation CO_2
 302 within ~ 700 kyr.

303

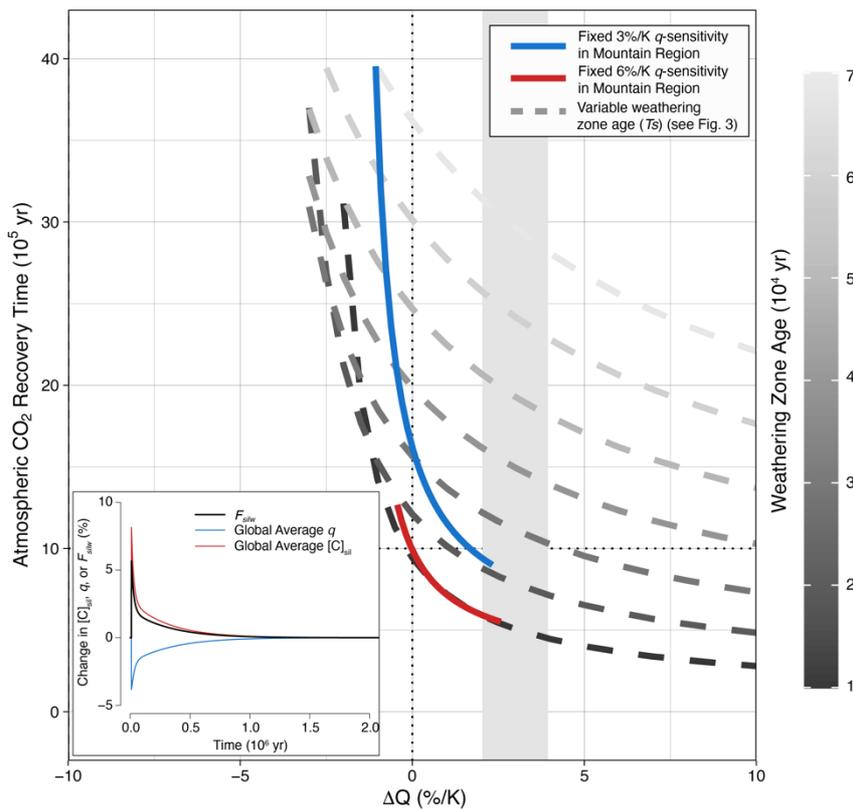
304 The above analysis suggests that, for the ocean-atmosphere system to recover to pre-
 305 perturbation CO_2 within 1 Ma, q -sensitivity must be greater than $-2 \%/K$ for any conceivable
 306 combination of weathering parameters; depending upon the precise model and
 307 parameterization, this value may be higher. For example, our preferred model of weathering—

308 using Maher and Chamberlain (2014)—requires a q -sensitivity of > 0 %/K for all reasonable
309 estimates of the global weathering zone age.

310 However, the above modeling results assume that the Earth's surface can be
311 characterized by single, mean values; such an assumption is likely incorrect. For example,
312 while the C4MIP ensemble global-mean q -sensitivity is 3.1 ± 0.9 %/K (similar to the CMIP5
313 ensemble mean; Zhang et al., 2014), the spatial variability across large catchments is enormous,
314 spanning -20 to +40 %/K (Dai & Trenberth, 2002; Scheff et al., 2017; Swann et al., 2016)
315 (Figure 2). High, regional q -sensitivity may coincide with particularly reactive rocks (*i.e.*, low
316 weathering zone ages and consequently high $[C]_{\text{sil}}$ -sensitivity) yielding a different CO_2
317 recovery time due to spatial co-variability in weathering zone reactivity and runoff change.
318 Indeed, consistently high tropical runoff is the basis for theories that posit that exposure of
319 reactive rocks (such as ophiolites or exposure of Large Igneous Province basalts) near the
320 equator is the primary mode of long-term atmospheric CO_2 control (Donnadieu et al., 2004;
321 Macdonald et al., 2019; Park et al., 2020; Swanson-Hysell & Macdonald, 2017).

322 Consequently, our estimate of the minimum q -sensitivity may be biased high because
323 we do not consider regions with coincident high q -sensitivity and high weathering zone
324 reactivity. To test this possibility, we modify CH2O-CHOO such that two distinct regions
325 contribute toward the global silicate weathering flux: Mountain Region consists of a highly
326 reactive weathering zone ($T_s = 1000$ yr) and contributes 50% of the initial, pre-perturbation
327 global F_{silw} and Lowland Region comprises the rest of the world and is characterized by low
328 weathering zone reactivity ($T_s = 39,000$ yr). Though this example is simplified, the Mountain
329 Region may be considered equivalent to the role of mountains today, which contribute half of
330 the global weathering flux (silicate and carbonate weathering combined) (Larsen et al., 2014).
331 We treat the Mountain Region as having a fixed, positive q -sensitivity and the Lowland Region
332 as having variable q -sensitivity. Globally, the q -sensitivity of mountains more likely tracks
333 changes in P than changes in ET because most precipitation in mountain ranges is partitioned
334 to q . In general, mountain ranges—particularly coastal ones—witness changes in P similar to
335 the zonal mean, such that subtropical ranges see declines in P (and likely q), whereas mid-
336 latitude ranges may see changes in P equal to or greater than 7 %/K (Shi & Durran, 2014). We
337 repeat the experiment above, treating the q -sensitivity of the Low-Land Region as an
338 independent parameter and injecting 1000 Pg C into the ocean-atmosphere system over 100
339 years. We test two cases: (1) where the Mountain Region has a fixed q -sensitivity of 3%/K and
340 (2) where the Mountain Region has a fixed q -sensitivity of 6%/K.

341 Even the coincidence of high weathering zone reactivity with high runoff sensitivity
 342 still requires that average global runoff sensitivity be $> 0\%/K$ in order for atmospheric CO_2 to
 343 recover to pre-perturbation levels within ~ 1 Ma (Figure 4). Though a greater Mountain Region
 344 q -sensitivity (6 vs. 3 $\%/K$) results in faster recovery times, the minimum q -sensitivity is still 0
 345 $\%/K$ to recover from a perturbation within 1 Myr. The different relationship between Δq and
 346 recovery time and compressed Δq variability in these simulations is due to how Δq is calculated
 347 for this experiment; in contrast to the first experiments above, where Δq is prescribed, here
 348 50% of the Earth experiences a fixed 3 or 6 $\%/K$ q -sensitivity. Though we vary the q -sensitivity
 349 for the Lowland region (*i.e.*, with low weathering zone reactivity and high T_s), variations in
 350 global Δq are damped, given the fixed q -sensitivity in the Mountain Region (*i.e.* with high
 351 weathering zone reactivity and low T_s). Further, any decreases in global q when the q -
 352 sensitivity of the Lowland Region is $< 0\%/K$ are small (see inset in Figure 2) and global average
 353 $[C]_{sil}$ increases due to the effect of rising temperatures that offset the small decrease in q .



354
 355
 356 **Figure 4:** Recovery time [10^5 y] for atmospheric CO_2 as a function of the average q -sensitivity
 357 ($\%/K$) given a 1000 Pg C-cycle perturbation over 100 years and two distinct weathering regions
 358 (outlined in text). Dashed lines use the standard parameters in Table S1 with variable
 359 weathering zone age (T_s) (see Figure 3); solid, red line assumes a fixed Mountain Region q -

360 sensitivity of 6 %/K; solid, blue line assumes a fixed Mountain Region q -sensitivity of 3%/K.
361 In both cases, the q -sensitivity of region 2 is permitted to vary between -10 and 10 %/K. Gray
362 shading is the C4MIP estimate of runoff sensitivity. We calculate Δq as the percentage change
363 in global q at the peak of the C-cycle perturbation relative to starting global q against the change
364 in global T between the peak of the perturbation and the initial condition. Inset shows how F_{silw}
365 (black line), global average q (blue line), and global average $[C]_{sil}$ (red line) change during a
366 perturbation when the Lowland Region has a -10 %/K q -sensitivity and the Mountain Region
367 has a low T_s (ie, highly reactive) and a fixed q -sensitivity of 6 %/K.

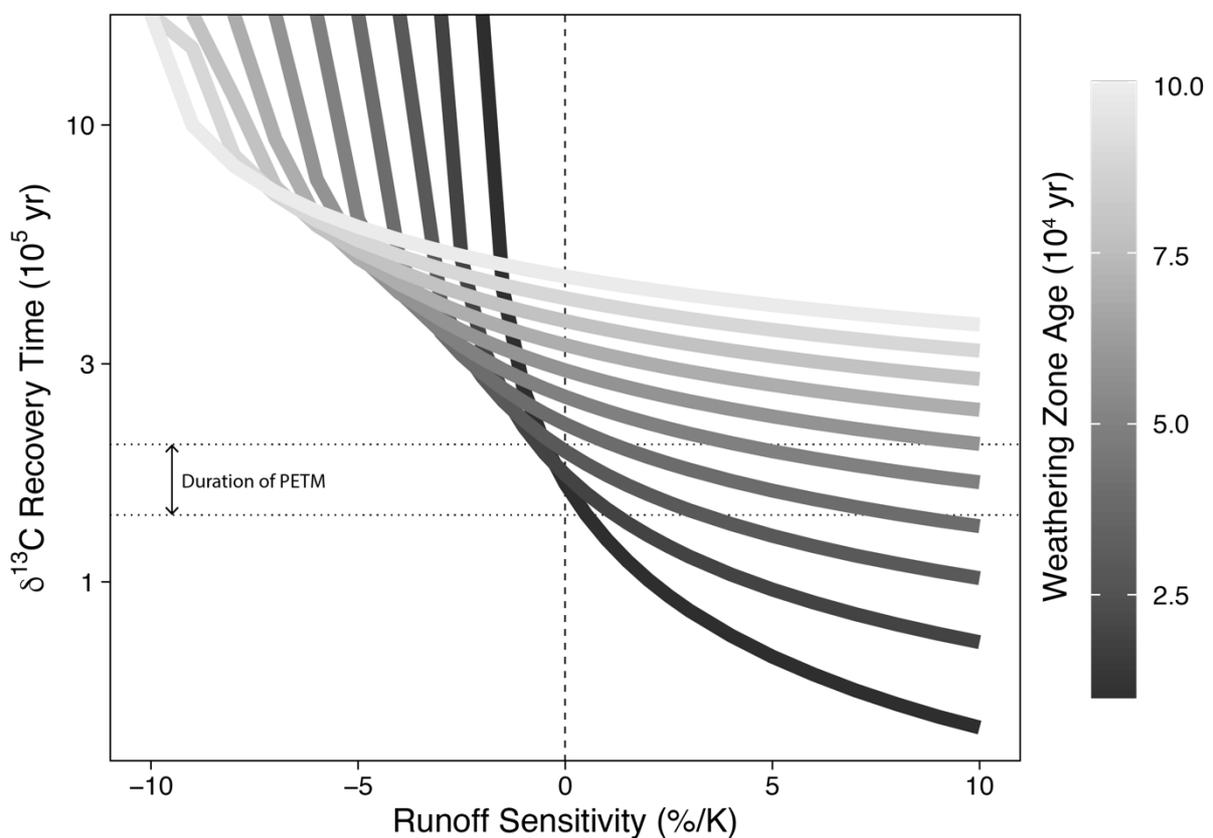
368

369 **4. Geologic Constraints on q -sensitivity**

370 We now use a well-studied past large carbon cycle perturbation—the Paleocene-Eocene
371 Thermal Maximum (PETM), ~ 55 Ma—to constrain the q response to a large carbon cycle
372 perturbation. Though the exact cause of the PETM remains debated, a substantial quantity of
373 carbon (5000-20000 Pg C) was released to the ocean-atmosphere system within 3000–10000
374 years, lowering global marine dissolved inorganic carbon (DIC) $\delta^{13}C$ by 3–4‰ (Cui et al.,
375 2011; Gutjahr et al., 2017; Panchuk et al., 2008; Penman et al., 2016). This negative carbon
376 isotope excursion is thought to have lasted $\sim 170 \pm 30$ ka (Zeebe & Lourens, 2019), at which
377 point the global marine DIC pool had recovered to pre-perturbation $\delta^{13}C$ values. Critically, the
378 recovery from the PETM was likely mediated by silicate weathering—as evidenced by an
379 excess burial of Si across the PETM (Penman, 2016)—and involved large-scale increases in
380 runoff in places (Chen et al., 2018; Foreman et al., 2012). The PETM thus provides an
381 opportunity to test our CH₂O-CHOO model and determine the most likely q -sensitivity
382 necessary to match the duration of the $\delta^{13}C$ negative excursion.

383 We force CH₂O-CHOO with net carbon emissions and net emissions $\delta^{13}C$ estimates
384 from Gutjahr et al. (2017), which also includes estimates of increased organic carbon burial
385 during the recovery phase (Bowen, 2013; Bowen & Zachos, 2010). As before, we prescribe a
386 wide-range of q -sensitivity estimates that determine how runoff responds to changes in
387 atmospheric CO₂. Because we also do not *a priori* know the average weathering zone age (T_s)
388 at the PETM, we vary this parameter as well, though evidence from a range of carbon cycle
389 models and isotopic data indicates that bulk Earth surface weatherability was lower in the early
390 Eocene, likely reflecting higher T_s (Caves et al., 2016; Froelich & Misra, 2014; Krissansen-
391 Totton & Catling, 2017; van der Ploeg et al., 2018; Vervoort et al., 2021).

392 Given these constraints, we find that, to match the duration of the PETM negative $\delta^{13}\text{C}$
393 excursion requires q -sensitivity to be equal to or greater than 0%/K if T_s is similar to today
394 (Figure 5). If, instead, T_s was higher in the late Paleocene, then q -sensitivity must be higher to
395 match the duration of the $\delta^{13}\text{C}$ negative excursion. Though our model lacks a number of critical
396 carbon cycle processes that are thought to modulate the impact of rapid CO_2 emissions (such
397 as seafloor carbonate sediments that buffer against acidic bottom waters), these effects are
398 likely to matter primarily for the initial stages of the perturbation, rather than mediating the
399 long-term removal of CO_2 by silicate weathering (Penman et al., 2020). We note that, while
400 the PETM provides a useful analogue with which to understand how q responds to CO_2 , we do
401 not expect the q -sensitivity at the PETM to exactly match that of today's Earth, due to
402 paleogeographic and floral changes that have occurred during the Cenozoic that would have
403 changed precisely how much precipitation is converted to q as CO_2 rises.
404



405
406
407 *Figure 5:* Estimated $\delta^{13}\text{C}$ recovery times (10^5 yr) as a function of the q -sensitivity and the
408 weathering zone age (grayscale). Horizontal dotted lines indicate the estimated $\delta^{13}\text{C}$ recovery
409 time based upon astrochronological tuning of the PETM $\delta^{13}\text{C}$ record (Zeebe & Lourens, 2019).
410

5. Implications

The geological record—and our understanding of how the Earth recovers from carbon cycle perturbations—provides long-term constraints on how q must respond to increases in atmospheric CO_2 . In a broad sense, our results bolster previous work pointing towards the importance of runoff in modulating the long-term carbon cycle and climate (Barron et al., 1989; François & Walker, 1992; Otto-Bliesner, 1995). Critically, our long-term perspective on the runoff response to CO_2 incorporates a number of processes that are thought to affect q but are difficult to constrain in the modern due to temporally limited instrumental records or experiments. For example, remotely sensed products of global discharge are affected by internal variability, which precludes their use currently in assessing how total runoff will respond to rising atmospheric CO_2 (Chandanpurkar et al., 2017, 2021). Experiments that seek to understand how plant responses might affect runoff—such as the Free Air CO_2 Enrichment (FACE) experiments—are relatively short-term and the long-term response of ecosystems may differ from the short-term response due to changes in nutrient demands and supply and non-linear plant responses to increasing CO_2 . In this sense, the known response of the long-term carbon cycle—and how this response is linked to q —provides a constraint on how global q must respond to rising CO_2 that avoids the inherent noisiness of the relatively short instrumental record.

Our finding that q -sensitivity must be greater than or equal to $0\%/K$ (when using our preferred model of weathering) holds implications for the processes that control changes in runoff with warming. Though PET should increase faster than P , stomatal conductance changes driven by CO_2 fertilization and increasing vapor pressure deficits may result in a greater fraction of P being partitioned to q (Novick et al., 2016; Roderick et al., 2015; Swann et al., 2016). This effect, however, is complicated by a number of factors that may instead drive greater plant water use, including a longer growing season (Mankin et al., 2019) and widespread greening that increases total leaf area (Zhu et al., 2016). How these factors will interact across the planet to produce a change in global q remains difficult to predict; across much of the Earth's surface, for example, models frequently do not even agree on the sign of the q change (Figure 2). For example, in much of the mid-latitudes, projected ensemble mean runoff changes are negligible, with little model agreement on the sign of the change (Elbaum et al., 2022; Scheff et al., 2017). Our results suggest that the processes on a global scale that tend towards greater q with increasing atmospheric CO_2 and warming—such as reductions in stomatal conductance—will be predominant in a warmer world, though there may be substantial spatial variability. Further, we note that our results likely hold on the millennial or

445 longer timescale, and, as such and given the potential complexity of the biospheric response to
446 warming, there may be long periods when global runoff may not increase in response to
447 warming.

448 Our findings also hold implications for understanding how paleogeographic changes
449 may have modified the strength of the silicate weathering negative feedback in the geologic
450 past. General circulation model simulations highlight that the runoff response to warming is
451 spatially complex; such results indicate the precise global q -sensitivity may vary with the
452 position of the continents (Otto-Bliesner, 1995). For example, models frequently predict that
453 subtropical areas should become drier (Burls & Fedorov, 2017; Mankin et al., 2019),
454 suggesting that a world with predominantly sub-tropical continents would perhaps see a
455 minimal increase or even decrease in global discharge. Our results suggest that either there are
456 additional mechanisms that keep global discharge from decreasing or that such a continental
457 configuration has never occurred on Earth during a major carbon cycle perturbation. If such an
458 Earth experienced a major perturbation, our results indicate that atmospheric CO₂ may have
459 never returned to pre-perturbation values.

460 Though we have attempted to test the robustness of our result by using different
461 parameters and even a different model of weathering (West, 2012), there are a number of
462 hypothesized feedbacks with warming and rising CO₂ that may impact weathering fluxes, but
463 are not—to our knowledge—yet incorporated into any model of weathering. For example,
464 warming is thought to increase the number of extreme precipitation events (Fischer & Knutti,
465 2016) which is likely to increase q relative to ET as P is rapidly converted to q . Though q
466 increases with these extreme events, much of the water may bypass the weathering zone,
467 limiting their impact on weathering. In turn, extreme events may also increase erosional
468 efficiency (Deal et al., 2017, 2018), increasing the availability of fresh minerals and thereby
469 enhancing silicate weathering by reducing average T_s . Though this process is not represented
470 in our model, we suspect that the impact of extreme events on silicate weathering is likely to
471 be minimal, as lower T_s is offset by a greater quantity of q that bypasses the weathering zone
472 via overland flow or exceptionally fast transit times. Additionally, other carbon fluxes may
473 change with a warming climate, such as erosion and burial of terrestrial organic carbon (Hilton,
474 2017) or increases in marine organic burial due to widespread anoxia (Lau et al., 2016).
475 However, these mechanisms also rely upon runoff to transport terrestrial organic matter to
476 continental shelves for burial and to delivery sufficient nutrients to drive marine anoxia (Them
477 et al., 2017), suggesting that increases in runoff are also necessary for these hypothesized
478 negative feedbacks on CO₂.

479 Our work highlights the tight coupling between the hydrological cycle and the long-
480 term carbon cycle and demonstrates that this coupling places a lower-bound on the globally
481 averaged runoff response to warming and rising CO₂. Whereas abundant research has
482 examined the links between the hydrological cycle and the short-term carbon cycle (Forzieri et
483 al., 2020; Lemordant et al., 2018; Novick et al., 2016), our work demonstrates that the operation
484 of the long-term carbon cycle is also critically linked to the hydrological cycle. It is this linkage
485 that has acted to remove excess CO₂ from the ocean-atmosphere system during perturbations,
486 thus maintaining Earth's habitability. Though our knowledge of weathering continues to
487 improve, ongoing model and observational work indicates the centrality of runoff in linking
488 the weathering of silicate rocks to the ultimate burial of carbon as calcium carbonate in the
489 marine environment. Thus, the importance of runoff for weathering indicates that, on long
490 timescales, runoff must increase as CO₂ rises.

491

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501

502 **Software Availability Statement:**

503 Model source code used for this research is available in Rugenstein and Winkler (2022) and
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505 **References:**

- 506 Arora, V. K., Boer, G. J., Friedlingstein, P., Eby, M., Jones, C. D., Christian, J. R., et al.
507 (2013). Carbon-concentration and carbon-climate feedbacks in CMIP5 earth system
508 models. *Journal of Climate*, 26(15), 5289–5314. [https://doi.org/10.1175/JCLI-D-12-](https://doi.org/10.1175/JCLI-D-12-00494.1)
509 00494.1
- 510 Arora, V. K., Katavouta, A., Williams, R. G., Jones, C. D., Brovkin, V., Friedlingstein, P., et
511 al. (2020). Carbon – concentration and carbon – climate feedbacks in CMIP6 models
512 and their comparison to CMIP5 models. *Biogeosciences*, 17, 4173–4222.
- 513 Barron, E. J., Hay, W. W., & Thompson, S. (1989). The hydrologic cycle: A major variable
514 during earth history. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 75(3), 157–
515 174. [https://doi.org/10.1016/0031-0182\(89\)90175-2](https://doi.org/10.1016/0031-0182(89)90175-2)
- 516 Baum, M., Fu, M., & Bourguet, S. (2022). Sensitive Dependence of Global Climate to
517 Continental Geometry. *Geophysical Research Letters*, 49(11), 1–8.
518 <https://doi.org/10.1029/2022gl098843>
- 519 Berner, R. A., & Kothavala, Z. (2001). GEOCARB III: A revised model of atmospheric CO₂
520 over Phanerozoic time. *American Journal of Science*, 301, 182–204. Retrieved from
521 <http://ajsonline.org/content/301/2/182.short>
- 522 Berner, Robert A., & Caldeira, K. (1997). The need for mass balance and feedback in the
523 geochemical carbon cycle. *Geology*, 25(10), 955–956. [https://doi.org/10.1130/0091-](https://doi.org/10.1130/0091-7613(1997)025<0955:TNFMBA>2.3.CO;2)
524 7613(1997)025<0955:TNFMBA>2.3.CO;2
- 525 Bowen, G. J. (2013). Up in smoke: A role for organic carbon feedbacks in Paleogene
526 hyperthermals. *Global and Planetary Change*, 109, 18–29.
527 <https://doi.org/10.1016/j.gloplacha.2013.07.001>
- 528 Bowen, G. J., & Zachos, J. C. (2010). Rapid carbon sequestration at the termination of the
529 Palaeocene–Eocene Thermal Maximum. *Nature Geoscience*, 3(12), 866–869.
530 <https://doi.org/10.1038/ngeo1014>
- 531 Brady, P. V., & Gíslason, S. R. (1997). Seafloor weathering controls on atmospheric CO₂ and
532 global climate. *Geochimica et Cosmochimica Acta*, 61(5), 965–973.
533 [https://doi.org/10.1016/S0016-7037\(96\)00385-7](https://doi.org/10.1016/S0016-7037(96)00385-7)
- 534 Burls, N. J., & Fedorov, A. V. (2017). Wetter subtropics in a warmer world: Contrasting past
535 and future hydrological cycles. *Proceedings of the National Academy of Sciences*,
536 114(49), 12888–12893. <https://doi.org/10.1073/pnas.1703421114>
- 537 Caves, J. K., Jost, A. B., Lau, K. V., & Maher, K. (2016). Cenozoic carbon cycle imbalances
538 and a variable silicate weathering feedback. *Earth and Planetary Science Letters*, 450,

539 152–163. <https://doi.org/10.1016/j.epsl.2016.06.035>

540 Caves Rügenstein, J. K., Ibarra, D. E., & von Blanckenburg, F. (2019). Neogene cooling
541 driven by land surface reactivity rather than increased weathering fluxes. *Nature*, *571*,
542 99–102. <https://doi.org/10.1038/s41586-019-1332-y>

543 Chandanpurkar, H. A., Reager, J. T., Famiglietti, J. S., & Syed, T. H. (2017). Satellite- and
544 reanalysis-based mass balance estimates of global continental discharge (1993-2015).
545 *Journal of Climate*, *30*(21), 8481–8495. <https://doi.org/10.1175/JCLI-D-16-0708.1>

546 Chandanpurkar, H. A., Reager, J. T., Famiglietti, J. S., Nerem, R. S., Chambers, D. P., Lo, M.
547 H., et al. (2021). The Seasonality of Global Land and Ocean Mass and the Changing
548 Water Cycle. *Geophysical Research Letters*, *48*(7).
549 <https://doi.org/10.1029/2020GL091248>

550 Chen, C., Guerit, L., Foreman, B. Z., Hassenruck-Gudipati, H. J., Adatte, T., Honegger, L., et
551 al. (2018). Estimating regional flood discharge during Palaeocene-Eocene global
552 warming. *Scientific Reports*, *8*(1), 1–8. <https://doi.org/10.1038/s41598-018-31076-3>

553 Colbourn, G., Ridgwell, A., & Lenton, T. M. (2015). The time scale of the silicate weathering
554 negative feedback on atmospheric CO₂. *Global Biogeochemical Cycles*, *29*, 583–596.
555 <https://doi.org/10.1002/2014GB005054>

556 Coogan, L. A., & Gillis, K. M. (2018). Low-Temperature Alteration of the Seafloor: Impacts
557 on Ocean Chemistry. *Annu. Rev. Earth Planet. Sci*, *46*, 21–45.
558 <https://doi.org/10.1146/annurev-earth-082517>

559 Cook, B. I., Smerdon, J. E., Seager, R., & Coats, S. (2014). Global warming and 21st century
560 drying. *Climate Dynamics*, *43*, 2607–2627. <https://doi.org/10.1007/s00382-014-2075-y>

561 Cui, Y., Kump, L. R., Ridgwell, A. J., Charles, A. J., Junium, C. K., Diefendorf, A. F., et al.
562 (2011). Slow release of fossil carbon during the Palaeocene–Eocene Thermal Maximum.
563 *Nature Geoscience*, *4*(7), 481–485. <https://doi.org/10.1038/ngeo1179>

564 Dai, A., & Trenberth, K. E. (2002). Estimates of Freshwater Discharge from Continents :
565 Latitudinal and Seasonal Variations. *Journal of Hydrometeorology*, *3*, 660–687.

566 Deal, E., Favre, A.-C., & Braun, J. (2017). Rainfall variability in the Himalayan orogen and
567 its relevance to erosion processes. *Water Resources Research*, *53*, 4004–4021.
568 <https://doi.org/10.1002/2013WR014979.Reply>

569 Deal, E., Botter, G., & Braun, J. (2018). Understanding the role of rainfall and hydrology in
570 determining fluvial erosion efficiency. *Journal of Geophysical Research: Earth Surface*.
571 <https://doi.org/10.1002/2017JF004393>

572 Donnadieu, Y., Goddérès, Y., Ramstein, G., Nédélec, A., & Meert, J. (2004). A ‘snowball

573 Earth' climate triggered by continental break-up through changes in runoff. *Nature*,
574 428(6980), 303–306. <https://doi.org/10.1038/nature02408>

575 Douville, H., Raghavan, K., Renwick, J., Allan, R. P., Arias, P. A., Barlow, M., et al. (2021).
576 Water Cycle Changes. In V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C.
577 Péan, S. Berger, et al. (Eds.), *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the*
578 *Intergovernmental Panel on Climate Change* (p. 239). Cambridge University Press.

579 Elbaum, E., Garfinkel, C. I., Adam, O., Morin, E., Rostkier-Edelstein, D., & Dayan, U.
580 (2022). Uncertainty in projected changes in precipitation minus evaporation: Dominant
581 role of dynamic circulation changes and weak role for thermodynamic changes.
582 *Geophysical Research Letters*. <https://doi.org/10.1029/2022gl097725>

583 Ficklin, D. L., & Novick, K. A. (2017). Historic and projected changes in vapor pressure
584 deficit suggest a continental-scale drying of the United States atmosphere. *Journal of*
585 *Geophysical Research: Atmospheres*, 122, 2061–2079.
586 <https://doi.org/10.1002/2016JD025855>

587 Fischer, E. M., & Knutti, R. (2016). Observed heavy precipitation increase confirms theory
588 and early models. *Nature Climate Change*, 6(11), 986–991.
589 <https://doi.org/10.1038/nclimate3110>

590 Foreman, B. Z., Heller, P. L., & Clementz, M. T. (2012). Fluvial response to abrupt global
591 warming at the Palaeocene/Eocene boundary. *Nature*, 1–4.
592 <https://doi.org/10.1038/nature11513>

593 Forzieri, G., Miralles, D. G., Ciais, P., Alkama, R., Ryu, Y., Duveiller, G., et al. (2020).
594 Increased control of vegetation on global terrestrial energy fluxes. *Nature Climate*
595 *Change*, 10. <https://doi.org/10.1038/s41558-020-0717-0>

596 François, L. M., & Walker, J. C. G. (1992). Modelling the Phanerozoic carbon cycle and
597 climate: constraints from the 87Sr/86Sr isotopic ratio of seawater. *American Journal of*
598 *Science*. <https://doi.org/10.2475/ajs.292.2.81>

599 Froelich, F., & Misra, S. (2014). Was the late Paleocene-early Eocene hot because Earth was
600 flat? An ocean lithium isotope view of mountain building, continental weathering,
601 carbon dioxide, and Earth's Cenozoic climate. *Oceanography*, 27(1), 36–49. Retrieved
602 from <http://eprints.esc.cam.ac.uk/2999/>

603 Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration – discharge
604 relationships reflect chemostatic characteristics of US catchments. *Hydrological*
605 *Processes*, 23, 1844–1864. <https://doi.org/10.1002/hyp>

606

607 Godsey, S. E., Hartmann, J., & Kirchner, J. W. (2019). Catchment chemostasis revisited:
608 Water quality responds differently to variations in weather and climate. *Hydrological*
609 *Processes*, 1–14. <https://doi.org/10.1002/hyp.13554>

610 Good, S. P., Noone, D., & Bowen, G. (2015). Hydrologic connectivity constrains partitioning
611 of global terrestrial water fluxes. *Science*, 349(6244), 175–177.

612 Graham, R. J., & Pierrehumbert, R. T. (2020). Thermodynamic and Energetic Limits on
613 Continental Silicate Weathering Strongly Impact the Climate and Habitability of Wet,
614 Rocky Worlds. Retrieved from <http://arxiv.org/abs/2004.14058>

615 Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälike, H., et al.
616 (2017). Very large release of mostly volcanic carbon during the Palaeocene–Eocene
617 Thermal Maximum. *Nature*, 548(7669), 573–577. <https://doi.org/10.1038/nature23646>

618 Held, I., & Soden, B. (2006). Robust responses of the hydrological cycle to global warming.
619 *Journal of Climate*, 19, 5686–5699.

620 Hilton, R. G. (2017). Climate regulates the erosional carbon export from the terrestrial
621 biosphere. *Geomorphology*, 277, 118–132.
622 <https://doi.org/10.1016/j.geomorph.2016.03.028>

623 Hilton, R. G., & West, A. J. (2020). Mountains, erosion and the carbon cycle. *Nature Reviews*
624 *Earth and Environment*. Springer US. <https://doi.org/10.1038/s43017-020-0058-6>

625 Ibarra, D. E., Caves, J. K., Moon, S., Thomas, D. L., Hartmann, J., Chamberlain, C. P., &
626 Maher, K. (2016). Differential weathering of basaltic and granitic catchments from
627 concentration–discharge relationships. *Geochimica et Cosmochimica Acta*, 190, 265–
628 293. <https://doi.org/10.1016/j.gca.2016.07.006>

629 Knutti, R., Rugenstein, M. A. A., & Hegerl, G. C. (2017). Beyond equilibrium climate
630 sensitivity. *Nature Geoscience*, 10, 727–736. <https://doi.org/10.1038/ngeo3017>

631 Krissansen-Totton, J., & Catling, D. C. (2017). Constraining climate sensitivity and
632 continental versus seafloor weathering using an inverse geological carbon cycle model.
633 *Nature Communications*, 8, 15423. <https://doi.org/10.1038/ncomms15423>

634 Kump, L. R., & Arthur, M. A. (1999). Interpreting carbon-isotope excursions: carbonates and
635 organic matter. *Chemical Geology*, 161(1–3), 181–198. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2541(99)00086-8)
636 [2541\(99\)00086-8](https://doi.org/10.1016/S0009-2541(99)00086-8)

637 Kump, L. R., Brantley, S. L., & Arthur, M. A. (2000). Chemical weathering, atmospheric
638 CO₂, and climate. *Annual Review of Earth and Planetary Sciences*, 28, 611–667.
639 Retrieved from <http://www.annualreviews.org/doi/abs/10.1146/annurev.earth.28.1.611>

640 Larsen, I. J., Montgomery, D. R., & Greenberg, H. M. (2014). The contribution of mountains

641 to global denudation. *Geology*, 42, 527–530. <https://doi.org/10.1130/G35136.1>

642 Lau, K. V., Maher, K., Altiner, D., Kelley, B. M., Kump, L. R., Lehrmann, D. J., et al.
643 (2016). Marine anoxia and delayed Earth system recovery after end-Permian extinction.
644 *Proceedings of the National Academy of Sciences*.
645 <https://doi.org/10.1073/pnas.1515080113>

646 Lemordant, L., Gentine, P., Swann, A. S., Cook, B. I., & Scheff, J. (2018). Critical impact of
647 vegetation physiology on the continental hydrologic cycle in response to increasing
648 CO₂. *Proceedings of the National Academy of Sciences*, 115(16), 201720712.
649 <https://doi.org/10.1073/pnas.1720712115>

650 Lenton, T. M., & Britton, C. (2006). Enhanced carbonate and silicate weathering accelerates
651 recovery from fossil fuel CO₂ perturbations. *Global Biogeochemical Cycles*, 20(3), 1–
652 12. <https://doi.org/10.1029/2005GB002678>

653 Li, L., Stewart, B., Zhi, W., Sadayappan, K., Ramesh, S., Kerins, D., et al. (2022). Climate
654 Controls on River Chemistry. *Earth's Future*, 10(6), 1–17.
655 <https://doi.org/10.1029/2021EF002603>

656 Macdonald, F. A., Swanson-Hysell, N. L., Park, Y., Lisiecki, L., & Jagoutz, O. (2019). Arc-
657 continent collisions in the tropics set Earth's climate state. *Science*, 364, 181–184.

658 Maher, K., & Chamberlain, C. P. (2014). Hydrologic regulation of chemical weathering and
659 the geologic carbon cycle. *Science*, 343(6178), 1502–1504.
660 <https://doi.org/10.1126/science.1250770>

661 Mankin, J. S., Seager, R., Smerdon, J. E., Cook, B. I., & Williams, A. P. (2019). Mid-latitude
662 freshwater availability reduced by projected vegetation responses to climate change.
663 *Nature Geoscience*. <https://doi.org/10.1038/s41561-019-0480-x>

664 Milly, P. C. D., & Dunne, K. A. (2016). Potential evapotranspiration and continental drying.
665 *Nature Climate Change*, 6, 946–949. <https://doi.org/10.1038/NCLIMATE3046>

666 Milly, P. C. D., & Dunne, K. A. (2020). Colorado River flow dwindles as warming-driven
667 loss of reflective snow energizes evaporation. *Science*, 9187(February), eaay9187.
668 <https://doi.org/10.1126/science.aay9187>

669 Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., et al.
670 (2016). The increasing importance of atmospheric demand for ecosystem water and
671 carbon fluxes. *Nature Climate Change*, 6(11), 1023–1027.
672 <https://doi.org/10.1038/nclimate3114>

673 Otto-Bliesner, B. L. (1995). Continental drift, runoff, and weathering feedbacks: Implications
674 from climate model experiments. *Journal of Geophysical Research*, 100(D6), 11537–

675 11548. <https://doi.org/10.1029/95JD00591>

676 Overpeck, J. T., & Udall, B. (2020). Climate change and the aridification of North America.
677 *Proceedings of the National Academy of Sciences*, 0, 202006323.
678 <https://doi.org/10.1073/pnas.2006323117>

679 Panchuk, K., Ridgwell, A., & Kump, L. R. (2008). Sedimentary response to Paleocene-
680 Eocene Thermal Maximum carbon release: A model-data comparison. *Geology*, 36,
681 315–318. <https://doi.org/10.1130/G24474A.1>

682 Park, Y., Maffre, P., Godderis, Y., Macdonald, F. A., Anttila, E. S. C. C., Swanson-Hysell,
683 N. L., et al. (2020). Emergence of the Southeast Asian islands as a driver for Neogene
684 cooling. *Proceedings of the National Academy of Sciences*, 117(41), 25319–25326.
685 <https://doi.org/10.1073/pnas.2011033117>

686 Pendergrass, A. G., & Hartmann, D. L. (2014). The atmospheric energy constraint on global-
687 mean precipitation change. *Journal of Climate*, 27(2), 757–768.
688 <https://doi.org/10.1175/JCLI-D-13-00163.1>

689 Penman, D. E. (2016). Silicate weathering and North Atlantic silica burial during the
690 Paleocene-Eocene Thermal Maximum. *Geology*, (9). <https://doi.org/10.1130/G37704.1>

691 Penman, D. E., Turner, K. S., Sexton, P., Norris, R., Dickson, A. J., Boulila, S., et al. (2016).
692 A carbonate compensation depth overshoot in the aftermath of the Paleocene-Eocene
693 Thermal Maximum. *Nature Geoscience*. <https://doi.org/10.1038/ngeo2757>

694 Penman, D. E., Rugenstein, J. K. C., Ibarra, D. E., & Winnick, M. J. (2020). Silicate
695 weathering as a feedback and forcing in Earth’s climate and carbon cycle. *Earth-Science*
696 *Reviews*, 209, 103298. <https://doi.org/10.1016/j.earscirev.2020.103298>

697 Piao, S., Friedlingstein, P., Ciais, P., de Noblet-Ducoudre, N., Labat, D., & Zaehle, S. (2007).
698 Changes in climate and land use have a larger direct impact than rising CO₂ on global
699 river runoff trends. *Proceedings of the National Academy of Sciences*, 104(39), 15242–
700 15247. <https://doi.org/10.1073/pnas.0707213104>

701 Rugenstein, J. K. C., & Winkler, A. J. (2022). CH2O-CHOO v.1.1. Zenodo.
702 <https://doi.org/10.5281/zenodo.7219627>.

703 van der Ploeg, R., Selby, D., Cramwinckel, M. J., Li, Y., Bohaty, S. M., Middelburg, J. J., &
704 Sluijs, A. (2018). Middle Eocene greenhouse warming facilitated by diminished
705 weathering feedback. *Nature Communications*, 9(1), 2877.
706 <https://doi.org/10.1038/s41467-018-05104-9>

707 Roderick, M. L., Greve, P., & Farquhar, G. D. (2015). On the assessment of aridity with
708 changes in atmospheric CO₂. *Water Resources Research*, 51(7), 5450–5463.

709 <https://doi.org/10.1002/2015WR017031>

710 Sagan, C., & Mullen, G. (1972). Earth and Mars: evolution of atmospheres and surface
711 temperatures. *Science*, *177*(4043), 52–56. <https://doi.org/10.1126/science.177.4043.52>

712 Scheff, J., & Frierson, D. M. W. (2014). Scaling potential evapotranspiration with
713 greenhouse warming. *Journal of Climate*, *27*(4), 1539–1558.
714 <https://doi.org/10.1175/JCLI-D-13-00233.1>

715 Scheff, J., Seager, R., Liu, H., & Coats, S. (2017). Are glacials dry? Consequences for
716 paleoclimatology and for greenhouse warming. *Journal of Climate*, *30*(17), 6593–6609.
717 <https://doi.org/10.1175/JCLI-D-16-0854.1>

718 Schlesinger, W. H., & Jasechko, S. (2014). Transpiration in the global water cycle.
719 *Agricultural and Forest Meteorology*, *189–190*, 115–117.
720 <https://doi.org/10.1016/j.agrformet.2014.01.011>

721 Shi, X., & Durran, D. R. (2014). The Response of Orographic Precipitation over Idealized
722 Midlatitude Mountains Due to Global Increases in CO₂. *Journal of Climate*, *27*(11),
723 3938–3956. <https://doi.org/10.1175/JCLI-D-13-00460.1>

724 Swann, A. L. S., Hoffman, F. M., Koven, C. D., & Randerson, J. T. (2016). Plant responses
725 to increasing CO₂ reduce estimates of climate impacts on drought severity. *Proceedings*
726 *of the National Academy of Sciences*, *113*(36), 10019–10024.
727 <https://doi.org/10.1073/pnas.1604581113>

728 Swanson-Hysell, N. L., & Macdonald, F. A. (2017). Tropical weathering of the Taconic
729 orogeny as a driver for Ordovician cooling. *Geology*, *45*(8), 719–722.
730 <https://doi.org/10.1130/G38985.1>

731 Them, T. R., Gill, B. C., Selby, D., Gröcke, D. R., Friedman, R. M., & Owens, J. D. (2017).
732 Evidence for rapid weathering response to climatic warming during the Toarcian
733 Oceanic Anoxic Event. *Scientific Reports*, *7*(1), 1–10. [https://doi.org/10.1038/s41598-](https://doi.org/10.1038/s41598-017-05307-y)
734 [017-05307-y](https://doi.org/10.1038/s41598-017-05307-y)

735 Torres, M. A., West, A. J., & Li, G. (2014). Sulphide oxidation and carbonate dissolution as a
736 source of CO₂ over geological timescales. *Nature*, *507*, 346–349.
737 <https://doi.org/10.1038/nature13030>

738 Uchikawa, J., & Zeebe, R. E. (2008). Influence of terrestrial weathering on ocean
739 acidification and the next glacial inception. *Geophys. Res. Lett.*, *35*(23).
740 <https://doi.org/10.1029/2008GL035963>

741 Ukkola, A. M., Prentice, I. C., Keenan, T. F., van Dijk, A. I. J. M., Viney, N. R., Myneni, R.
742 B., & Bi, J. (2016). Reduced streamflow in water-stressed climates consistent with CO₂

743 effects on vegetation. *Nature Climate Change*, 6, 75–78.
744 <https://doi.org/10.1038/nclimate2831>

745 Vervoort, P., Kirtland Turner, S., Rochholz, F., & Ridgwell, A. (2021). Earth System Model
746 Analysis of How Astronomical Forcing Is Imprinted Onto the Marine Geological
747 Record: The Role of the Inorganic (Carbonate) Carbon Cycle and Feedbacks.
748 *Paleoceanography and Paleoclimatology*, 36(10), 1–20.
749 <https://doi.org/10.1029/2020pa004090>

750 Volk, T. (1987). Feedbacks between weathering and atmospheric CO₂ over the last 100
751 million years. *American Journal of Science*. <https://doi.org/10.2475/ajs.287.8.763>

752 Walker, J. C. G., Hays, P. B., & Kasting, J. F. (1981). A negative feedback mechanism for
753 the long-term stabilization of Earth's surface temperature. *Journal of Geophysical*
754 *Research*, 86(C10), 9776–9782.

755 Wang-Erlandsson, L., van der Ent, R. J., Gordon, L. J., & Savenije, H. H. G. (2014).
756 Contrasting roles of interception and transpiration in the hydrological cycle – Part 1:
757 Temporal characteristics over land. *Earth System Dynamics*, 5(2), 441–469.
758 <https://doi.org/10.5194/esd-5-441-2014>

759 Wei, Z., Yoshimura, K., Wang, L., Miralles, D. G., Jasechko, S., & Lee, X. (2017).
760 Revisiting the contribution of transpiration to global terrestrial evapotranspiration.
761 *Geophysical Research Letters*, 44(6), 2792–2801.
762 <https://doi.org/10.1002/2016GL072235>

763 West, A. J. (2012). Thickness of the chemical weathering zone and implications for erosional
764 and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology*, 40(9), 811–
765 814. <https://doi.org/10.1130/G33041.1>

766 White, A. F., & Blum, A. E. (1995). Effects of climate on chemical weathering in
767 watersheds. *Geochimica et Cosmochimica Acta*, 59(9), 1729–1747.
768 [https://doi.org/10.1016/0016-7037\(95\)00078-E](https://doi.org/10.1016/0016-7037(95)00078-E)

769 Winkler, A. J., Myneni, R. B., Hannart, A., Sitch, S., Haverd, V., Lombardozzi, D., et al.
770 (2021). Slowdown of the greening trend in natural vegetation with further rise in
771 atmospheric CO₂. *Biogeosciences*, 18(17), 4985–5010. [https://doi.org/10.5194/bg-18-](https://doi.org/10.5194/bg-18-4985-2021)
772 [4985-2021](https://doi.org/10.5194/bg-18-4985-2021)

773 Winnick, M., & Maher, K. (2018). Relationships between CO₂, thermodynamic limits on
774 silicate weathering, and the strength of the silicate weathering feedback. *Earth and*
775 *Planetary Science Letters*, 485, 111–120.
776 <https://doi.org/https://doi.org/10.1016/j.epsl.2018.01.005>

- 777 Zeebe, R. E., & Caldeira, K. (2008). Close mass balance of long-term carbon fluxes from ice-
778 core CO₂ and ocean chemistry records. *Nature Geoscience*, *1*(5), 312–315.
779 <https://doi.org/10.1038/ngeo185>
- 780 Zeebe, R. E., & Lourens, L. J. (2019). Solar System chaos and the Paleocene–Eocene
781 boundary age constrained by geology and astronomy. *Science*, *365*, 926–929.
- 782 Zhang, X., Tang, Q., Zhang, X., & Lettenmaier, D. P. (2014). Runoff sensitivity to global
783 mean temperature change in the CMIP5 Models. *Geophysical Research Letters*, *41*,
784 5492–5498. <https://doi.org/10.1002/2014GL061184>. Received
- 785 Zhu, Z., Piao, S., Myneni, R. B., Huang, M., Zeng, Z., Canadell, J. G., et al. (2016). Greening
786 of the Earth and its drivers. *Nature Climate Change*, *6*, 791–795.
787 <https://doi.org/10.1038/NCLIMATE3004>
- 788

789 **Supporting Information References**

- 790 Arora, V.K., Boer, G.J., Friedlingstein, P., Eby, M., Jones, C.D., Christian, J.R., Bonan, G.,
791 Bopp, L., Brovkin, V., Cadule, P., Hajima, T., Ilyina, T., Lindsay, K., Tjiputra, J.F., Wu,
792 T., 2013. Carbon-concentration and carbon-climate feedbacks in CMIP5 earth system
793 models. *J. Clim.* *26*, 5289–5314. <https://doi.org/10.1175/JCLI-D-12-00494.1>
- 794 Arora, V.K., Katavouta, A., Williams, R.G., Jones, C.D., Brovkin, V., Friedlingstein, P.,
795 Schwinger, J., Bopp, L., Boucher, O., Cadule, P., Chamberlain, M.A., Christian, J.R.,
796 Delire, C., Fisher, R.A., Hajima, T., Ilyina, T., Joetzjer, E., Kawamiya, M., Koven, C.D.,
797 Krasting, J.P., Law, R.M., Lawrence, D.M., Lenton, A., Lindsay, K., Pongratz, J.,
798 Raddatz, T., Séférian, R., Tachiiri, K., Tjiputra, J.F., Wiltshire, A., Wu, T., Ziehn, T.,
799 2020. Carbon – concentration and carbon – climate feedbacks in CMIP6 models and
800 their comparison to CMIP5 models. *Biogeosciences* *17*, 4173–4222.
- 801 Berner, R.A., 2006. GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂
802 and CO₂. *Geochim. Cosmochim. Acta* *70*, 5653–5664.
803 <https://doi.org/10.1016/j.gca.2005.11.032>
- 804 Brady, P. V., 1991. The effect of silicate weathering on global temperature and atmospheric
805 CO₂. *J. Geophys. Res.* *96*. <https://doi.org/10.1029/91jb01898>
- 806 Brook, G., Folkoff, M., Box, E., 1983. A World Model of Soil Carbon Dioxide. *Earth Surf.*
807 *Process. Landforms* *8*, 79–88.
- 808 Caves Rügenstein, J.K., Ibarra, D.E., von Blanckenburg, F., 2019. Neogene cooling driven by
809 land surface reactivity rather than increased weathering fluxes. *Nature* *571*, 99–102.
810 <https://doi.org/10.1038/s41586-019-1332-y>

811 Gaillardet, J., Dupré, B., Louvat, P., Allegre, C., 1999. Global silicate weathering and CO₂
812 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.

813 Graham, R.J., Pierrehumbert, R.T., 2020. Thermodynamic and Energetic Limits on
814 Continental Silicate Weathering Strongly Impact the Climate and Habitability of Wet,
815 Rocky Worlds.

816 Knutti, R., Rugenstein, M.A.A., Hegerl, G.C., 2017. Beyond equilibrium climate sensitivity.
817 *Nat. Geosci.* 10, 727–736. <https://doi.org/10.1038/ngeo3017>

818 Kump, L.R., Brantley, S.L., Arthur, M.A., 2000. Chemical weathering, atmospheric CO₂,
819 and climate. *Annu. Rev. Earth Planet. Sci.* 28, 611–667.

820 Larsen, I.J., Montgomery, D.R., Greenberg, H.M., 2014. The contribution of mountains to
821 global denudation. *Geology* 42, 527–530. <https://doi.org/10.1130/G35136.1>

822 Lenton, T.M., Daines, S.J., Mills, B.J.W., 2018. COPSE reloaded: An improved model of
823 biogeochemical cycling over Phanerozoic time. *Earth-Science Rev.* 178, 1–28.
824 <https://doi.org/10.1016/j.earscirev.2017.12.004>

825 Maher, K., Chamberlain, C.P., 2014. Hydrologic regulation of chemical weathering and the
826 geologic carbon cycle. *Science* (80-.). 343, 1502–1504.
827 <https://doi.org/10.1126/science.1250770>

828 Manabe, S., Wetherald, R.T., Milly, P.C.D., Delworth, T.L., Stouffer, R.J., 2004. Century-
829 scale change in water availability: CO₂-quadrupling experiment. *Clim. Change* 64, 59–
830 76.

831 Milliman, J.D., Droessler, A.W., 1996. Neritic and pelagic carbonate sedimentation in the
832 marine environment: ignorance is not bliss. *Geol. Rundschau* 85, 496–504.

833 Moon, S., Chamberlain, C.P., Hilley, G.E., 2014. New estimates of silicate weathering rates
834 and their uncertainties in global rivers. *Geochim. Cosmochim. Acta* 134, 257–274.
835 <https://doi.org/10.1016/j.gca.2014.02.033>

836 Myhre, G., Highwood, E.J., Shine, K.P., Stordal, F., 1998. New estimates of radiative forcing
837 due to well mixed greenhouse gases. *Geophys. Res. Lett.* 25, 2715–2718.

838 Prentice, I.C., Harrison, S.P., 2009. Ecosystem effects of CO₂ concentration: Evidence from
839 past climates. *Clim. Past* 5, 297–307. <https://doi.org/10.5194/cp-5-297-2009>

840 Scheff, J., Seager, R., Liu, H., Coats, S., 2017. Are glacials dry? Consequences for
841 paleoclimatology and for greenhouse warming. *J. Clim.* 30, 6593–6609.
842 <https://doi.org/10.1175/JCLI-D-16-0854.1>

843 Shields, G.A., Mills, B.J.W., 2017. Tectonic controls on the long-term carbon isotope mass
844 balance. *Proc. Natl. Acad. Sci.* 114, 4318–4323.

845 <https://doi.org/10.1073/pnas.1614506114>

846 Volk, T., 1987. Feedbacks between weathering and atmospheric CO₂ over the last 100
847 million years. *Am. J. Sci.* <https://doi.org/10.2475/ajs.287.8.763>

848 Wallmann, K., 2001. Controls on the Cretaceous and Cenozoic evolution of seawater
849 composition, atmospheric CO₂ and climate. *Geochim. Cosmochim. Acta* 65, 3005–
850 3025. [https://doi.org/10.1016/S0016-7037\(01\)00638-X](https://doi.org/10.1016/S0016-7037(01)00638-X)

851 West, A.J., 2012. Thickness of the chemical weathering zone and implications for erosional
852 and climatic drivers of weathering and for carbon-cycle feedbacks. *Geology* 40, 811–
853 814. <https://doi.org/10.1130/G33041.1>

854 Winnick, M., Maher, K., 2018. Relationships between CO₂, thermodynamic limits on silicate
855 weathering, and the strength of the silicate weathering feedback. *Earth Planet. Sci. Lett.*
856 485, 111–120. <https://doi.org/https://doi.org/10.1016/j.epsl.2018.01.005>

857 Zhang, Xuejun, Tang, Q., Zhang, Xuezhen, Lettenmaier, D.P., 2014. Runoff sensitivity to
858 global mean temperature change in the CMIP5 Models. *Geophys. Res. Lett.* 41, 5492–
859 5498. <https://doi.org/10.1002/2014GL061184>.Received

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