

1 Tectonic controls on the long-term carbon isotope mass balance

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18 G.S. designed the study, B.M. computed numerical results, and both authors contributed to

19 the analysis and writing.

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21

22 **Abstract**

23 **The long-term, steady-state marine carbon isotope record reflects changes to the**  
24 **proportional burial rate of organic carbon relative to total carbon on a global scale. For**  
25 **this reason, times of high  $\delta^{13}\text{C}$  are conventionally interpreted to be oxygenation events**  
26 **caused by excess organic burial. Here we show that the carbon isotope mass balance is**  
27 **also significantly affected by tectonic uplift and erosion via changes to the inorganic**  
28 **carbon cycle that are independent of changes to the isotopic composition of carbon input.**  
29 **This view is supported by inverse co-variance between  $\delta^{13}\text{C}$  and a range of uplift proxies,**  
30 **including seawater  $^{87}\text{Sr}/^{86}\text{Sr}$ , that demonstrates how erosional forcing of carbonate**  
31 **weathering outweighs that of organic burial on geological time scales. A model of the**  
32 **long-term carbon cycle shows that increases in  $\delta^{13}\text{C}$  need not be associated with increased**  
33 **organic burial and that alternative tectonic drivers (erosion, outgassing) provide testable**  
34 **and plausible explanations for sustained deviations from the long-term  $\delta^{13}\text{C}$  mean. Our**  
35 **approach emphasizes the commonly overlooked difference between how net and gross**  
36 **carbon fluxes affect the long-term carbon isotope mass balance, and may lead to**  
37 **reassessment of the role that the  $\delta^{13}\text{C}$  record plays in reconstructing the oxygenation of**  
38 **Earth's surface environment.**

39

40 **Significance**

41 The carbon isotope record has played a major role in reconstructing the oxygen and carbon  
42 dioxide content of the ancient atmosphere. However, known oxygenation events are not always  
43 reflected in the isotopic record of marine carbonate rocks, while conventional interpretations  
44 imply that less organic matter is buried when erosion rates are high, which is hard to explain.  
45 Here we show that both issues can be resolved if limestone weathering makes up a  
46 proportionately greater fraction of the global carbon cycle at high erosion rates. We argue that  
47 the link between carbon isotopes and oxygenation is more tenuous than commonly assumed,  
48 and propose a case-by-case re-examination of Earth's oxygenation history.

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## 55 **Introduction**

56 Earth's highly oxygenated atmosphere derives largely from the splitting of the water molecule  
57 during photosynthesis. Respiration and decay reverse this process, consuming oxygen, but the  
58 burial of organic matter in sediments allows oxygen to accumulate in the atmosphere. Net  
59 oxygenation may also arise from burial of reduced sulphur species, but the organic carbon  
60 burial flux has been the major source of oxygen throughout the Phanerozoic (1-6).

61

62 Because photosynthesis results in  $^{13}\text{C}$ -depleted organic carbon, the carbon isotope composition  
63 of past oceans has played an important role in tracing the oxygenation of Earth's surface  
64 environment. The conventional interpretation of C-isotope mass balance (7) presumes that  
65 prolonged intervals of high carbonate  $\delta^{13}\text{C}$  are the result of elevated rates of organic carbon  
66 burial (removing a larger fraction of  $^{13}\text{C}$ -depleted organic matter), and so correspond to an  
67 excess of oxygen production over consumption, which is in large part due to the oxidation of  
68 organic matter during surface weathering. This paradigm has led to the view that atmospheric  
69 oxygen levels rose at three crucial junctures in Earth history: at  $\sim 2.1$  Ga (8-9),  $\sim 0.8$  Ga (10-11)  
70 and  $\sim 0.3$  Ga (7,12), and this has become generally accepted (13).

71

72 This paradigm encounters difficulties. Firstly, although Earth's oxygenation history does not  
73 rely solely on carbon isotope data, it is remarkable that independent evidence for oxygenation  
74 does not always coincide with high  $\delta^{13}\text{C}$  (14). The Ediacaran-Cambrian faunal radiation  
75 (Cambrian Explosion), which is commonly attributed to oxygenation, is strangely accompanied  
76 by low, rather than high  $\delta^{13}\text{C}$  (Fig. 1), while the many fluctuations in atmospheric oxygen  
77 between 15% and 32% that have been identified using the Phanerozoic carbon isotope record  
78 (12), lack corroborating evidence (14). Although such inconsistencies are widely  
79 acknowledged, alternative explanations to explain global trends in  $\delta^{13}\text{C}$  are uncommon. One

80 possibly viable alternative attributes  $\delta^{13}\text{C}$  fluctuations to the amount of diagenetically  
81 precipitated (and isotopically light) carbonate cement worldwide (14-15). Such large changes  
82 remain unsubstantiated, while the link to the global carbon cycle must appeal to a sampling  
83 bias, wherein a great mass of isotopically light material can be buried (to drive a positive  
84 excursion) yet does not lower the bulk isotopic composition of the carbonates which are  
85 analyzed. We argue that the preservation of a  $\delta^{13}\text{C}$  signal that is correlated with other global  
86 processes is evidence against such sampling errors, and must be the result of definable system  
87 interactions (Fig. 1).

88

89 A second problem stems from the driving mechanism for increased organic burial during times  
90 of high  $\delta^{13}\text{C}$ . It is widely supposed that higher rates of organic burial are caused by increased  
91 nutrient input and/or sedimentation rates through weathering and erosion (5,11,16-17).  
92 However, long-term carbon isotope trends exhibit low, not high values during the collisional  
93 phases of supercontinent formation, while  $\delta^{13}\text{C}$  shows an unexpected inverse relationship with  
94 erosion proxies, such as seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  and reconstructed sediment masses (Fig. 1, see SI  
95 for correlations), best illustrated by the Ediacaran-Ordovician orogenic interval of  
96 exceptionally high sedimentary fluxes, which are independently verified by zircon isotope  
97 studies (see SI). The C isotope record implies therefore that erosional forcing of organic burial  
98 does not control the long-term C isotope mass balance, and that any such effect may be  
99 outweighed by an erosional forcing of carbonate burial.

100

### 101 **The long-term carbon isotope mass balance**

102 Figure 2 shows a representation of the long-term carbon cycle, which forms the basis for  
103 isotope mass balance calculations (18). Carbon enters the atmosphere/ocean system by four  
104 routes: oxidative weathering of fossil carbon ( $F_{\text{wg}}$ ), carbonate weathering ( $F_{\text{wc}}$ ) and

105 metamorphic degassing of sedimentary organic carbon ( $F_{mg}$ ) and carbonates ( $F_{mc}$ ). Carbon  
106 leaves the surface pool via burial of organic carbon ( $F_{bg}$ ) and inorganic carbonates ( $F_{bc}$ ), with  
107 the fraction of total burial leaving via the organic route denoted  $f_{org}$ . The dashed lines in figure  
108 2 show an important difference between net (solid lines) and gross (all lines) fluxes in the  
109 carbon cycle, which arises because the carbonate weathering-precipitation cycle is a  $CO_2$   
110 neutral process on long time-scales (19) (see SI).

111

112 The C-isotope mass balance (eq. 1) is based around the principle that on time scales greater  
113 than the residence time of carbon in the ocean (about  $10^5$  years), the quantity and isotopic  
114 composition of carbon entering and exiting the atmosphere-ocean system (A) must be the same  
115 (18):

116

$$117 \quad \delta^{13}C_{in} = \delta^{13}C_{org} \cdot f_{org} + \delta^{13}C_{carb} (1 - f_{org}) \quad (1)$$

118

119 Standard calculations then assume that the average isotopic composition of carbon input  
120 ( $\delta^{13}C_{in}$ ) is constant and approximately equal to  $\delta^{13}C_{mantle}$  or about  $-6\% \pm 1\%$ . Rearranging  
121 equation (1) then allows the proportion of carbon buried as organic matter ( $f_{org}$ ) to be read  
122 directly from the carbonate C isotope record (20). Knowledge of  $f_{org}$ , and the total input ( $\approx$   
123 output) rate of carbon,  $F_{total}$ , then allows the rate of organic carbon burial, and hence oxygen  
124 production to be estimated (9,10):

125

$$126 \quad F_{bg} = F_{total} \times (\delta^{13}C_{carb} - \delta^{13}C_{in}) / \Delta B \quad (2)$$

127

128 Following this reasoning, positive  $\delta^{13}C$  excursions are commonly interpreted as organic C  
129 burial events, whereby the resultant oxygenation is quantified using the assumptions that total

130 C throughput and net fluxes (the net carbon flux on geological time scales excludes the  
131 carbonate weathering flux) were similar to the present day, and that  $f_{\text{org}}$  approximates the  
132 proportion of outgassed  $\text{CO}_2$  (including weathering sources) that is reduced to organic carbon  
133 (9,15). For example, the sustained baseline increase of  $\sim 5\text{-}6\%$  during the early Neoproterozoic  
134 (11) is interpreted to imply an approximate doubling of organic burial due to increased  
135 phytoplankton body size (10) or high sedimentation rates (11). For the  $\sim 2.1$  Ga Lomagundi  
136 Event of high  $\delta^{13}\text{C}$ , the total excess oxygen produced has been estimated at a massive 12-22  
137 times the present inventory of atmospheric oxygen (8,9), with organic burial rates thought to  
138 increase by  $>20$  times over the course of the isotope excursion (21).

139

140 Such large increases in organic carbon burial are difficult to reconcile with the operation of the  
141 long-term carbon cycle. Whilst organics contribute only around 20-25% of gross carbon burial  
142 (i.e.  $f_{\text{org}} \approx 0.20\text{-}0.25$ ), they constitute more than 50% (19,6) and even as much as 72% (22) of  
143 the net carbon sink. Even a doubling of global organic carbon burial over geological timescales  
144 would therefore require a massive reorganization of the carbon cycle, alongside a  
145 contemporaneous increase in carbon sources through weathering and degassing, due to the  
146 impossibility of the other net sink (carbonate deposition following silicate weathering) being  
147 reduced below zero.

148

#### 149 **A physical erosion control on the carbon isotope mass balance**

150 We propose here that long-term variation in  $f_{\text{org}}$ , and hence  $\delta^{13}\text{C}$ , may sometimes be driven by  
151 changes in the inorganic, rather than the organic side of the carbon cycle. Because the carbonate  
152 weathering – deposition cycle is  $\text{CO}_2$  neutral on time scales relevant to the C-isotope mass  
153 balance, increasing the carbonate weathering (and deposition) rates acts to decrease  $f_{\text{org}}$  without  
154 impacting the net carbon fluxes responsible for driving climate. Although this is not the first

155 study to link changes in carbonate weathering to  $\delta^{13}\text{C}$ , for example, it has been shown that a  
156 transient increase in carbonate weathering rates would drive an increase in  $\delta^{13}\text{C}_{\text{in}}$  (23), our  
157 proposition differs from previous work by highlighting how sustained changes in carbonate  
158 deposition rates can alter  $f_{\text{org}}$  directly.

159

160 Such changes in the inorganic carbon cycle may be brought about by variation in erosion rates,  
161 driving step changes in carbonate weathering, and therefore gross carbon throughput. Whilst  
162 changes in erosion rate may also initially affect the net fluxes of silicate weathering and organic  
163 C burial, these must eventually return to balance the carbon cycle at steady state via temperature  
164 and nutrient feedbacks. There is no such requirement for carbonate weathering. This key  
165 difference between the net and gross carbon fluxes may explain why the erosional forcing of  
166 organic burial does not keep pace with carbonate burial during the early Palaeozoic and other  
167 orogenic events (Fig. 1).

168

169

170 Considering that mountains dominate global denudation rates (24), and that carbonate  
171 weathering is proportionately more important at higher erosion rates (25), we argue that  $f_{\text{org}}$   
172 (and hence the  $\delta^{13}\text{C}$  composition of the atmosphere-ocean system) will be lowered by tectonic  
173 uplift and erosion, unless compensated for by increased rates of net carbon flux (outgassing).  
174 Conversely, during periods of low denudation rates,  $\delta^{13}\text{C}$  values will tend to be higher, although  
175 the overall weathering flux and organic burial rates may be lower. This is apparent when  
176 considering the evidence for low  $\delta^{13}\text{C}$  during times of supercontinent formation and high  $\delta^{13}\text{C}$   
177 during times of supercontinent stability (16, 26), and can be observed by rearranging equation  
178 (2), assuming that erosion affects  $F_{\text{total}}$ :

179



180  $\delta^{13}\text{C}_{\text{carb}} = (F_{\text{bg}} \times \Delta B)/F_{\text{total}} + \delta^{13}\text{C}_{\text{in}}$  (3)

181

182 Taking average values from the literature for carbon fluxes ( $F_{\text{wg}} = 7.75 \times 10^{12}$  mol/yr,  $F_{\text{wc}} =$   
183  $24 \times 10^{12}$  mol/yr;  $F_{\text{mg}} = 1.25 \times 10^{12}$  mol/yr;  $F_{\text{mc}} = 8 \times 10^{12}$  mol/yr;  $F_{\text{bg}} = 9 \times 10^{12}$  mol/yr;  $F_{\text{total}} = F_{\text{wc}} +$   
184  $F_{\text{mc}} + F_{\text{wg}} + F_{\text{mg}} = 41 \times 10^{12}$  mol/yr (19, 27), equation (3) suggests that trends in the long-term  
185  $\delta^{13}\text{C}$  average of  $\sim -1\text{‰}$  to  $\sim +5\text{‰}$  can be explained by varying the carbonate weathering flux  
186 between 1.5 times and 0.2 times the present day rate, respectively, without requiring any  
187 change in the rate of organic carbon burial. Such changes are within the limits of published  
188 estimates based on the Sr isotope record and/or sedimentation rates (see SI). Note that this  
189 mechanism does not require changes in  $\delta^{13}\text{C}_{\text{in}}$ .

190

### 191 **Modelling the carbon isotope mass balance**

192 To illustrate this idea, we compute the steady states of the long-term carbon cycle model with  
193 respect to the relative global erosion rate (Figure 3). The flux calculations follow the  
194 GEOCARB and COPSE models (6, 26) under present day conditions, including both direct  
195 erosion and temperature effects on weathering fluxes. The isotope mass balance calculations  
196 in our model do not differ from those employed in Berner's analysis (5), but critically our  
197 model takes into account the effects of erosion on carbonate weathering. This is in line with  
198 the above discussion, and with direct evidence for considerable carbonate weathering in areas  
199 of high erosion and relief, e.g. the mountainous and foreland areas of the Andes (28). See SI  
200 for further model discussion.

201

202 An important consideration in this work is that changes in erosion rate also alter the rate of  
203 organic carbon burial via changes to the phosphorus cycle. To explore this further we link the  
204 rate of organic carbon burial in the model to the availability of phosphorus (22, 6). Phosphorus

205 enters the surface system via the weathering of silicate, carbonate and organic C-bearing rocks,  
206 and the strength of the relationship between erosion and organic C burial depends on the P  
207 delivery from the weathering of each individual rock type.

208

209 Recent studies of P delivery from different rock types (29, 30) suggest that silicates play the  
210 major role, delivering more than 50% of riverine P (see SI). The model run showing this setup  
211 (M1) is shown in bold in figure 3. When the weathering of silicates is chiefly responsible for P  
212 delivery, an increase in erosion will not greatly affect the steady state P delivery or organic C  
213 burial, because the global silicate weathering rate is tightly controlled at steady state by the rate  
214 of CO<sub>2</sub> release (which remains constant in the model), and by any imbalance in the organic C  
215 cycle.

216

217 Dashed lines in figure 3 show results when silicates are assumed to contribute only ~17% of  
218 global P delivery (M2), as was assumed in the original COPSE model, based on crustal  
219 inventories rather than supply rates (6). The dotted lines (M3) show a more extreme case where  
220 all P delivery results from carbonate weathering. These configurations show that if most P is  
221 supplied by the weathering of carbonates, or follows a similar erosional forcing to carbonates  
222 (i.e. preferentially weathered at high erosion rates) (25), then an increase in erosion rate would  
223 significantly increase P delivery, and therefore organic C burial, at steady state. This would act  
224 to counter the direct effect of increased erosion and carbonate weathering/deposition on  $\delta^{13}\text{C}$ ,  
225 but only as far as carbon mass balance can allow.

226

227 We conclude from this analysis that changes in erosion rates most likely exert a powerful first-  
228 order control on long term carbonate  $\delta^{13}\text{C}$ , which is only partially nullified by associated  
229 changes in the phosphorus cycle and organic carbon burial.

230

231 We acknowledge that the long-term effects of erosion on global P delivery and organic carbon  
232 burial are still poorly constrained. Uncertainties exist in the various temperature and erosion  
233 effects on individual chemical weathering fluxes, the degree of preferential chemical  
234 weathering of accessory apatite minerals, and the possibility that changes in sedimentation rate  
235 may impact organic carbon burial differently to the burial of carbonates. In particular, it has  
236 been proposed that increased rates of sedimentation will enhance the preservation of buried  
237 organic carbon and phosphorus (5). Our model calculates the rate of organic carbon burial  
238 based on a relationship between ocean phosphate, new production and sedimentation rate (31),  
239 but we have also run an alternative model setup to further explore this idea, wherein we  
240 strengthen this relationship by giving the burial rates of organic carbon and phosphorus an  
241 additional linear dependence on the global erosion rate. The model results for ocean phosphate  
242 concentration are altered under these assumptions, but the steady-state burial rates of carbon  
243 and phosphorus are not affected, as they are ultimately constrained by the supply flux of P from  
244 weathering (see SI for more details).

245

246 Our model run M1 shows what we consider to be the current best guess for these mechanisms  
247 (see SI for more details and other model runs), but a model is not unequivocal proof, and it is  
248 clearly theoretically possible for erosion to increase organic C burial more than it increases the  
249 burial rate of carbonates (e.g. model run M3). However, if this were the case we would expect  
250  $\delta^{13}\text{C}$  values to increase with increasing erosion rates, but this is effectively falsified by the anti-  
251 correlation of  $\delta^{13}\text{C}$  and all available erosion proxies. We therefore conclude that although  
252 erosion rates must certainly increase the rate of P delivery and organic C burial, such increases  
253 must be less than the increases to the burial rate of carbonates.

254

255 Figure 4 shows a series of time-dependent model runs where a +3‰ positive excursion in  $\delta^{13}\text{C}$   
256 is caused by either increasing organic carbon burial (via increased P delivery), or decreasing  
257 the erosion rate. Increasing  $\delta^{13}\text{C}$  via an organic C burial event (Figure 4. A-E) results in a  
258 decrease in the atmosphere/ocean carbon reservoir, i.e. a decrease in atmospheric  $\text{pCO}_2$ , and  
259 global cooling. Driving a similar positive excursion via a reduction in erosion rates (Figure 4.  
260 F-J) causes a warming event due to the weakening of silicate weathering. Importantly, we show  
261 that a positive  $\delta^{13}\text{C}$  excursion may be coincident with either an increase, or decrease in the rate  
262 of organic carbon burial. This should be a serious consideration for work aiming to tie the C  
263 isotope record to global biogeochemical events.

264

265 An important factor influencing the time-dependent response of the model is the assumption  
266 of ‘rapid recycling’ of isotope signals due to the predominant weathering of recently-deposited  
267 sediments. This idea has been explored in early carbon and sulphur cycle models (7), and is  
268 included in the GEOCARB models (5). We include this effect here by reducing the size of the  
269 crustal pools of organic carbon and carbonates to around 10% of the total crustal inventory,  
270 allowing for much quicker variation in isotopic composition (RR on, solid lines in figure 4).  
271 This follows Berner (5, 7). Dashed lines assume no rapid recycling, i.e. that the isotopic  
272 signature of weathered material represents the whole crustal inventory. As may be expected,  
273 the rapid recycling model acquires steady state around an order of magnitude quicker than the  
274 non-RR model. However, the choice of models does not affect the qualitative dynamics we  
275 wish to demonstrate.

276

277 The isotopic composition of carbon inputs ( $\delta^{13}\text{C}_{\text{in}}$ ) is not fixed in our model, but responds to  
278 the changing composition of the crustal reservoirs. Although changes to  $\delta^{13}\text{C}_{\text{in}}$  (e.g. due to  
279 preferential weathering of high- $\delta^{13}\text{C}$  lithologies) have been shown to drive C isotope

280 excursions (20, 23), the mechanism explored in this paper does not depend on variations in  
281  $\delta^{13}\text{C}_{\text{in}}$ . As an example we run the model with this parameter fixed (Figure S7), which shows  
282 the same qualitative results.

283

#### 284 **Interrogating carbon isotope excursions**

285 A positive carbon isotope excursion caused by changes to the inorganic carbon cycle has  
286 different climatic effects from one caused by increasing the burial rate of organics: notably an  
287 increase in  $\text{CO}_2$  and surface temperature, rather than a decrease. Such testable distinctions  
288 allow us to constrain the causes of specific carbon isotope events, and suggest that major, but  
289 short-lived  $\delta^{13}\text{C}$  events, which coincide with global cooling, such as the late Ordovician  
290 Hirnantian event, could potentially relate to excess organic burial. The longer Permo-  
291 Carboniferous glaciations also occurred at a time of generally high  $\delta^{13}\text{C}$ , and are thus consistent  
292 with an elevated organic burial flux, perhaps associated with the evolution of a modern land  
293 biota (32). However, relatively low erosion rates throughout this period imply that rates of  
294 organic C burial need not have been as high as previously thought – potentially resolving  
295 conflicts over the prediction of hyperambient  $\text{O}_2$  levels (5). By contrast, glaciation during the  
296 Cenozoic is associated with decreasing  $\delta^{13}\text{C}$ , and so appears to be more consistent with the  
297 notion that the erosional forcing of carbonate deposition outweighed that of organic burial.

298

299 Some times of elevated  $\delta^{13}\text{C}$  do not coincide with glaciation, and this is the case for the post-  
300 glacial Lomagundi Event of exceptionally high  $\delta^{13}\text{C}$  during the Palaeoproterozoic . Such high  
301  $\delta^{13}\text{C}$  values may result from a hugely increased oxidative weathering flux (21), following the  
302 Great Oxidation Event, which could have been self-sustained by oxygenic siderite (iron  
303 carbonate) weathering (22). Although not related to decreased erosion rates, the Lomagundi  
304 Event can still be viewed as a time of proportionately higher net carbon flux relative to gross

305 carbon throughput, in the same way as we argue for other times of high baseline  $\delta^{13}\text{C}$ , such as  
306 during the Tonian Period of supercontinent peneplanation. Note that in none of these cases  
307 does high  $\delta^{13}\text{C}$  imply net oxygenation. Previously, these well-established  $\delta^{13}\text{C}$  events were  
308 first-order determinants in our understanding of Earth's oxygenation history.

309

310 Despite our emphasis here on erosional controls on  $\delta^{13}\text{C}$ , we view the carbon isotope mass  
311 balance as a proportional parameter, whereby changes to the long-term norm correspond to  
312 changes in the proportion that carbonate weathering makes up of the global carbon cycle. In  
313 this regard, the anti-correlation between  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  over the past billion years could  
314 reflect the dependence of both these parameters on the competing tectonic influences of  
315 volcanism versus uplift, rather than erosion *per se*.

316

## 317 **Conclusions**

318 The carbon isotope record is most commonly viewed in terms of changing organic carbon  
319 burial rates, and less in terms of the proportional organic component of the carbon cycle. By  
320 viewing  $\delta^{13}\text{C}$  as a combination of net and gross carbon fluxes (and removing the common  
321 assumption that carbonate / silicate / organic weathering systematics are invariantly  
322 proportional), we show that higher proportional organic burial (higher  $f_{\text{org}}$ ) can result from a  
323 decreased global weathering (carbonate) flux to the ocean and may not be driven directly by  
324 changes in the organic carbon burial flux. Moreover, it appears that tectonic controls may  
325 plausibly be the underlying drivers of carbon isotope trends that were previously attributed  
326 either to organic carbon burial or to the changing isotopic composition of carbon sources. This  
327 is evidenced by the anti-correlation between carbonate  $\delta^{13}\text{C}$  and erosion proxies such as  
328  $^{87}\text{Sr}/^{86}\text{Sr}$  and reconstructed sediment abundance. There seems to be no systematic relationship  
329 between  $\delta^{13}\text{C}$  and oxygenation through carbon burial, and we suggest therefore that the

330 oxygenation history of the Earth be reassessed on a case-by-case basis in order to better take  
331 into account the distinction between net and gross fluxes.

332

### 333 **References**

334 1. Kump LR., Garrels RM (1986) Modeling Atmospheric O<sub>2</sub> in the Global Sedimentary

335 Redox Cycle. *American Journal of Science* 286: 337-360.

336 2. Bottrell SH, Newton, RJ (2006) Reconstruction of changes in global sulfur cycling from

337 marine sulfate isotopes. *Earth Science Reviews* 75: 59-83.

338 3. Smith RW, Bianchi TS, Allison M, Savage C, Galy V (2015) High rates of organic carbon

339 burial in fjord sediments globally. *Nat Geosci* 8: 450-453.

340 4. Berner RA, Canfield DE (1989) A new model for atmospheric oxygen over Phanerozoic

341 time. *Amer J Sci* 289: 333-361.

342 5. Berner RA (2006) GEOCARBSULF: A combined model for Phanerozoic atmospheric O<sub>2</sub>

343 and CO<sub>2</sub>. *Geochim et Cosmochim Acta* 70: 5653-5664.

344 6. Bergman NM, Lenton TM, Watson AJ (2004) COPSE: A new model of biogeochemical

345 cycling over Phanerozoic time. *Amer J Sci* 304: 397-437.

346 7. Berner RA (1987) Models for carbon and sulfur cycles and atmospheric oxygen:

347 application to Paleozoic geologic history. *Amer J Sci* 287: 177-196.

348 8. Karhu JA, Holland HD (1996) Carbon isotopes and the rise of atmospheric oxygen.

349 *Geology* 24: 867-870.

350 9. Holland HD (2002) Volcanic gases, black smokers, and the Great Oxidation Event.

351 *Geochim et Cosmochim Acta* 66: 3811-3826.

352 10. Knoll AH, Hayes JM, Kaufman AJ, Swett K, Lambert IB (1986) Secular variations in

353 carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland.

354 *Nature* 321: 832-838.

- 355 11. Des Marais DJ, Strauss H, Summons RE, Hayes JM (1992) Carbon isotope evidence for  
356 the stepwise oxidation of the Proterozoic environment. *Nature* 359: 605-609.
- 357 12. Berner RA (2009) Phanerozoic atmospheric oxygen: new results using the  
358 GEOCARBSULF model. *Amer J Sci* 309: 603-606.
- 359 13. Lyons TW, Reinhard CT, Planavsky NJ (2014) The rise of oxygen in Earth's ocean and  
360 atmosphere. *Nature* 506: 307-315.
- 361 14. Schrag DP, Higgins JA, Macdonald FA, Johnston DT (2013) Authigenic Carbonate and  
362 the History of the Global Carbon Cycle. *Science* 339: 540-543.
- 363 15. Hayes JM, Waldbauer JR (2006) The carbon cycle and associated redox processes  
364 through time. *Phil. Trans. R. Soc. B* 361: 931-950.
- 365 16. Campbell IH, Allen CM (2008) Formation of supercontinents linked to increases in  
366 atmospheric oxygen. *Nat Geosci* 1: 554-558.
- 367 17. Galy V, Peucker-Ehrenbrink B, Eglinton T (2015) Global carbon export from the  
368 terrestrial biosphere controlled by erosion. *Nature* 521: 204-207.
- 369 18. Garrels RM, Lerman A (1984) Coupling the sedimentary sulfur and carbon cycles - an  
370 improved model. *Amer J Sci* 284: 989-1007.
- 371 19. Berner RA (1991) A model for atmospheric CO<sub>2</sub> over Phanerozoic time. *Amer J Sci* 291:  
372 339-376.
- 373 20. Kump LR, Arthur MA (1999) Interpreting carbon-isotope excursions: carbonates and  
374 organic matter. *Chem Geol* 161: 181-198.
- 375 21. Bekker A, Holland HD (2012) Oxygen overshoot and recovery during the early  
376 Paleoproterozoic. *EPSL* 317-318: 295-304.
- 377 22. Bachan A, Kump LR (2015) The rise of oxygen and siderite oxidation during the  
378 Lomagundi Event. *Proc Natl Acad Sci USA* 112: 6562-6567.



- 379 23. Kump LR et al (1999) A weathering hypothesis for glaciation at high atmospheric pCO<sub>2</sub>  
380 during the late Ordovician. *Palaeogeog, Palaeoclimat, Palaeoecol* 152: 173-187.
- 381 24. Larsen IJ, Montgomery DR, Greenberg HM (2014) The contribution of mountains to  
382 global denudation. *Geology* 42: 527-530.
- 383 25. Jacobson AD, Blum JD (2003) Relationship between mechanical erosion and atmospheric  
384 CO<sub>2</sub> consumption in the New Zealand Southern Alps. *Geology* 31: 865-868.
- 385 26. Berner RA (1994) Geocarb II: A revised model of atmospheric CO<sub>2</sub> over Phanerozoic  
386 time. *Amer J Sci* 294: 56-91.
- 387 27. Kasting JF (2013) What caused the rise of atmospheric O<sub>2</sub>? *Chem Geol* 362: 13-25.
- 388 28. Moquet J-S, et al (2011) Chemical weathering and atmospheric/soil CO<sub>2</sub> uptake in the  
389 Andean and Foreland Amazon basins. *Chem Geol* 287: 1-26.
- 390 29. Hartmann J, Moosdorf N, Lauerwald R, Hinderer M, West AJ (2014) Global chemical  
391 weathering and associated P-release – The role of lithology, temperature and soil properties  
392 *Chem Geol* 363: 145-163.
- 393 30. Compton J, et al (2000) Variations in the global phosphorus cycle. In *Marine*  
394 *Authigenesis: From Global to Microbial*, SEPM Special Publication 66: 21-33.
- 395 31. Van Cappellen P, Ingall ED (1994) Benthic phosphorus regeneration, net primary  
396 production, and ocean anoxia – a model of the coupled marine biogeochemical cycles of  
397 carbon and phosphorus *Paleoceanography* 9: 677-692.
- 398 32. Lenton TM et al (2016) Earliest land plants created modern levels of atmospheric oxygen.  
399 *Proc Natl Acad Sci USA* 113(35): 9704-9709.
- 400 33. Gradstein FM, Ogg JG, Schmitz MD, Ogg GM (Eds) *The Geologic Time Scale 2012:*  
401 *volume 1*. Elsevier, 435pp.

- 402 34. Hay WW et al (2006) Evaporites and the salinity of the ocean during the Phanerozoic:  
403 Implications for climate, ocean circulation and life. *Palaeogeog, Palaeoclimat, Palaeoecol*  
404 240: 3-46.
- 405 35. Hayes JM, Strauss H, Kaufman AJ (1999) The abundance of <sup>13</sup>C in marine organic matter  
406 and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800  
407 Ma. *Chem Geol* 161: 103-125.
- 408 36. Veizer J (1985) Carbonates and ancient oceans: isotopic and chemical record on time  
409 scales of 10<sup>7</sup> – 10<sup>8</sup> years. In: The carbon cycle and atmospheric CO<sub>2</sub>: Natural variations,  
410 Archean to Present. Eds: E.T. Sundquist, W.S. Broecker. *AGU Geophysical Monograph* 32:  
411 595-601.
- 412 37. Worsley TR, Moody JB, Nance RD (1985) Proterozoic to Recent tectonic tuning of  
413 biogeochemical cycles. In: The carbon cycle and atmospheric CO<sub>2</sub>: Natural variations,  
414 Archean to Present. Eds: E.T. Sundquist, W.S. Broecker. *AGU Geophysical Monograph*  
415 32: 561-572.
- 416 38. Rothman DH (2002) Atmospheric carbon dioxide levels for the last 500 million years.  
417 *Proc Natl Acad Sci USA* 99: 4167-4171.
- 418 39. Brasier MD, Lindsay JF (2001) Did supercontinent amalgamation trigger the “Cambrian  
419 Explosion”? In: The ecology of the Cambrian radiation. Eds: A.Y. Zhuravlev, R. Riding.  
420 Columbia University Press, New York, pp. 69-89.
- 421 40. Squire RJ, Campbell IH, Allen CM, Wilson CJL (2006) Did the Transgondwanan  
422 supermountain trigger the explosive radiation of animals on Earth? *EPSL* 250: 116-133.
- 423 41. Bradley DC (2011) Secular trends in the geologic record and the supercontinent cycle.  
424 *Earth Sci Rev* 108: 16-33.
- 425 42. Peters SE, Gaines RR (2012) Formation of the ‘Great Unconformity’ as a trigger for the  
426 Cambrian explosion. *Nature* 484: 363-366.

- 427 43. Spencer CJ et al (2014) Proterozoic onset of crustal reworking and collisional tectonics:  
428 Reappraisal of the zircon oxygen isotope record. *Geology* 42: 451-454.
- 429 44. Berner RA (2004), *The Phanerozoic Carbon Cycle: CO<sub>2</sub> and O<sub>2</sub>*, Oxford Univ. Press, New  
430 York, USA.
- 431 45. Dilek Y, Furnes H (2011) Ophiolite genesis and global tectonics: Geochemical and  
432 tectonic fingerprinting of ancient oceanic lithosphere. *GSA Bulletin* 123: 387-411.
- 433 46. Condie K (2011) *Earth as an evolving planetary system*. Elsevier Academic Press.  
434 Cambridge MA, USA.
- 435 47. Scotese CR (2001) *Atlas of Earth History. PALEOMAP project*. Arlington, TX, USA.
- 436 48. Cawood PA, Hawkesworth CJ, Dhuime B (2013) The continental record and the  
437 generation of continental crust. *GSA Bulletin* 125: 14-32.
- 438 49. Krissansen-Totton J, Buick R, Catling DC (2015) A statistical analysis of the carbon  
439 isotope record from the Archean to the Phanerozoic and implications for the rise of oxygen.  
440 *Amer J Sci* 315: 275-316.
- 441 50. Sleep NH, Zahnle K (2001) Carbon dioxide cycling and implications for climate on  
442 ancient Earth. *J Geophys Res* 106: 1373-1399.
- 443 51. Royer DL, Donnadieu Y, Park J, Kowalczyk J, Godderis Y (2014) Error analysis of CO<sub>2</sub>  
444 and O<sub>2</sub> estimates from the long-term geochemical model GEOCARBSULF. *Amer J Sci* 314:  
445 1259-1283.
- 446 52. Mills B, Watson AJ, Goldblatt C, Boyle R, Lenton TM (2011) Timing of Neoproterozoic  
447 glaciations linked to transport-limited global weathering. *Nat Geosci* 4: 861-864.
- 448 53. Li G, Elderfield H (2013) Evolution of carbon cycle over the past 100 million years.  
449 *Geochim Cosmochim Acta* 103: 11-25.
- 450 54. Lenton TM, Watson AJ (2000) Redfield Revisited: 1) Regulation of nitrate, phosphate  
451 and oxygen in the ocean. *Global Biogeochemical Cycles* 14: 225-248.

- 452 55. Hartmann J, Dürr HH, Moosdorf N, Meybeck M, Kempe S (2012) The geochemical  
453 composition of the terrestrial surface (without soils) and comparison with the upper  
454 continental crust. *Int J Earth Sci* 101(1): 365-376.
- 455 56. Caldeira K, Kasting JF (1992) The life span of the biosphere revisited. *Nature* 360: 721-  
456 723.
- 457 57. Shields GA (2007) A normalised seawater strontium isotope curve: possible implications  
458 for Neoproterozoic-Cambrian weathering rates and the further oxygenation of the Earth.  
459 *eEarth* 2: 35-42.

460

461

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469 point moving average of 1 Myr bins over the Phanerozoic (Fig. 1).

470

471

472

473 **Figure legends**

474

475 **Fig. 1.** Phanerozoic records of marine carbonate  $\delta^{13}\text{C}$  (33), seawater Sr isotope composition  
476 (33) and mass of sedimentary material (two shades correspond to measured and estimated total  
477 mass, respectively) (34). Diverse tectonic proxies identify the Ediacaran-Ordovician interval  
478 as a time of maximal uplift and erosion, but minimal  $\delta^{13}\text{C}$  (see SI).

479

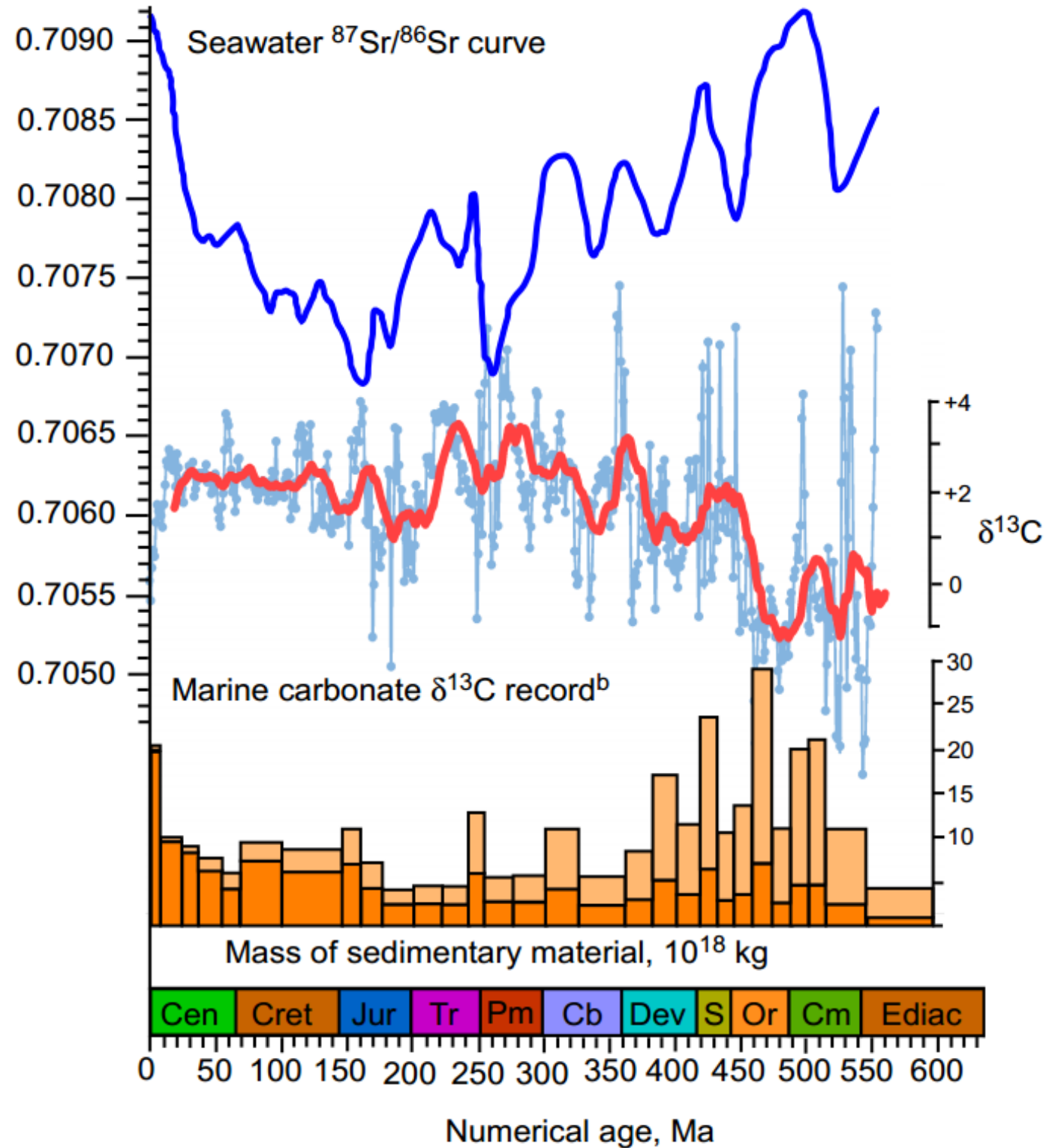
480 **Fig. 2.** Long term carbon cycle showing isotope fractionation. A is atmosphere and ocean  
481 carbon, G is buried organic carbon and C is buried carbonate carbon.  $F_b$  refers to burial fluxes,  
482  $F_w$  to weathering and  $F_m$  to metamorphic/degassing fluxes.  $\delta_x$  denotes the isotopic fractionation  
483 of reservoir X, and  $\Delta B$  is the fractionation effect applied to buried organic carbon, taken to  
484 represent an average value over the Phanerozoic (35). *Sil* and *Carb* show alkalinity fluxes from  
485 silicate and carbonate weathering, respectively, which are combined to calculate  $F_{bc}$  (see SI).  
486 Dashed lines denote the ‘null’ carbonate weathering – deposition cycle.

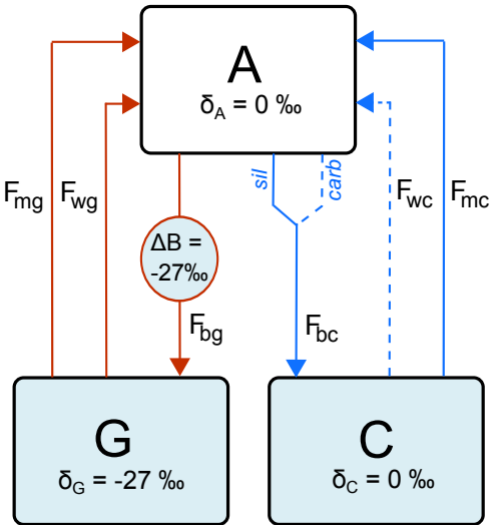
487

488 **Fig. 3.** Steady states of the long-term carbon cycle model. The system shown in Figure 2 is run  
489 to steady state for different values of the relative global uplift/erosion rate. Bold lines (M1)  
490 show results when silicate weathering delivers around 58% of ocean phosphate (29, see SI),  
491 dashed lines (M2) show results when when silicate weathering delivers only 17% of ocean  
492 phosphate (6), and dotted lines (M3) show results when all P delivery is instead from carbonate  
493 weathering. The equations governing the response of fluxes to reservoir sizes and global  
494 temperature follow current models (6, 26). See SI for full model description, MATLAB code,  
495 and further evaluation.

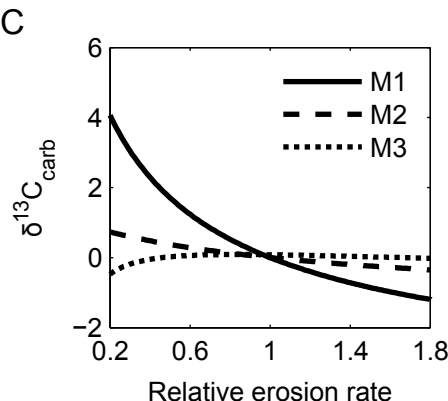
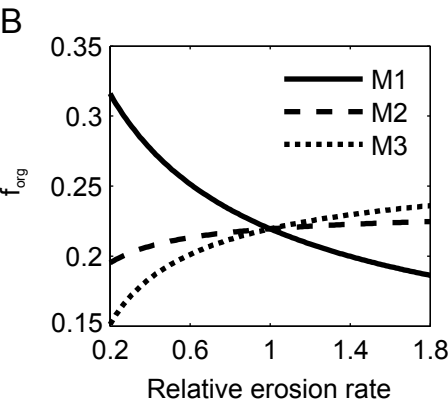
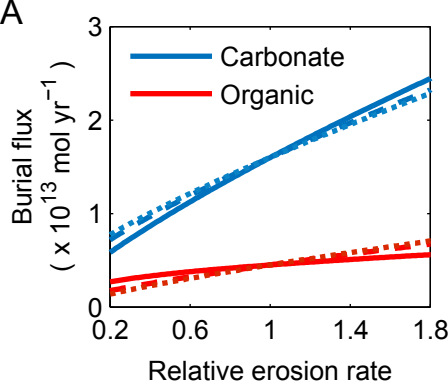
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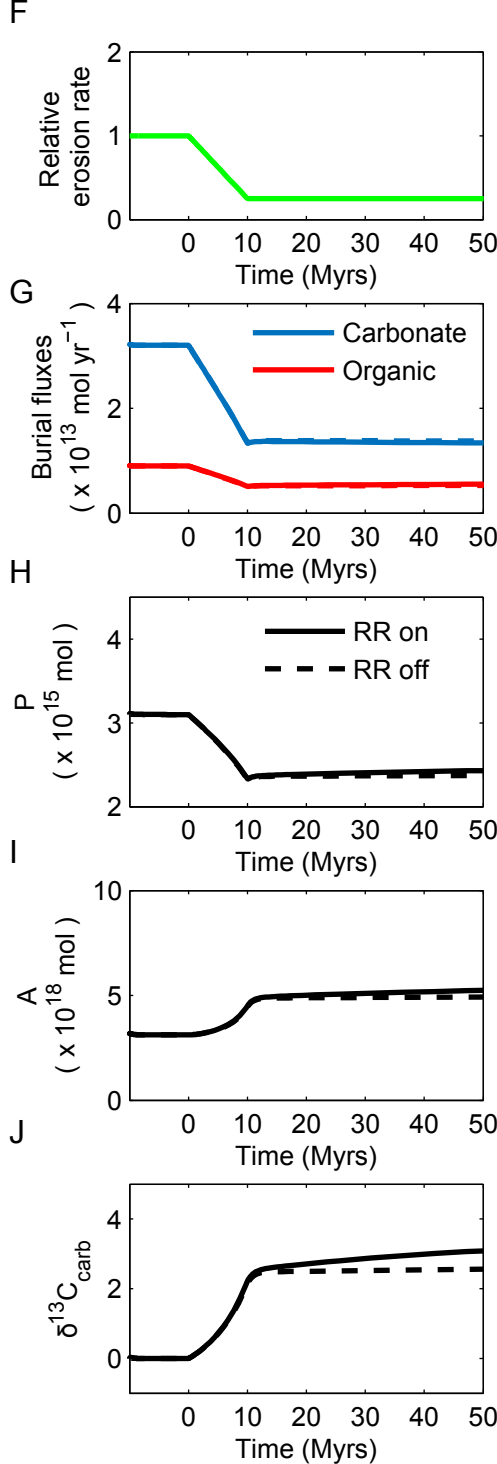
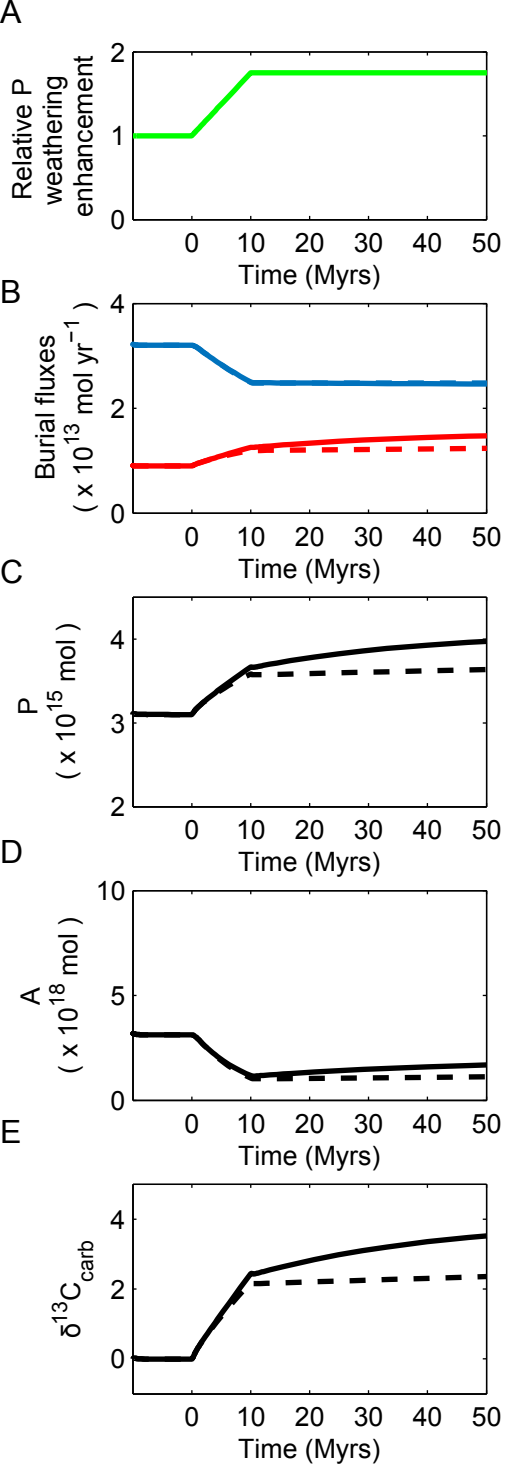
497 **Fig. 4.** Comparison of positive  $\delta^{13}\text{C}$  excursions driven by burial and erosion events. Panels  
498 show A: Relative model forcing factor. B, Burial fluxes for carbonate ( $F_{bc}$ , blue) and organic  
499 carbon ( $F_{bg}$ , red). C, Ocean phosphate. D, Atmosphere and ocean carbon. E,  $\delta^{13}\text{C}$  of  
500 atmosphere/ocean carbon reservoir. Panels F-J repeat these quantities for the second model  
501 scenario. A positive  $\delta^{13}\text{C}$  excursion is driven by increased organic carbon burial, via  
502 enhancement of phosphorus weathering (A-E), and is compared to a positive  $\delta^{13}\text{C}$  excursion  
503 driven by a change in erosion (F-J). Both forcings (green lines) are ramped over a 10 Myr  
504 period, beginning at  $t=0$ . Solid lines show rapid recycling model (RR on, see text), dashed lines  
505 show no rapid recycling. Note that the positive excursion driven by organic C burial is  
506 associated with a decrease in atmosphere/ocean carbon (panel D), whilst the excursion driven  
507 by erosion is associated with an increase in the carbon reservoir (panel I). P input from  
508 weathering follows Hartmann et al. (2014) (29). Full model output is included in the SI.











# 1 **Supporting Information**

2 SI Materials and Methods

3

## 4 **Co-variation of erosion rates and carbonate $\delta^{13}\text{C}$ .**

5 Inverse correlation between carbonate  $\delta^{13}\text{C}$  and seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios has been noted in  
6 previous studies (36-38), and similar correlations with the reconstructed rate of sediment  
7 deposition (34) and the 'relative uplift/erosion' parameter from long term carbon cycle models  
8 (5, 6) can be observed using scatter plots (Figure S1). Computing the Pearson product moment  
9 correlation coefficient (PMCC) for these datasets gives values of  $\sim -0.5$  to  $-0.4$ , and fitting a  
10 linear regression model (red lines in Figure S1) to the data results in a negative slope, with  $R^2$   
11 values between 0.17 and 0.25. Together, these tests confirm a weak but observable negative  
12 correlation in all cases. Efforts to remove the sedimentary recycling 'memory flux' from the  
13  $^{87}\text{Sr}/^{86}\text{Sr}$  record have resulted in an improved correlation with  $\delta^{13}\text{C}$  (38). We do not expect a  
14 strong correlation between erosion proxies and  $\delta^{13}\text{C}$  due in part to heterogeneities in both  
15 datasets, driven by the spatial nature of paleoenvironments, and by sampling and preservation  
16 errors. But more importantly, erosion is not the only driving force behind C isotope variation:  
17 the argument in this paper is that erosion, via the changing proportion that carbonate weathering  
18 makes of total carbon throughput, acts as a base-level control over  $\sim 100$  Myr time scales, which  
19 is supported by the correlations we show here.

20

21 Reconstructing paleo-erosion fluxes is difficult, and each method has its own caveats: Sr  
22 isotope ratios are controlled by the age and distribution of weathered material, which is  
23 undoubtedly influenced by erosion, but has other drivers. Similarly, the observed abundances  
24 of sedimentary rocks are subject to preservation and sampling bias. However, over  $\sim 100$  Myr  
25 time scales, the Wilson cycle of supercontinent formation and break-up is widely accepted to

26 have led to a prolonged period of mountain uplift during the Late Precambrian and early  
27 Paleozoic (39-42), followed by a time of supercontinent stability and low erosion rates during  
28 the late Paleozoic and Early Mesozoic (43). The relative erosion rate used to drive long-term  
29 carbon cycle models (e.g. GEOCARBSULF (5), Figure S1 B) uses a quadratic curve to  
30 represent Phanerozoic erosion, analogous to the Wilson cycle and the long-term average  
31 variation in sediment mass and Sr isotope ratios (44).

32

33 This long-term dynamic is independently evidenced by records of orogenies, collisions and  
34 paleogeographies (45-48), and has recently been elucidated by the study of zircon hafnium and  
35 oxygen isotope compositions. Zircon  $\epsilon\text{Hf}$  and  $\delta^{18}\text{O}$  values (48, 43) highlight the Ediacaran-  
36 Cambrian interval of low carbonate  $\delta^{13}\text{C}$  as a time of exceptional uplift (unroofing) of deep  
37 crustal roots and of sediment reworking, respectively, providing independent and quantitative  
38 support for the Wilson cycle dynamic (Figure S2). Consistent with this interpretation, the  
39 earlier ‘Tonian’ interval of exceptionally high  $\delta^{13}\text{C}$  (10,11) is interpreted as a time of relative  
40 tectonic quiescence (48): This peak in carbonate  $f_{\text{org}}$ , confirmed most recently by Krissansen-  
41 Totton et al. (49), occurred during the initial rifting phase of the greatly denuded supercontinent  
42 Rodinia (Fig. S2). We conclude that despite the difficulty in reconstructing variation in past  
43 erosion rates, the established long-term cyclic changes over the Phanerozoic show a marked  
44 inverse correlation with average  $\delta^{13}\text{C}$  since 500 Ma, and possibly earlier.

45

#### 46 **Net and gross fluxes in the long-term carbon cycle**

47 The representation of the long term carbon cycle, which forms the basis for isotope mass  
48 balance calculations (1, 7, 8) (ms Figure 2), considers changes in the following fluxes: carbon  
49 inputs to the surface system via oxidative weathering of fossil carbon ( $F_{wg}$ ), carbonate  
50 weathering ( $F_{wc}$ ), metamorphic degassing of sedimentary organic carbon ( $F_{mg}$ ), and degassing

51 of carbonates ( $F_{mc}$ ), and carbon outputs via burial of organic carbon ( $F_{bg}$ ) and burial of  
52 inorganic carbonates ( $F_{bc}$ ).

53 The rate of change of the reservoir of CO<sub>2</sub> in the atmosphere and ocean (A) is:

54

$$55 \quad \frac{dA}{dt} = F_{source} - F_{sink} = F_{wg} + F_{wc} + F_{mg} + F_{mc} - F_{bg} - F_{bc} \quad (1)$$

56

57 For CO<sub>2</sub> steady state,  $F_{sink}$  will be close to  $F_{source}$  and  $\frac{dA}{dt} = 0$ . Burial of carbonates ( $F_{bc}$ ) is  
58 calculated assuming marine alkalinity balance, i.e. that input from weathering of terrestrial  
59 carbonate and silicate rocks will be balanced by total carbonate deposition (19), i.e.

60

$$61 \quad F_{bc} = F_{wc} + F_{sil\ weathering} \quad (2)$$

62

63 Carbonate weathering ( $F_{wc}$ ) absorbs one CO<sub>2</sub> molecule for every CaCO<sub>3</sub> molecule dissolved,  
64 according to the following reversible reaction:

65



67

68 Calcium carbonate deposition simply reverses the effect of carbonate weathering (eq. 3) and  
69 so the carbonate weathering-precipitation cycle is a CO<sub>2</sub> neutral process on long time-scales;  
70 this is highlighted by the dashed lines in Figure 2 (see manuscript). This means that the  
71 remaining ‘net’ CO<sub>2</sub> sources must be completely balanced by the two ‘net’ carbon sinks, which  
72 are: organic carbon burial and carbonate deposition following Ca-Mg-silicate weathering.  
73 Therefore, the stability of the atmosphere and ocean carbon reservoir over geological  
74 timescales is determined by:

75

76  $\frac{dA}{dt} = (F_{wg} + F_{mg} + F_{mc}) - (F_{bg} + F_{sil\ weathering})$  (4)

77

78 The carbonate weathering flux, and the rate of carbonate deposition following carbonate  
79 weathering, are not required for the standard calculation of carbon cycle stability. But these  
80 fluxes are essential when considering changes in  $\delta^{13}\text{C}$  – the isotopic signature of carbon  
81 liberated during the weathering of carbonates is controlled by the crustal value, whilst the  
82 signature of buried carbonates reflects the value in the surface system. Therefore, these terms  
83 cannot be removed from the equation governing the change to atmosphere and ocean  $\delta^{13}\text{C}$ .

84

85 Low-temperature alteration of the ocean crust is an additional net carbon sink, with increased  
86 importance in early Earth history (50), but because it does not impart an isotopic fractionation  
87 it may be absorbed into the silicate weathering term without significantly altering our analysis.

88

89 The net carbon fluxes drive climate, but the gross fluxes (i.e. including the carbonate  
90 weathering-deposition cycle) control  $\delta^{13}\text{C}$ . Moreover, these gross fluxes may potentially have  
91 changed by an order of magnitude over the Phanerozoic (due to erosion rate changes – see  
92 manuscript) without significantly impacting our picture of the net changes in global carbon  
93 cycling and, by extension, climate. Current isotope mass balance models (5, 51) correctly base  
94 their  $\delta^{13}\text{C}$  inversion on the changing gross carbon cycle fluxes, but their analysis assumes that  
95 erosion rates do not affect the rate of carbonate weathering, and that rates of erosion over the  
96 Phanerozoic have followed a simple cubic trajectory and remained within 0.5 – 1 times the  
97 present day rate (44). Implicit in their analysis is therefore the assumption that gross carbon  
98 fluxes have remained similar to the present day, and that  $\delta^{13}\text{C}$  changes must then reflect a  
99 change in the net fluxes. For this reason, the predicted rates of organic carbon burial (and

100 oxygen release) in all previous isotope mass balance studies have closely followed the  
101 measured variations in carbonate  $\delta^{13}\text{C}$ .

102

### 103 **Carbon cycle modelling**

104 We develop a simple carbon cycle model to test the effects of changes to net and gross carbon  
105 fluxes. This model incorporates the temperature dependence of weathering rates and the  
106 recycling of crustal material, and is essentially a reduced version of the GEOCARB and  
107 COPSE models (19, 5, 6) which considers only the carbon cycle and its variation around the  
108 present day steady state. The model code is included here for use with Matlab.

109

#### 110 A) Flux calculations

111 Each flux in the model is defined by a present day rate,  $F(0)$ , and a set of multipliers that define  
112 dependence of the relative rate on other model variables. This follows the approaches used in  
113 the most common biogeochemical box models for Phanerozoic climate.

114

115 Carbonate and Silicate weathering ( $F_{wc}$  and  $F_{sil\ weathering}$ ) are assumed to have a temperature  
116 dependence as described in the GEOCARB models (19, 26, 5), with the linear functional form  
117 for relative river runoff rate approximated with an exponential (52), to avoid nonphysical  
118 negative values when temperature is very low. Dependence of weathering rates on the relative  
119 erosion rate ( $U$ ) follows (53), with a weaker dependence for silicate weathering, as observed  
120 in field studies (25). The dependence of carbonate weathering rate on the crustal carbonate  
121 inventory,  $C$ , follows the COPSE model (6). Here  $T$  is temperature in Kelvin.

122

$$123 \quad F_{wc} = F_{wc}(0) \times U^{0.9} \times \frac{C}{C(0)} \times e^{0.05(T-288)} \quad (5)$$

$$124 \quad F_{sil\ weathering} = F_{sil\ weathering}(0) \times U^{0.33} \times e^{\frac{7537.69(T-288)}{288T}} \times (e^{0.03(T-288)})^{0.65} \quad (6)$$

125

126 Weathering of organic carbon ( $F_{wg}$ ) depends on the relative uplift/erosion rate  $U$ , and on the  
127 relative abundance of organic carbon in the crust ( $G$ ). Degassing of organic carbon ( $F_{mg}$ ), and  
128 degassing of carbonates ( $F_{mc}$ ) are assumed to depend on the crustal inventories of these species,  
129 and the material subduction rate, termed  $D$ . These follow COPSE (6).

130

$$131 \quad F_{wg} = F_{wg}(0) \times U^{0.9} \times \frac{G}{G(0)} \quad (7)$$

$$132 \quad F_{mg} = F_{mg}(0) \times D \times \frac{G}{G(0)} \quad (8)$$

$$133 \quad F_{mc} = F_{mc}(0) \times D \times \frac{C}{C(0)} \quad (9)$$

134

135 Burial of organic carbon follows the COPSE model, wherein carbon burial scales with bulk  
136 sedimentation rate, which has a quadratic dependence on phosphate-limited primary  
137 production (6, 31, 54).

138

$$139 \quad F_{bg} = F_{bg}(0) \times \left( \frac{P}{P(0)} \right)^2 \quad (10)$$

140

141 Burial of carbonates follows equation (2) above.

142

#### 143 B) Phosphorus delivery and burial

144 Following the COPSE model, it is assumed that phosphorus input from weathering is related  
145 to the relative rates of silicate, carbonate and organic C weathering.

146



$$F_{Pinput} = F_{Pinput}(0) \times OB \times \left( \%sil \left( \frac{F_{sil\ weathering}}{F_{sil\ weathering}(0)} \right) + \%carb \left( \frac{F_{wc}}{F_{wc}(0)} \right) + \%org \left( \frac{F_{wg}}{F_{wg}(0)} \right) \right) \quad (11)$$

Here *%sil*, *%carb* and *%org* are the fractions of present day P weathering from each rock type. *OB* is an arbitrary enhancement of P weathering used to test increased organic C burial. Based on the size of each rock reservoir, the COPSE model assumed that *%sil* =  $\frac{2}{12}$ , *%carb* =  $\frac{5}{12}$ , *%org* =  $\frac{5}{12}$ . Hartmann et al. (29, 55) estimate P fluxes directly, and show total P release of  $\sim 2.7 \times 10^{10}$  mol/yr from silicate weathering, and  $\sim 1 \times 10^{10}$  mol/yr from carbonates. The organically-derived P flux is difficult to measure, and Compton et al. (30) give  $\sim 1.3 \times 10^{10}$  mol/yr as a maximum. The COPSE model assumes that total P delivery is  $4.35 \times 10^{10}$  mol/yr, which would indicate organic P input of  $0.65 \times 10^{10}$  mol/yr, when taking silicate and carbonate weathering into account. For this work we set organic P delivery at  $1 \times 10^{10}$  mol/yr, as a compromise between these estimates. This gives a total P input of  $4.7 \times 10^{10}$  mol/yr, and sets *%sil* = 0.58, *%carb* = 0.21, *%org* = 0.21. We test the model using both these newly-derived P fluxes and the original COPSE input fractions.

The COPSE model calculates P burial via organic, calcium-bound and iron-sorbed forms. 86% of the combined burial flux is through the organic and Ca-bound routes, which are both linked linearly to organic C burial (6). The Fe-bound P burial flux has a complex relationship to ocean anoxia, which is difficult to represent in a non-dimensional model and is beyond the scope of the current study, we therefore simplify the burial function to be a single term, dependent on organic C burial rate.

$$F_{poutput} = F_{poutput}(0) \times \left( \frac{F_{bg}}{F_{bg}(0)} \right) \quad (12)$$

169 The organic C burial and P cycling in the model is a simplified system based on the dynamics  
 170 of the marine system, but intended to represent the biosphere as a whole. The qualitative  
 171 relationship between total P weathering and organic C burial over long timescales is not altered  
 172 by the evolving land biosphere (6), but additional complexities and feedbacks may affect the  
 173 quantitative dynamics – potentially resulting in the strengthening or weakening of the  
 174 relationship between erosion and  $\delta^{13}\text{C}$  values at different points in Earth history.

175

### 176 C) Reservoir calculations

177 Total atmosphere and ocean carbon,  $A$ , is calculated following equation (1). The crustal  
 178 reservoirs of oxidised carbonate ( $C$ ) and reduced organic carbon ( $G$ ) are calculated by summing  
 179 their respective sources and sinks.

$$180 \quad \frac{dA}{dt} = F_{wg} + F_{wc} + F_{mg} + F_{mc} - F_{bg} - F_{bc} \quad (13)$$

$$181 \quad \frac{dG}{dt} = F_{bg} - F_{wg} - F_{mg} \quad (14)$$

$$182 \quad \frac{dC}{dt} = F_{bc} - F_{wc} - F_{mc} \quad (15)$$

$$183 \quad \frac{dP}{dt} = F_{pinput} - F_{poutput} \quad (16)$$

184

185 In order to track the isotope composition of each reservoir ( $\delta R$ , its  $\delta^{13}\text{C}$  value), the quantity  
 186  $R \times \delta R$  is calculated for each reservoir  $R$ .  $\delta^{13}\text{C}$  is then calculated by dividing the  $R \times \delta R$  value  
 187 by the size of the reservoir.

188

$$189 \quad \frac{d(A\delta A)}{dt} = F_{wg} \times \delta G + F_{wc} \times \delta C + F_{mg} \times \delta G + F_{mc} \times \delta C$$

$$190 \quad -F_{bg} \times (\delta A - \Delta B) - F_{bc} \times \delta A \quad (17)$$

$$191 \quad \frac{d(G \times \delta G)}{dt} = F_{bg} \times (\delta A - \Delta B) - F_{wg} \times \delta G - F_{mg} \times \delta G \quad (18)$$

$$192 \quad \frac{d(C \times \delta C)}{dt} = F_{bc} \times \delta A - F_{wc} \times \delta C - F_{mc} \times \delta C \quad (19)$$

193

194 The above equations show the importance of changes in carbonate weathering for calculation  
 195 of  $\delta^{13}\text{C}$  values: although the identity  $F_{bc} = F_{wc} + F_{sil\ weathering}$  can be used to cancel out  $F_{wc}$   
 196 in equation (11), the same cannot be applied to equation (14) due to the difference in isotopic  
 197 compositions.

198

#### 199 D) Parameter values and rapid recycling

200 Size of reservoirs at present day follows GEOCARB (19, 5) and COPSE (6), considering  
 201 only the ‘young’ rock reservoirs for  $C$  and  $G$ , which constitute the vast majority of interaction  
 202 with the surface system, and are approximately 10% of the total carbon inventory. This setup  
 203 mimics the ‘rapid recycling’ model of (7), which is applied in current GEOCARB modelling  
 204 (51). In rapid recycling, the larger, ancient rock reservoirs are assumed to remain constant in  
 205 size, and are therefore omitted from the analysis. The key feature of rapid recycling is that  
 206 isotopic signatures recorded in young sediments are more quickly recycled to the surface  
 207 system through weathering. Therefore, atmosphere/ocean  $\delta^{13}\text{C}$  responds more quickly to  
 208 changes in carbon fluxes (see manuscript figure 4), but eventually reaches the same steady  
 209 state. Rapid recycling is removed from the model by increasing the sizes of the modelled  
 210 crustal organic carbon ( $G$ ) and carbonate carbon ( $C$ ) pools by a factor of 10, to represent the  
 211 entire reservoir. i.e. replacing equation 21 and 22 with 21\* and 22\*.

$$212 \quad A(0) = 3.193 \times 10^{18} \text{ mol} \quad (20)$$

$$213 \quad G(0) = 1.25 \times 10^{20} \text{ mol} \quad (\text{rapid recycling}) \quad (21)$$

$$214 \quad C(0) = 5 \times 10^{20} \text{ mol} \quad (\text{rapid recycling}) \quad (22)$$

$$215 \quad G(0) = 1.25 \times 10^{21} \text{ mol} \quad (\text{no rapid recycling}) \quad (21^*)$$

$$216 \quad C(0) = 5 \times 10^{21} \text{ mol} \quad (\text{no rapid recycling}) \quad (22^*)$$

217  $P(0) = 3.1 \times 10^{15} \text{ mol P}$  (23)

218  $\delta A(0) = 0 \text{ ‰}$  (24)

219  $\delta G(0) = -27 \text{ ‰}$  (25)

220  $\delta C(0) = 0 \text{ ‰}$  (26)

221

222 The magnitude of present day carbon fluxes is taken from an assessment of the current  
223 literature, taking average values (see manuscript).

224

225  $F_{bg}(0) = 9 \times 10^{12} \text{ mol yr}^{-1}$  (27)

226  $F_{wg}(0) = 7.75 \times 10^{12} \text{ mol yr}^{-1}$  (28)

227  $F_{mg}(0) = 1.25 \times 10^{12} \text{ mol yr}^{-1}$  (29)

228  $F_{wc}(0) = 24 \times 10^{12} \text{ mol yr}^{-1}$  (30)

229  $F_{mc}(0) = 8 \times 10^{12} \text{ mol yr}^{-1}$  (31)

230  $F_{sil\ weathering}(0) = 8 \times 10^{12} \text{ mol yr}^{-1}$  (32)

231 P outputs are assumed to equal inputs at the present day (pre-industrial).

232  $F_{pinput}(0) = 4.7 \times 10^{10} \text{ mol yr}^{-1}$  (33)

233  $F_{poutput}(0) = 4.7 \times 10^{10} \text{ mol yr}^{-1}$  (34)

234

235 E) Temperature approximation

236 The CO<sub>2</sub> and temperature approximation follows (56), as in the COPSE model (6). This  
237 calculation takes into account the solar insolation (fixed here), atmospheric pCO<sub>2</sub>, and a  
238 dynamic albedo function. A small correction, *tempcorrect*, is made to give T(0)=288K, as in  
239 COPSE, and average surface temperature is calculated from the black body equation, where  $\sigma$   
240 is the Stefan-Boltzmann constant.

241

242  $pCO_2 = \frac{A}{A(0)} \times 280 \times 10^{-6}$  (35)

243  $SOLAR = 1368 \text{ W m}^{-2}$  (36)

244  $ALBEDO = 1.4891 - 0.0065979 \times T + (8.567 \times 10^{-6})T^2$  (37)

245  $tempcorrect = 0.194$  (38)

246  $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$  (39)

248  $T_{CO_2} = 815.17 + (4.895 \times 10^7)T^{-2} - (3.9787 \times 10^5)T^{-1}$   
 249  $-6.7084(\log(CO_2atm))^{-2} + 73.221(\log(CO_2atm))^{-1}$   
 247  $-30882T^{-1}(\log(CO_2atm))^{-1}$  (40)

250  $T = \left( \frac{SOLAR(1-ALBEDO)}{4\sigma} \right)^{1/4} + T_{CO_2} + tempcorrect$  (41)

251

252 F) Model code

253 The attached model code consists of two Matlab scripts: solver.m and equations.m. To run the  
 254 model, run the solver script in Matlab. Modifications to the model may require alteration of  
 255 either script, but the scenarios explored in this paper require only modification of the solver  
 256 script. A ‘user panel’ is defined at the beginning of the solver script, containing all of the values  
 257 that must be changed to create the output for this work. Output figures are generated  
 258 automatically but these and any workspace data must be saved manually if required. The model  
 259 uses the Matlab ODE solver suite for ‘stiff’ systems (ODE15s).

260

261 **Full model output**

262 Figures S3 to S6 show complete model output for the scenarios explored in the manuscript.  
 263 Figures S3 shows the full model output for ms Figure 3. Figure S4 shows the sensitivity to  
 264 rapid recycling, under the Hartmann et al. (29) P inputs. Figure S5 shows the full model output  
 265 for ms Figure 4 (A-D): Carbon isotope excursion driven by an organic C burial event. Figure

266 S6 shows the full model output for ms Figure 4 (E-H): Carbon isotope excursion driven by an  
267 erosion rate change.

268

269 A) Effect of an additional direct link between global erosion rates and organic carbon  
270 burial.

271 Whilst sedimentation rates (and therefore organic C burial rates) appear to correlate with  
272 primary production (31), it is possible that a global increase in erosion rates may enhance  
273 organic carbon burial by a greater factor than is considered in our model through additional  
274 preservation effects (5). We explore this idea by giving the rate of organic C burial an additional  
275 direct dependence on the global uplift/erosion rate in figure S4. Aside from the concentration  
276 of ocean phosphate (shown in magenta), the steady state results are unchanged and plot over  
277 the original model runs. This is because increased preservation of organic carbon results in an  
278 increased phosphate sink, which is self-limiting. The organic C burial rate in our model adjusts  
279 so that the amount of phosphate buried is equal to the phosphate input, which is unchanged in  
280 the new scenario.

281 This discussion is by no means complete, and the drivers of organic C burial rates at the global  
282 scale remain complex and incompletely understood. But as we note in the manuscript, a strong  
283 link between the global erosion rate and the rate of organic C burial is effectively falsified by  
284 the anti-correlation between carbonate  $\delta^{13}\text{C}$  and erosion/sedimentation proxies.

285

286 B) Effect of fixing the  $\delta^{13}\text{C}$  value of carbon inputs.

287 Figure S7 shows the same scenario as figure S6, but with the isotopic value of carbon inputs  
288 ( $\delta^{13}\text{C}_{\text{in}}$ ) fixed at -6‰. Under this assumption (red lines), the response of  $\delta^{13}\text{C}_{\text{carb}}$  to the reduction  
289 in erosion rate is reduced by around 1‰, but is qualitatively similar. This confirms that the  
290 mechanism we describe in the manuscript does not rely on changes in the  $\delta^{13}\text{C}$  value of carbon

291 inputs, although these changes do contribute to the values of  $\delta^{13}\text{C}_{\text{carb}}$  predicted by our model.  
292  $\delta^{13}\text{C}_{\text{in}}$  is affected both by the changes to carbonate and organic carbon weathering fluxes  
293 brought about by erosion rate changes, and by the changing isotopic composition of the crustal  
294 carbon reservoirs themselves.

## Figure legends

295

296

297 **Fig. S1.** Correlations between carbonate  $\delta^{13}\text{C}$  and rates of sediment deposition (A),  
298 erosion/uplift parameter used in long term models (B) and  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater. The  $\delta^{13}\text{C}$   
299 data follows (33), and is averaged over the bins used in the study of (34) for panel A, and  
300 over 10 Myr bins for panels B and C.

301 **Fig. S2.** Secular trends in key isotopic parameters in zircons and marine carbonates (57, 48,  
302 43). Magmatic zircon abundances reveal when five supercontinents formed through  
303 orogenic collision (grey shading above), leading to greatly increased reworking of sediment  
304 during magmatism (red arrows mark resultant increases in zircon  $\delta^{18}\text{O}$ ). The zircon Hf and  
305 seawater Sr isotope records anti-correlate, confirming that the Ediacaran-Ordovician  
306 interval was a time of exceptional erosional unroofing of crustal roots (48). The  $\delta^{13}\text{C}$  ( $f_{\text{org}}$ )  
307 minimum at  $\sim 500$  Ma (49), shown as a dashed green line, occurred during the peak in  
308 Gondwanan orogenesis.  $\delta^{13}\text{C}$  ( $f_{\text{org}}$ ) maxima (49), shown as dashed red lines, coincide with  
309 the existence of Pangea and Rodinia, respectively, before onset of break-up.

310 **Fig. S3.** Full model output for ms figure 3 showing steady states for changes in the relative  
311 uplift rate. Organic carbon reservoirs and fluxes are coloured red and carbonate reservoirs  
312 and fluxes are coloured blue. 'deltaA' denotes the isotopic composition of reservoir A (‰  
313 relative to PDB). As in the manuscript, M1 shows P input ratios derived from (29), M2 shows  
314 ratios from COPSE and M3 assumes that P weathering follows the same relationships to  
315 uplift and temperature as carbonate weathering.

316 **Fig. S4.** Full model output for ms figure 3 showing steady states for changes in the relative  
317 uplift rate. This figure shows effect of rapid recycling on steady states: solid lines show RR



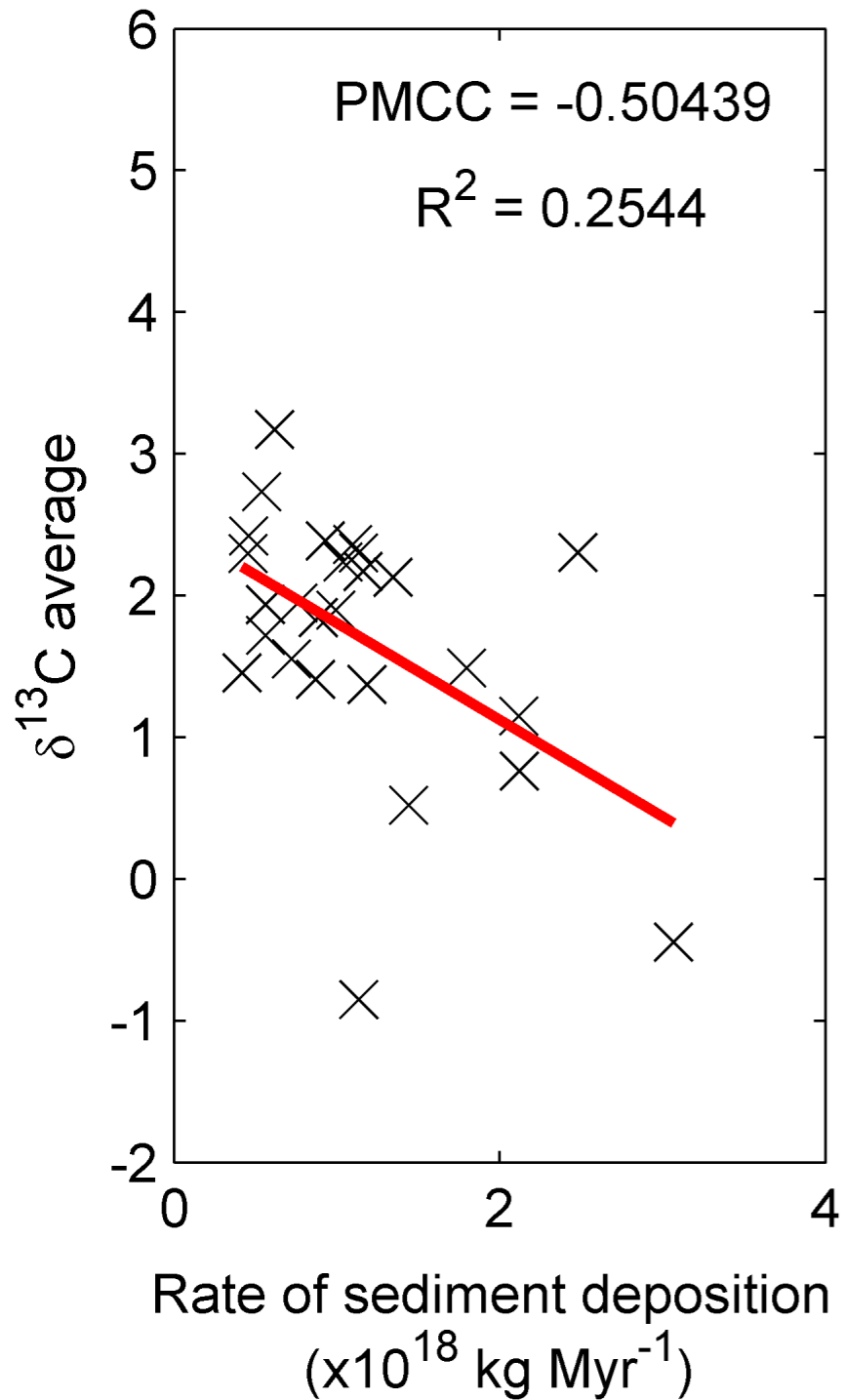
318 on, fainter lines show RR off. Note that surface reservoir steady states are unchanged, but  
319 crustal reservoirs now show larger bulk values instead of 'young' values. The figure also  
320 shows a scenario in which the rate of organic carbon burial has an additional linear  
321 dependency on the relative uplift/erosion rate. This changes only the values for ocean  
322 phosphate (shown in magenta).

323 **Fig. S5.** Full model output for ms figure 4 A-D (case 1) showing system response over time to  
324 an increase in organic C burial rate. Organic carbon reservoirs and fluxes are coloured red  
325 and carbonate reservoirs and fluxes are coloured blue. 'deltaA' denotes the isotopic  
326 composition of reservoir A (‰ relative to PDB). Green lines show forcing functions for uplift  
327 and relative P weathering enhancement.

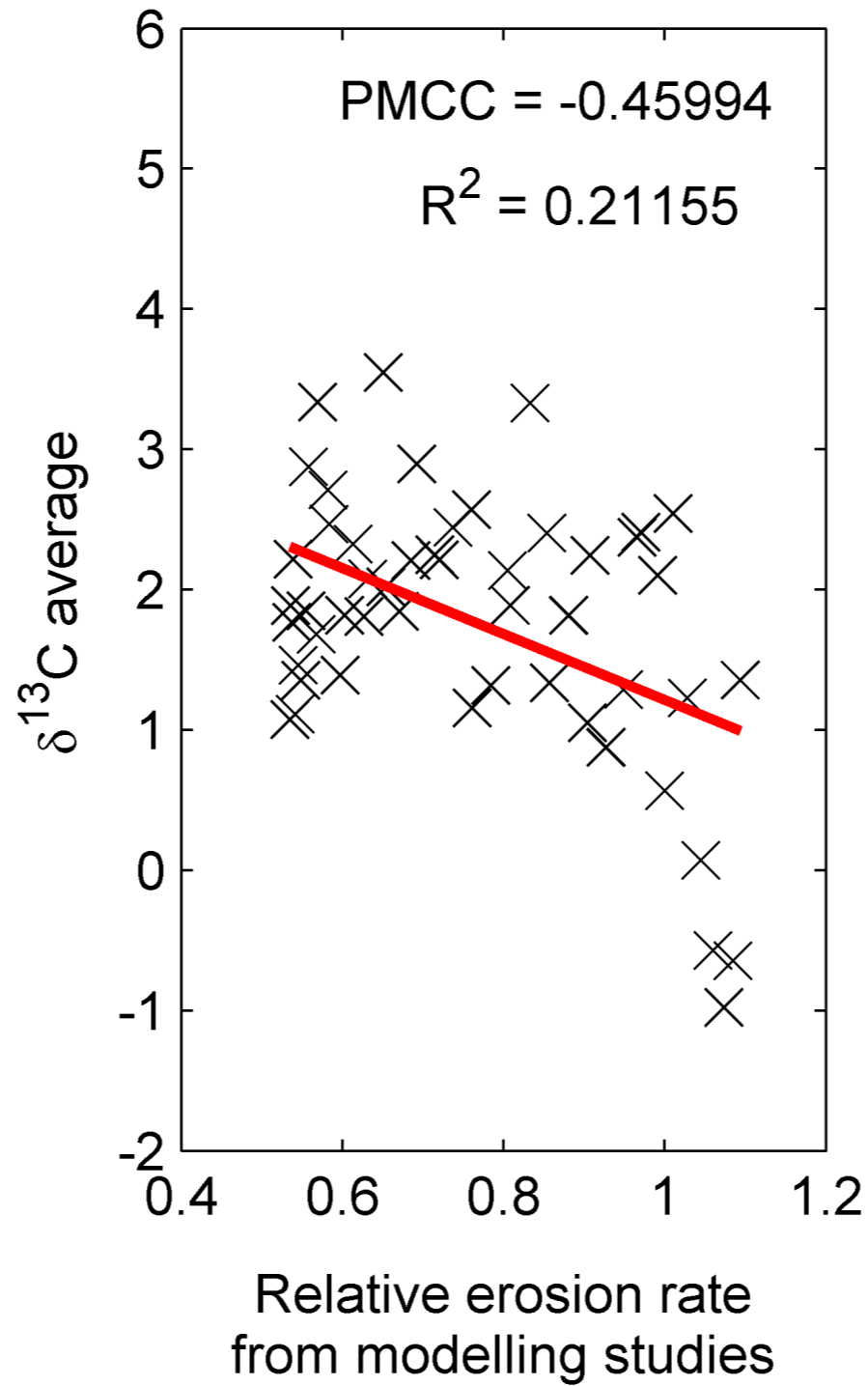
328 **Fig. S6.** Full model output for ms figure 4 E-H (case 2) showing system response over time to  
329 a decrease in the uplift/erosion rate. Organic carbon reservoirs and fluxes are coloured red  
330 and carbonate reservoirs and fluxes are coloured blue. 'deltaA' denotes the isotopic  
331 composition of reservoir A (‰ relative to PDB). Green lines show forcing functions for uplift  
332 and relative P weathering enhancement.

333 **Fig. S7.** Additional model output for ms figure 4 E-H (case 2) showing system response over  
334 time to a decrease in the uplift/erosion rate when the  $\delta^{13}\text{C}$  value of carbon inputs is fixed at  
335  $-6\text{‰}$  (red lines), compared to full model (black lines).

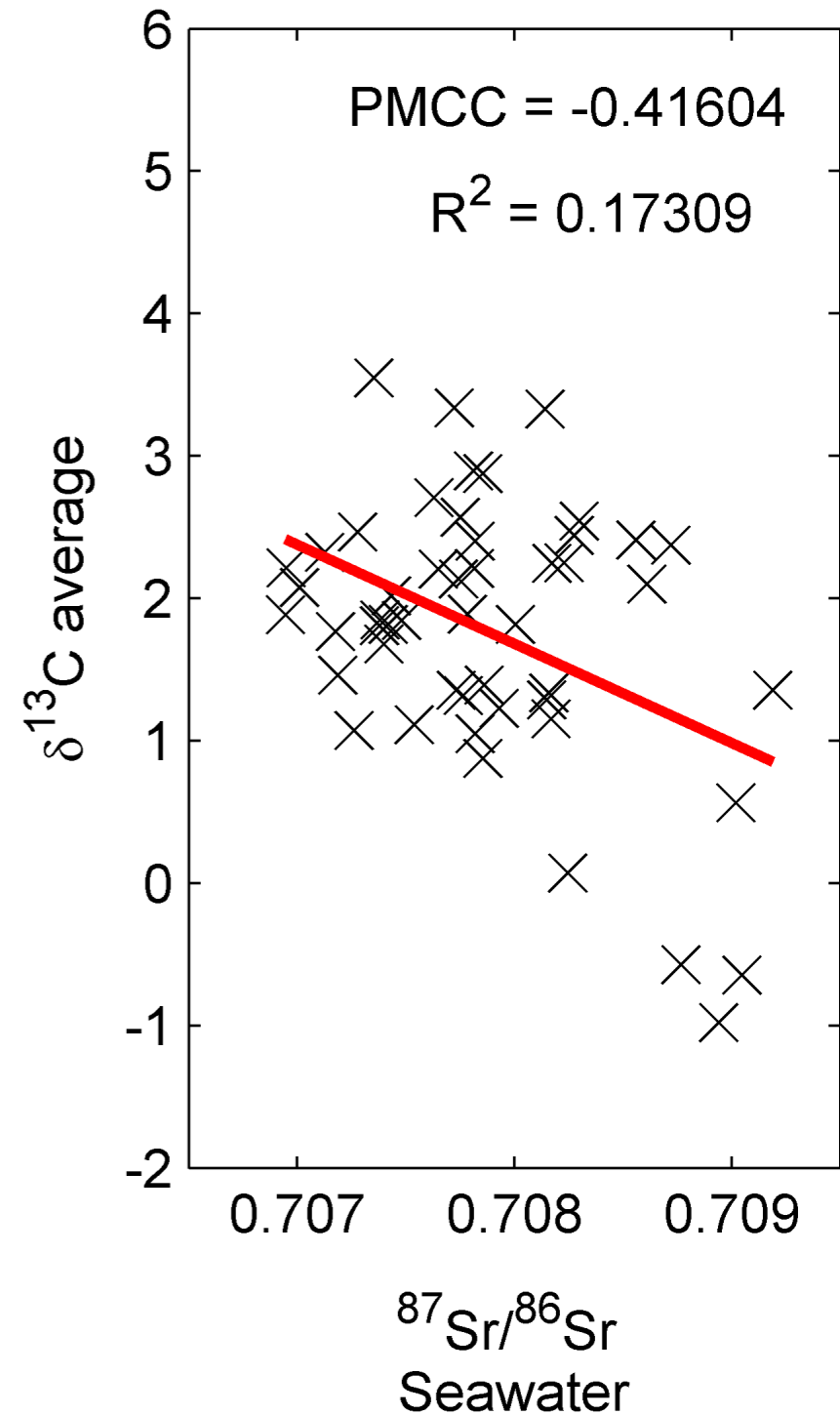
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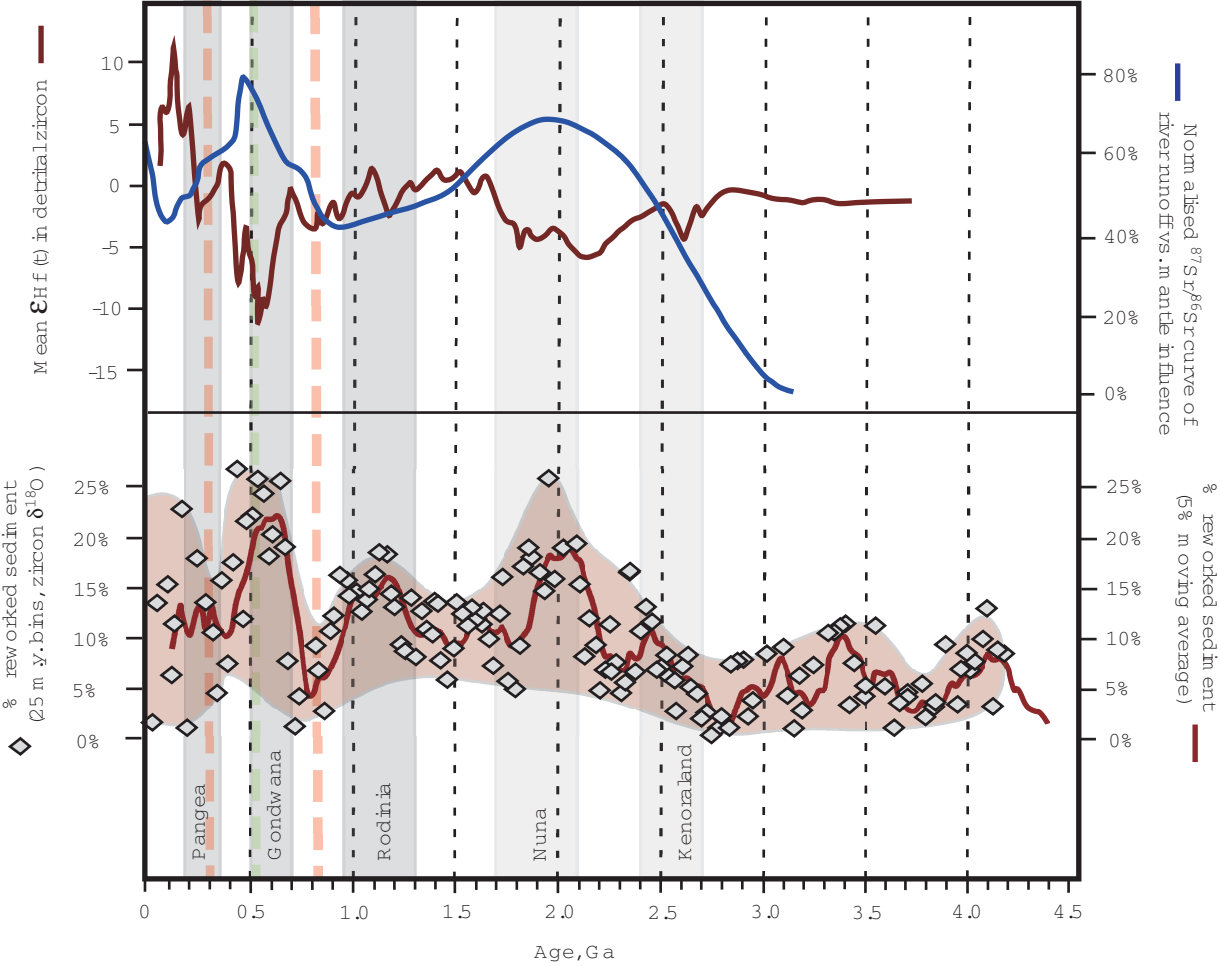


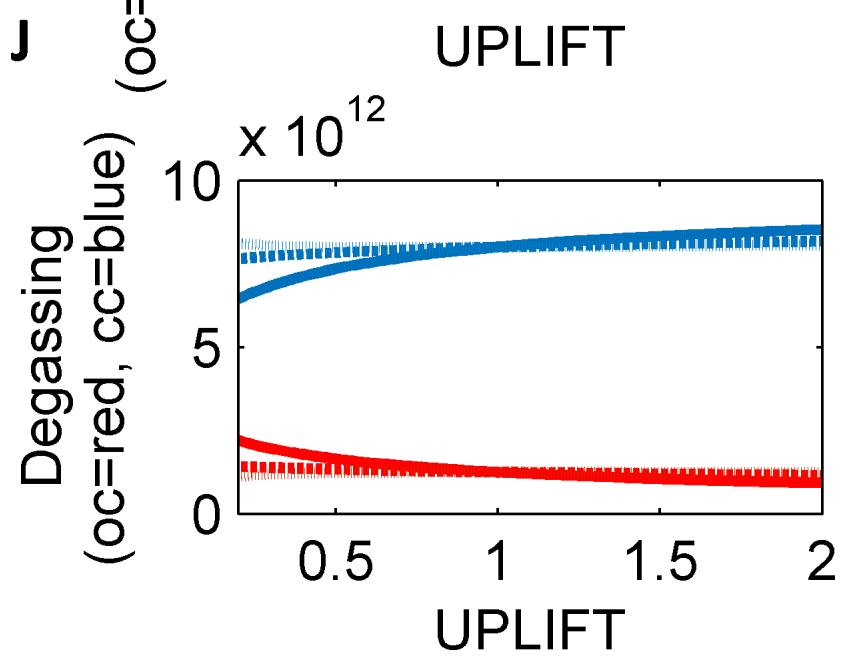
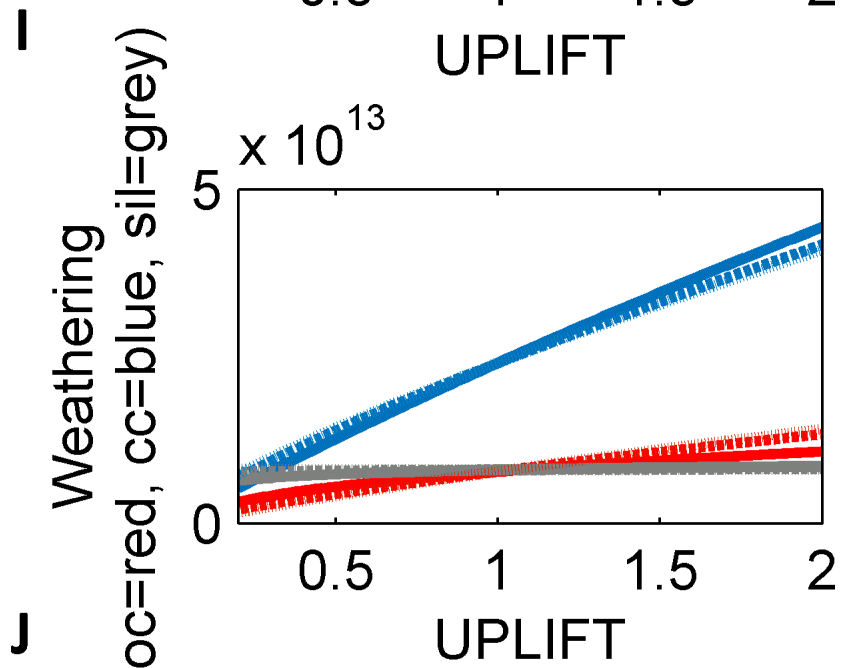
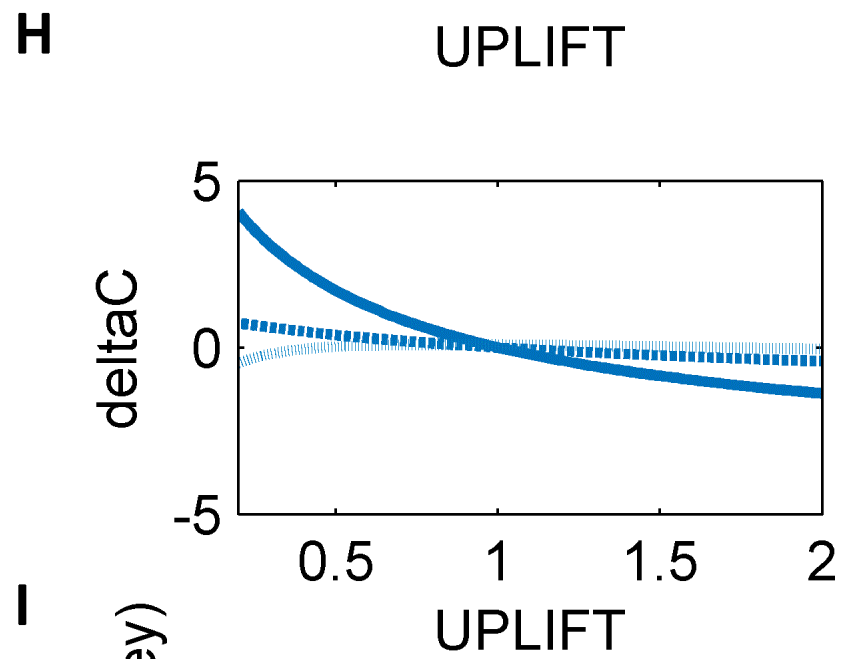
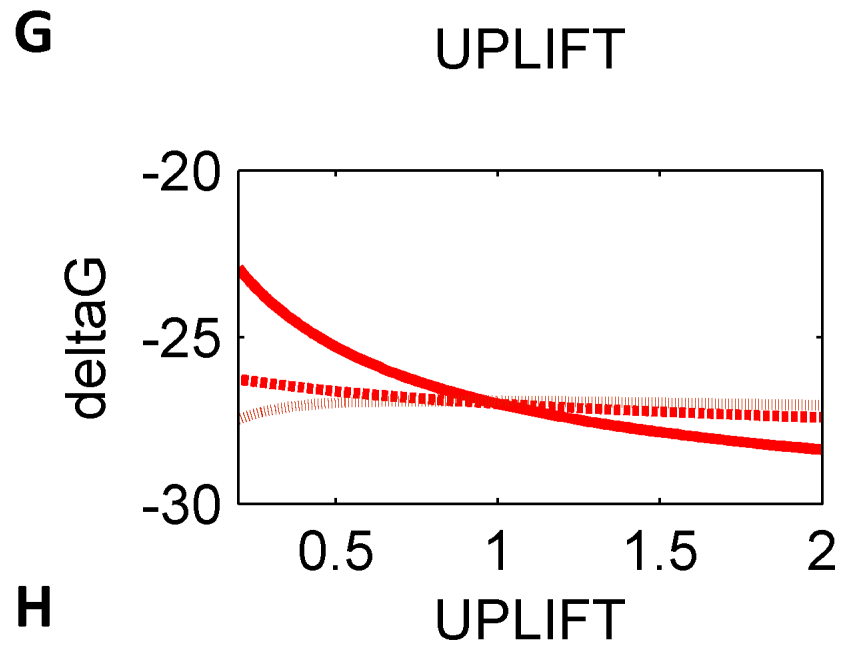
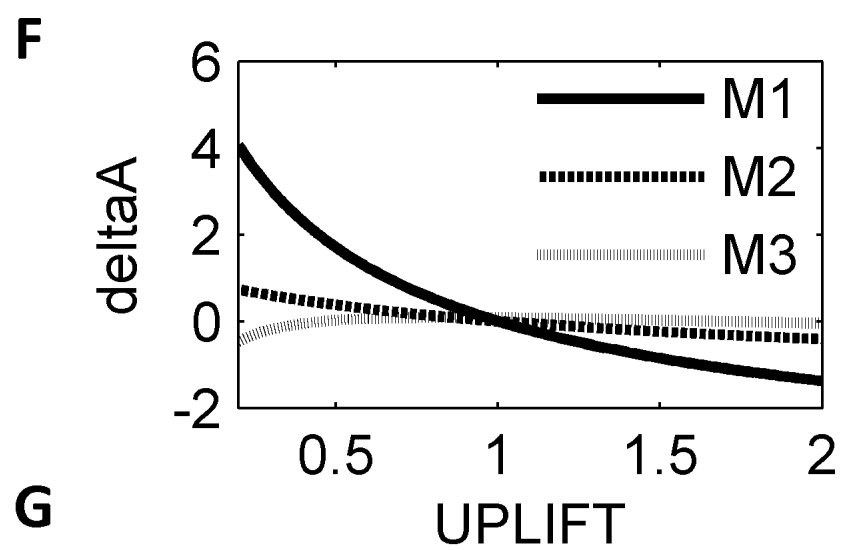
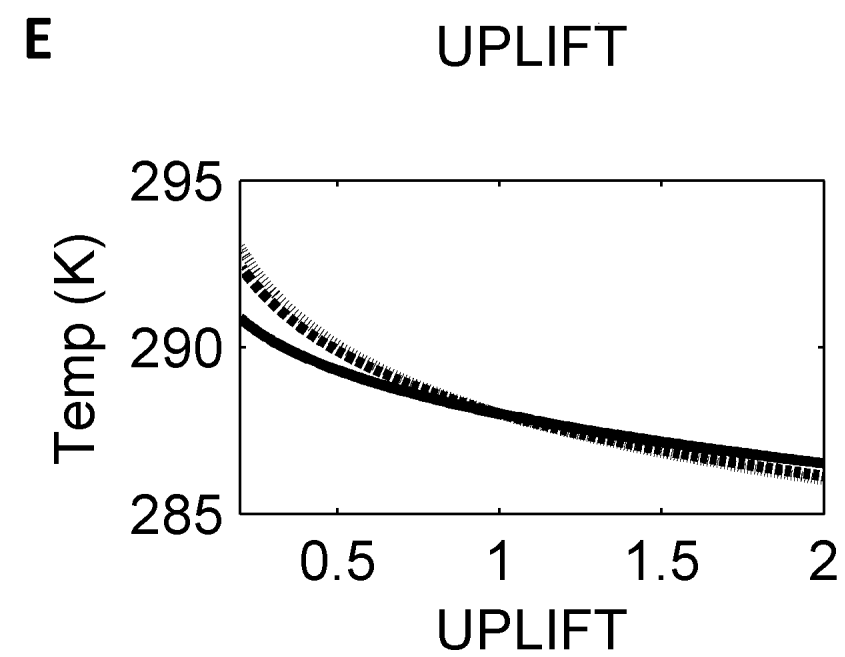
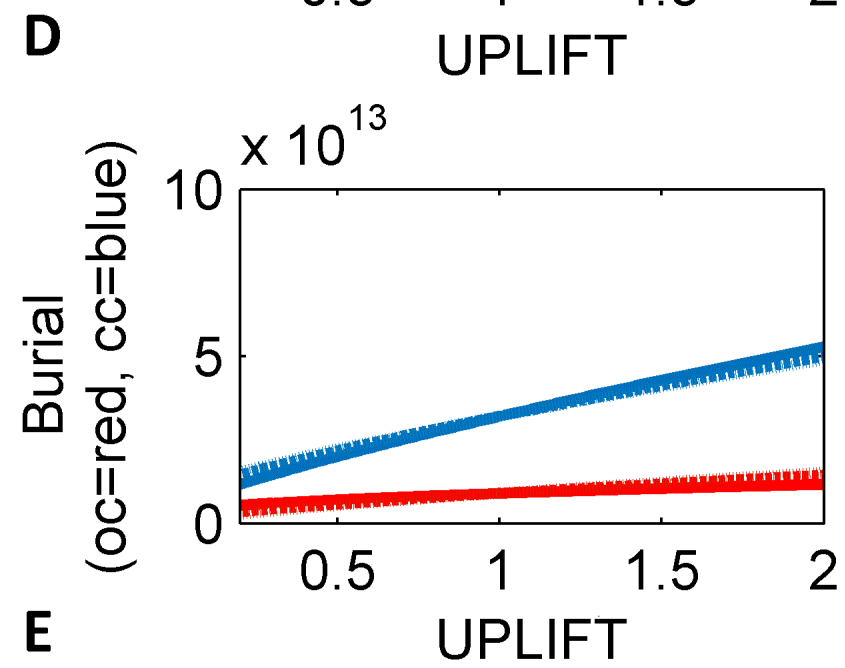
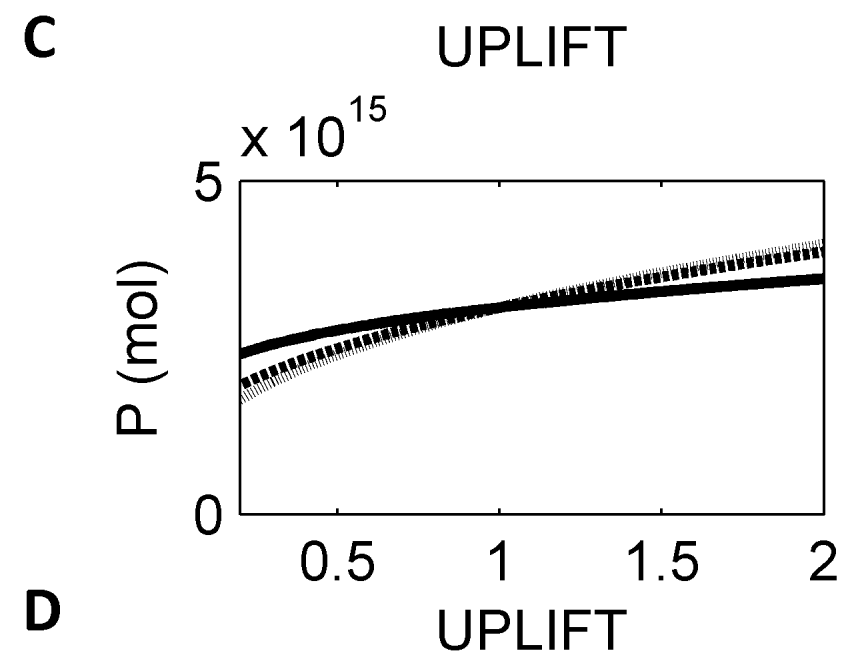
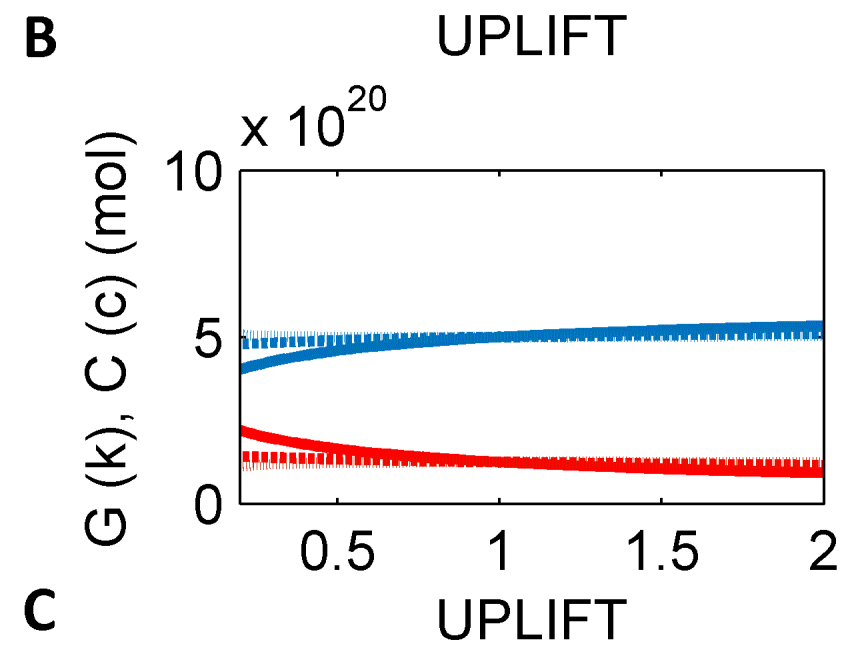
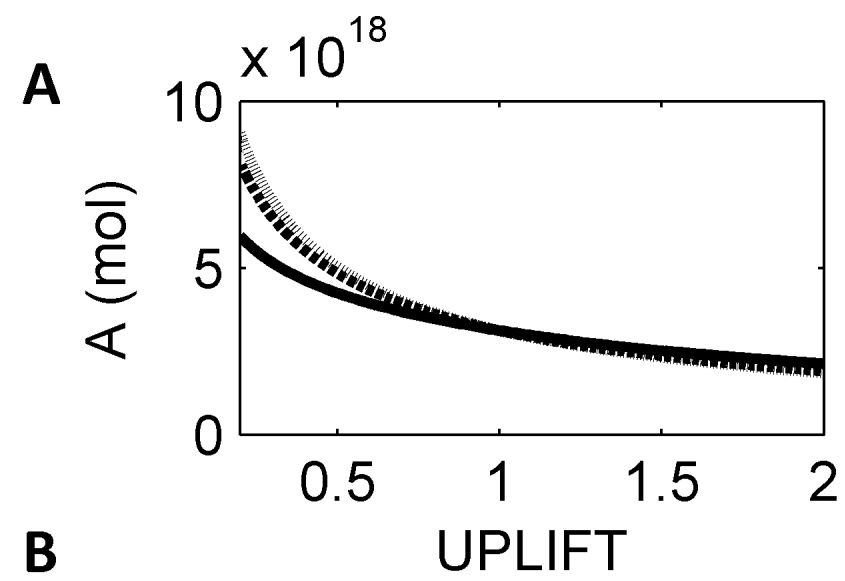
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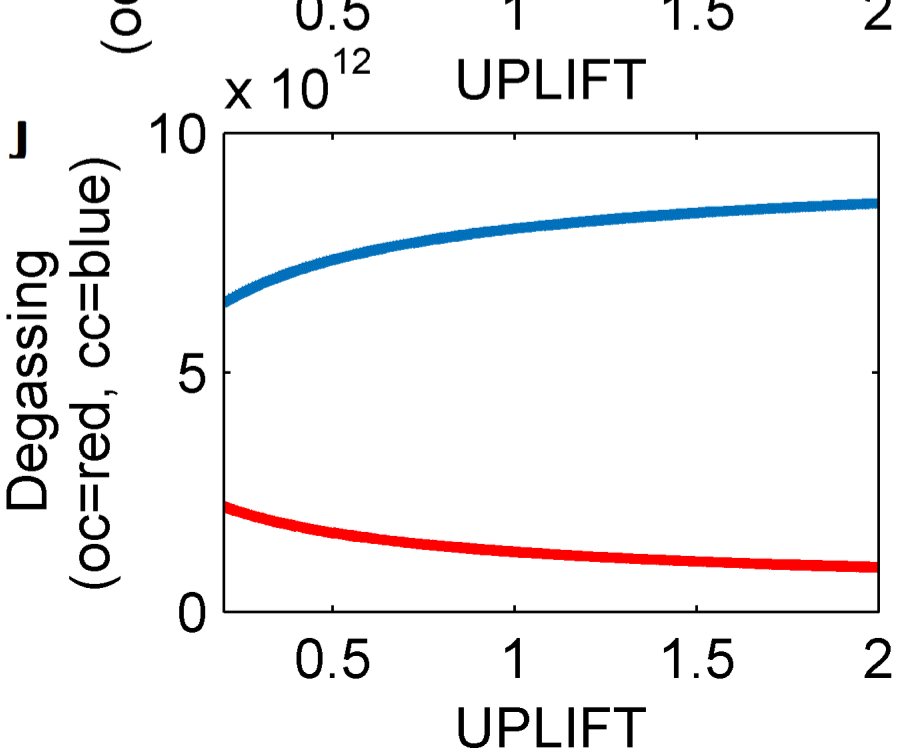
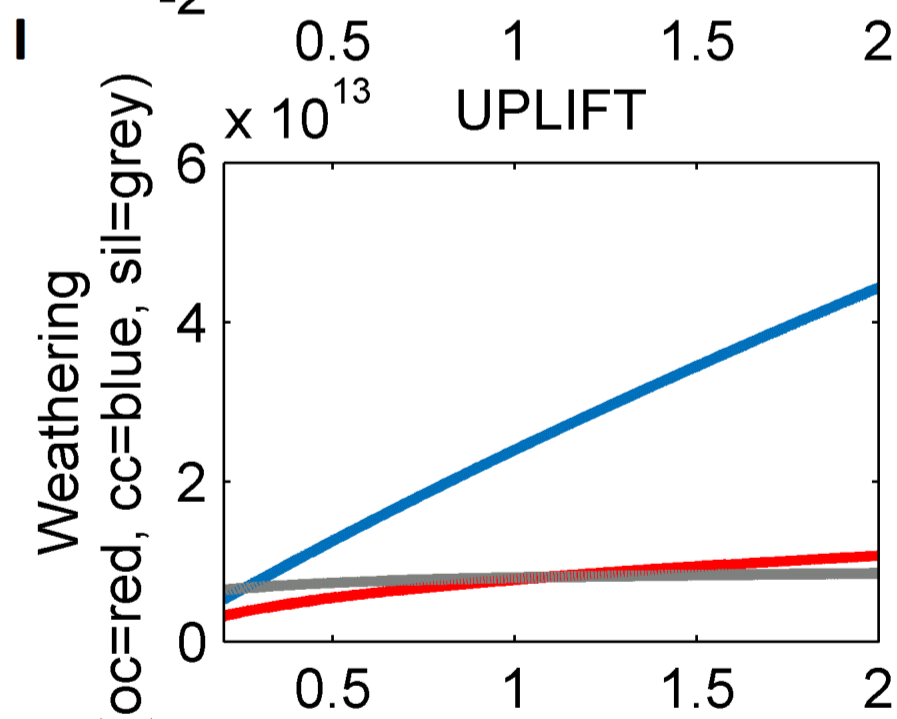
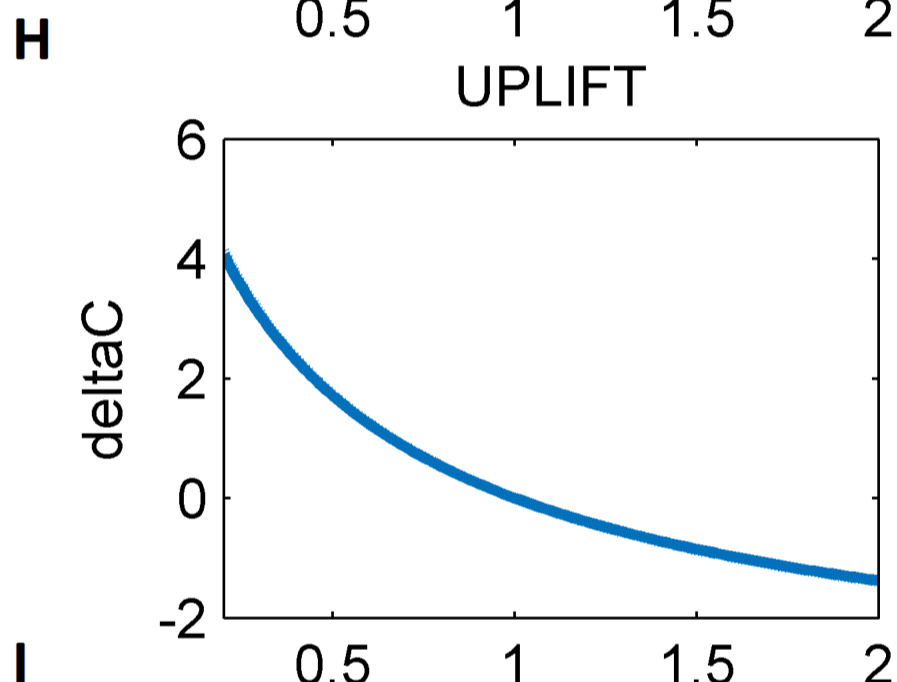
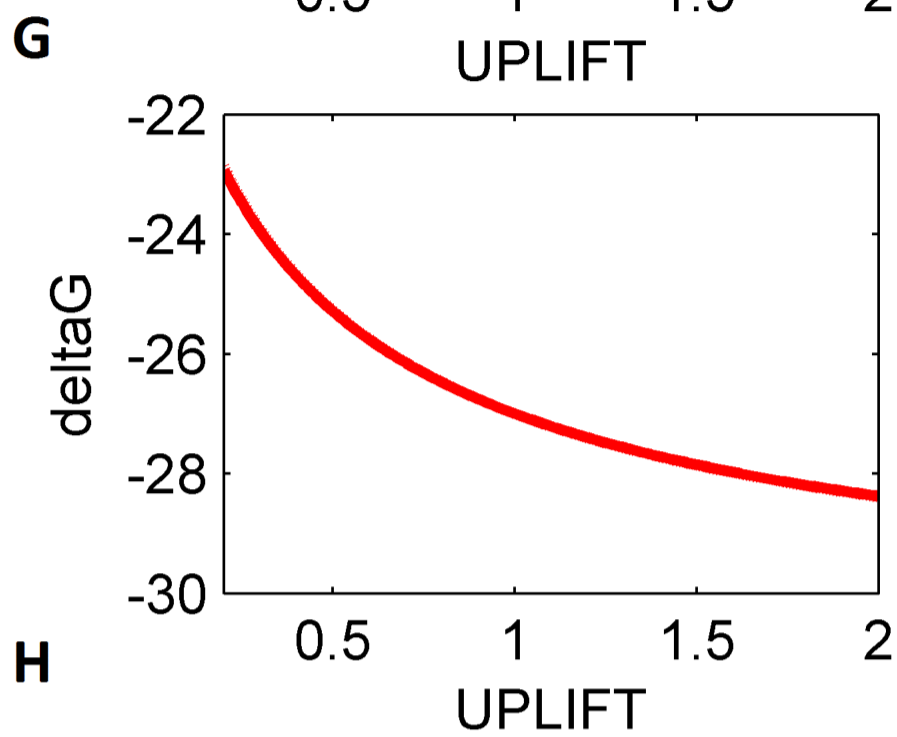
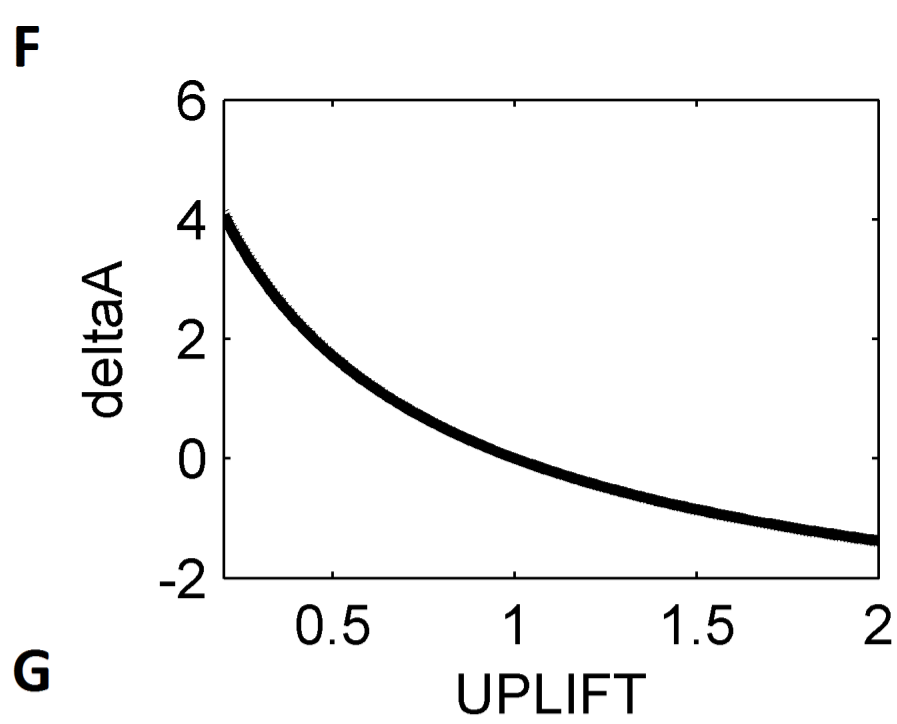
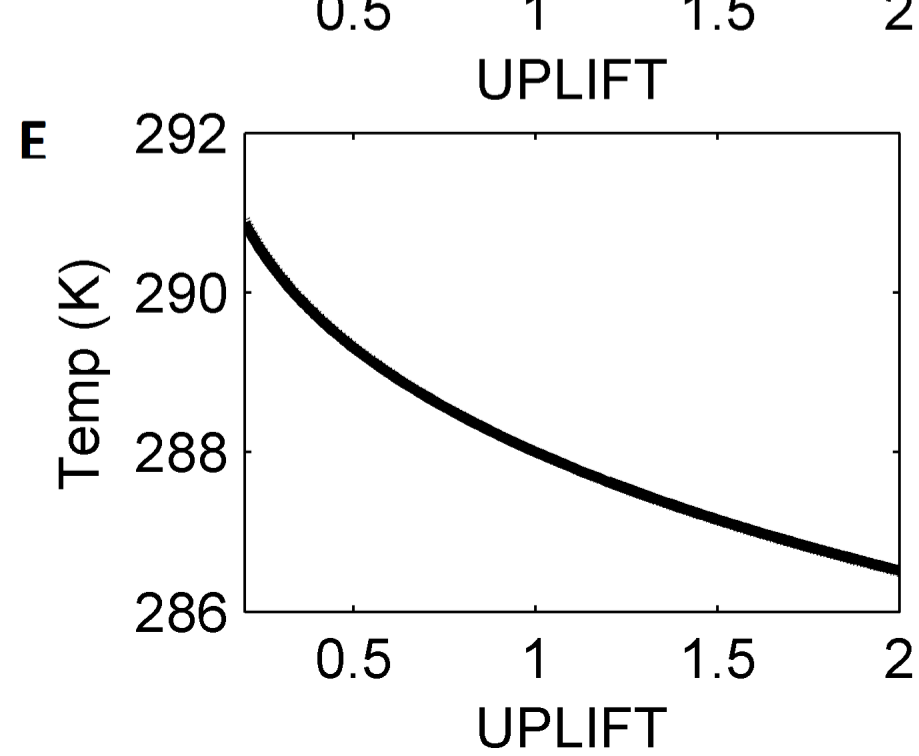
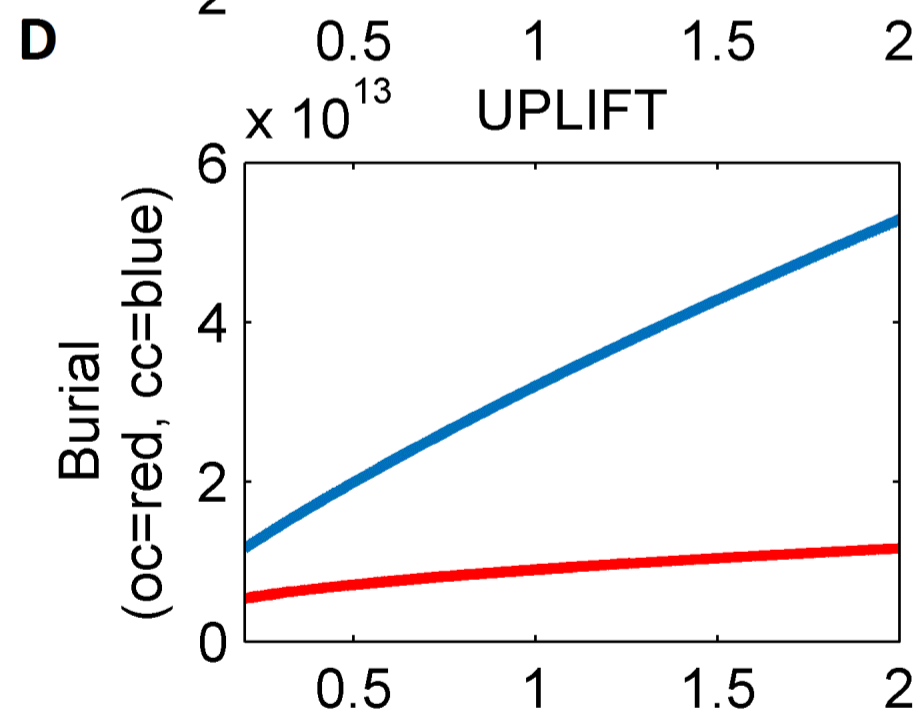
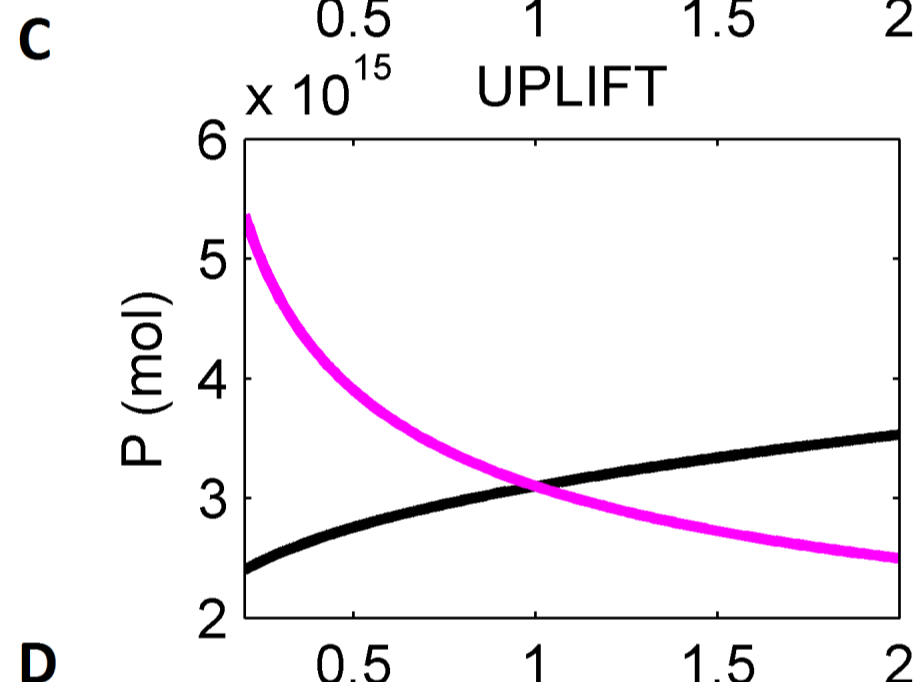
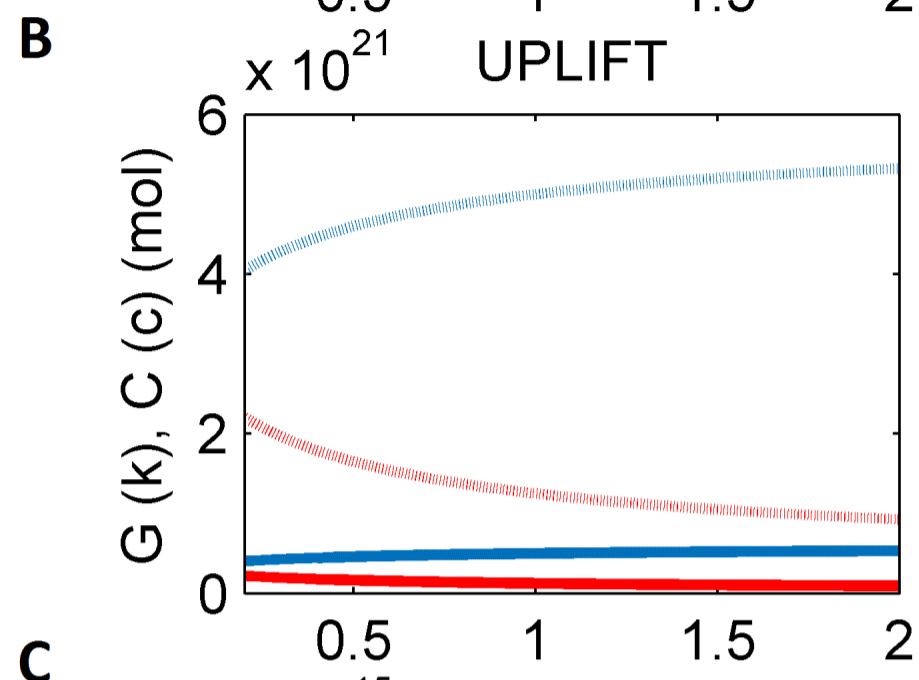
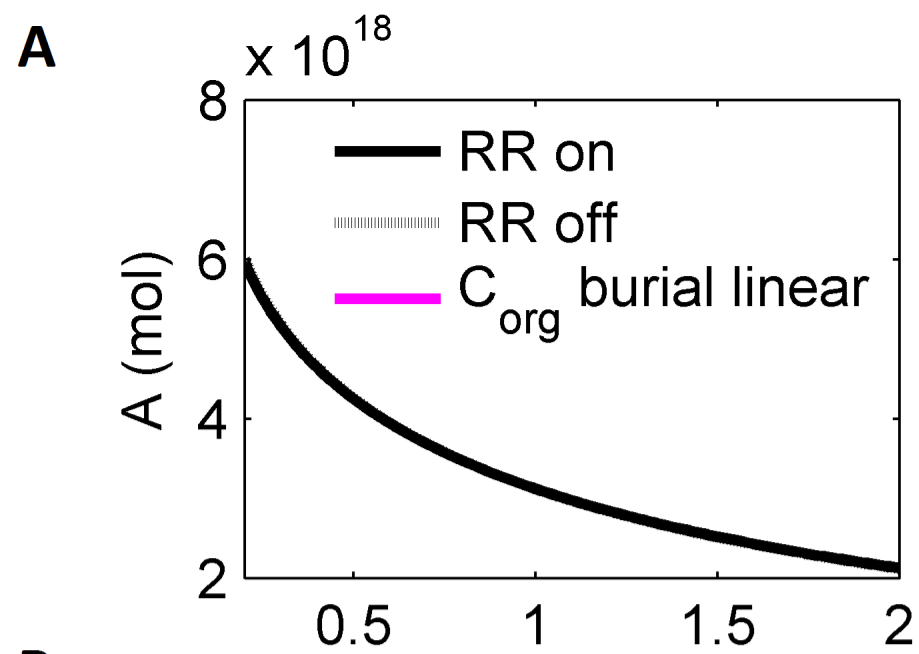


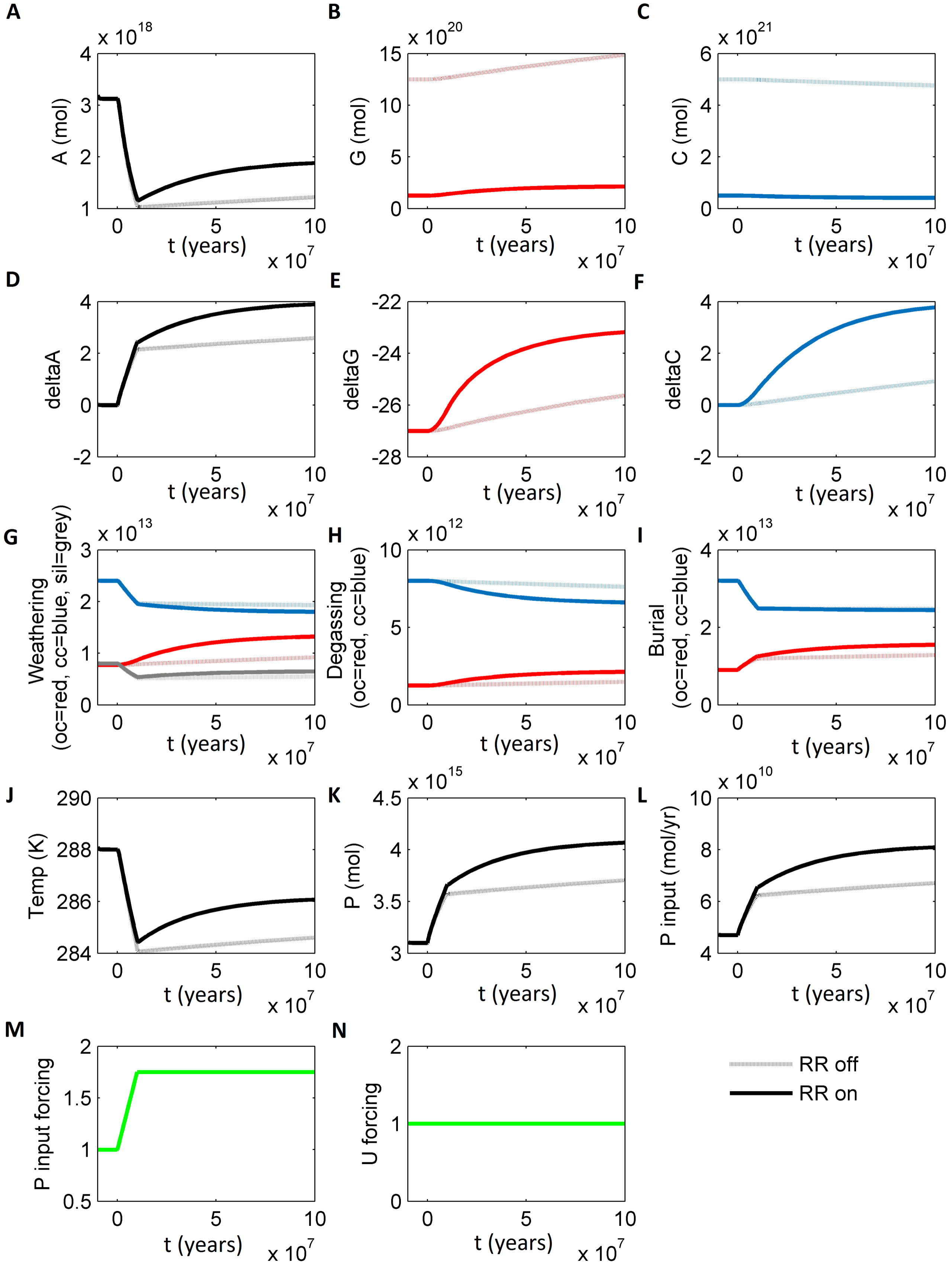
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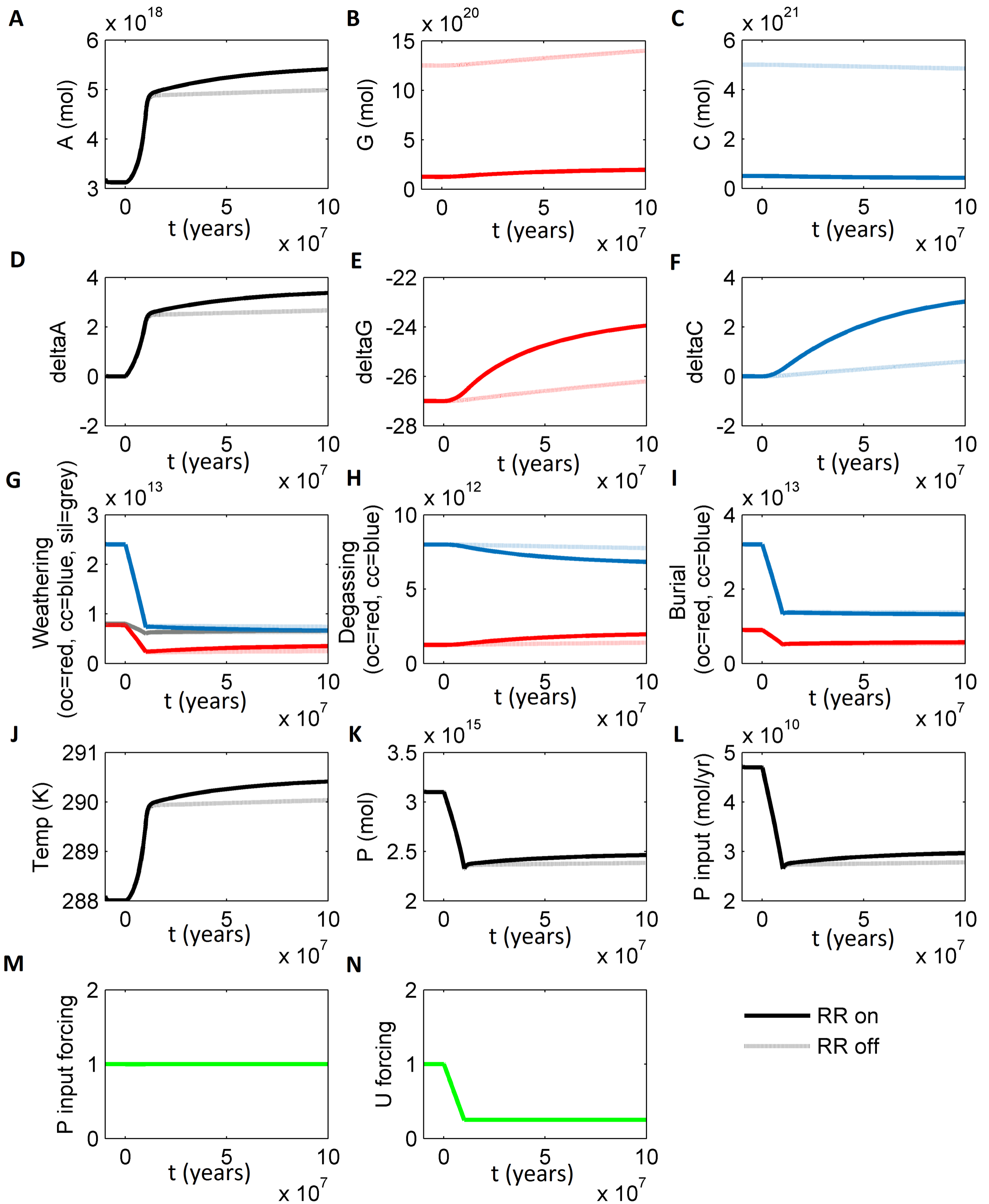


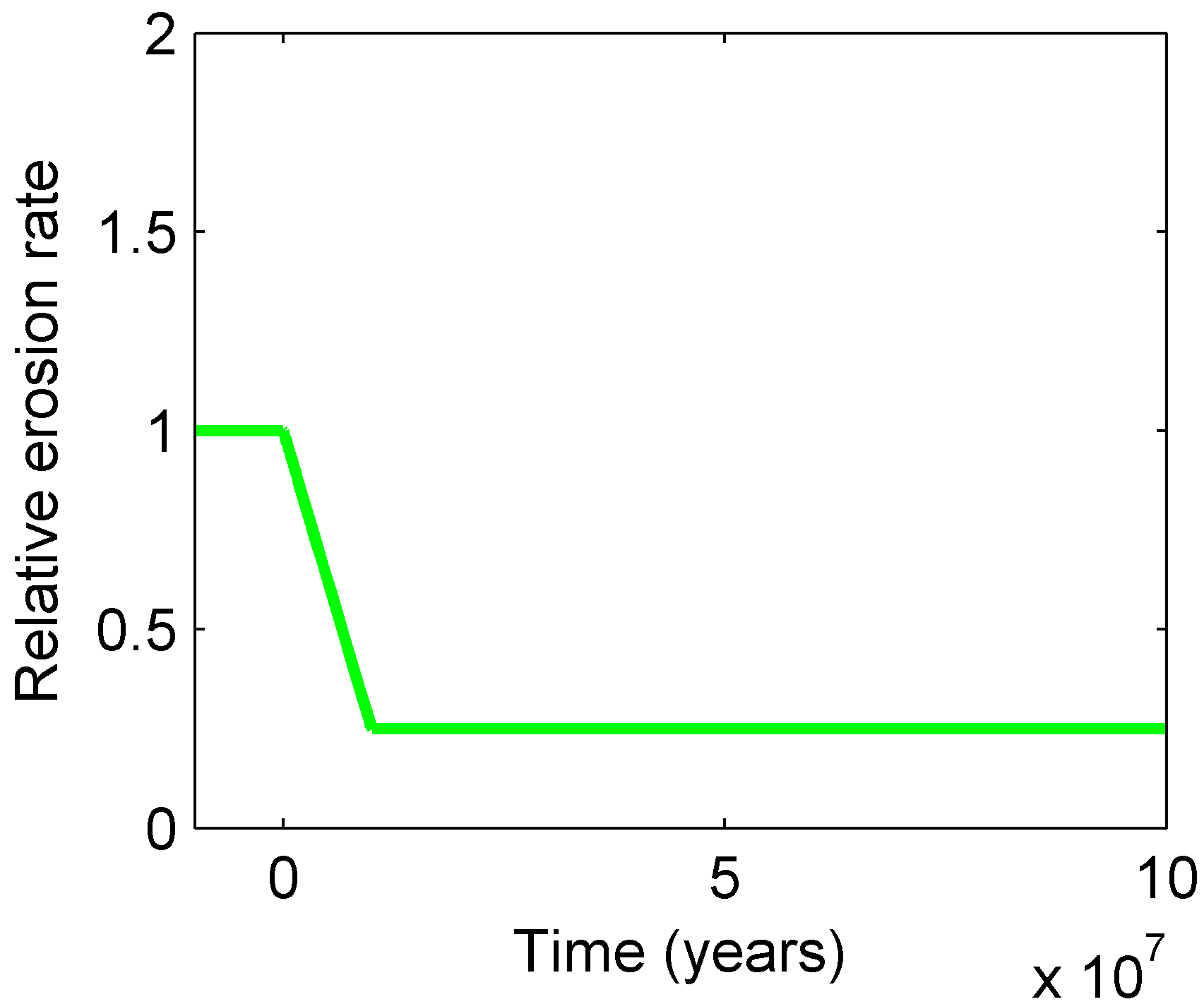










**A****B**