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Tectonic controls on the long-term carbon isotope mass balance

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

carbon isotopes | mass balance | tectonics | carbonate weathering | long-term carbon cycle

Introduction

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

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

This paradigm encounters difficulties. Firstly, although Earth's oxygenation history does not rely solely on carbon isotope data, it is remarkable that independent evidence for oxygenation does not always coincide with high $\delta^{13}C$ (14). The Ediacaran-Cambrian faunal radiation (Cambrian Explosion), which is commonly attributed to oxygenation, is strangely accompanied by low, rather than high $\delta^{13}C$ (Fig. 1), while the many fluctuations in atmospheric oxygen between 15% and 32% that have been identified using the Phanerozoic carbon isotope record (12), lack corroborating evidence (14). Although such inconsistencies are widely acknowledged, alternative explanations to explain global trends in $\delta^{13}C$ are uncommon. One possibly viable alternative attributes $\delta^{13}C$ fluctuations to the amount of diagenetically precipitated (and isotopically light) carbonate cement worldwide (14-15). Such large changes remain unsubstantiated, while the link to the global carbon cycle must appeal to a sampling bias, wherein a great mass of isotopically light material can be buried (to drive a positive excursion) yet does not lower the bulk isotopic composition of the carbonates which are analyzed. We argue that the preservation of a $\delta^{13}C$ signal that is correlated with other global processes is evidence against such sampling errors, and must be the result of definable system interactions (Fig. 1).

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

Significance

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

Reserved for Publication Footnotes

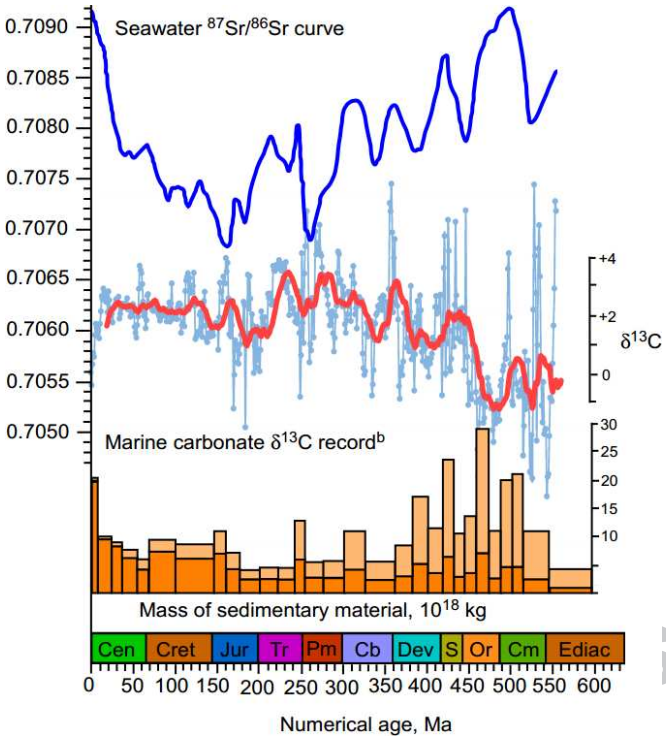

Fig. 1. Phanerozoic recordsof marine carbonate $\delta^{13}C$ (33), seawater Sr isotope composition (33) and mass of sedimentary material (two shades correspond to measured and estimated total mass, respectively) (34). Diverse tectonic proxies identify the Ediacaran-Ordovician interval as a time of maximal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

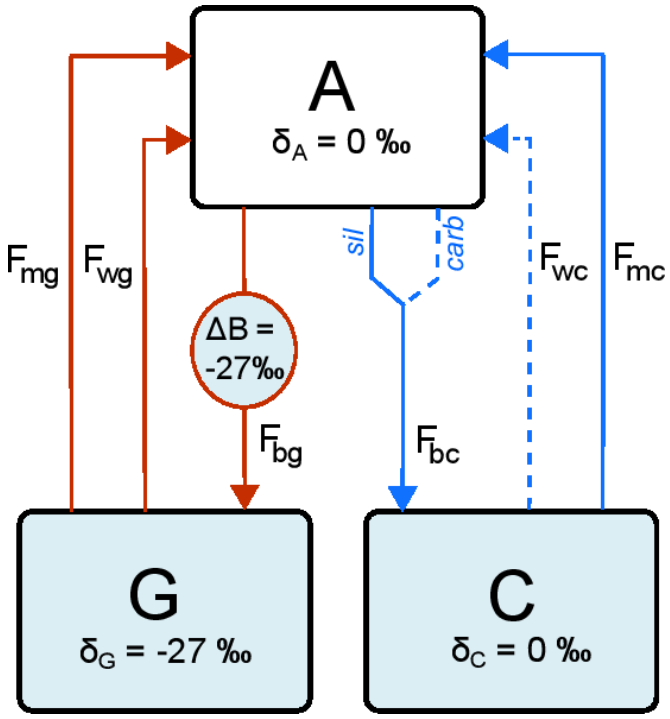

Fig. 2. Long term carbon cycle showing isotope fractionation. A is atmosphere and ocean carbon, G is buried organic carbon and C is buried carbonate carbon. F_b refers to burial fluxes, F_w to weathering and F_m to metamorphic/degassing fluxes. δ_x denotes the isotopic fractionation of reservoir X, and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

that any such effect may be outweighed by an erosional forcing of carbonate burial.

The long-term carbon isotope mass balance

Figure 2 shows a representation of the long-term carbon cycle, which forms the basis for isotope mass balance calculations (18). Carbon enters the atmosphere/ocean system by four routes: oxidative weathering of fossil carbon (F_{wg}), carbonate weathering (F_{wc}) and metamorphic degassing of sedimentary organic carbon (F_{mg}) and carbonates (F_{mc}). Carbon leaves the surface pool via burial of organic carbon (F_{bg}) and inorganic carbonates (F_{bc}), with the fraction of total burial leaving via the organic route denoted f_{org}. The dashed lines in figure 2 show an important difference between net (solid lines) and gross (all lines) fluxes in the carbon cycle, which arises because the carbonate weathering-precipitation cycle is a CO_2 neutral process on long time-scales (19) (see SI).

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

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

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

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

Following this reasoning, positive $\delta^{13}C$ excursions are commonly interpreted as organic C burial events, whereby the resultant oxygenation is quantified using the assumptions that total C throughput and net fluxes (the net carbon flux on geological time scales excludes the carbonate weathering flux) were similar to the present day, and that f_{org} approximates the proportion of outgassed CO_2 (including weathering sources) that is reduced to organic carbon (9,15). For example, the sustained baseline increase of ~5-6‰ during the early Neoproterozoic (11) is interpreted to imply an approximate doubling of organic burial due to increased phytoplankton body size (10) or high sedimentation rates (11). For the ~2.1 Ga Lomagundi Event of high $\delta^{13}C$, the total excess oxygen produced has been estimated at a massive 12-22 times the present inventory of atmospheric oxygen (8,9), with organic burial rates thought to increase by >20 times over the course of the isotope excursion (21).

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

A physical erosion control on the carbon isotope mass balance

We propose here that long-term variation in f_{org}, and hence $\delta^{13}C$, may sometimes be driven by changes in the inorganic, rather than the organic side of the carbon cycle. Because the

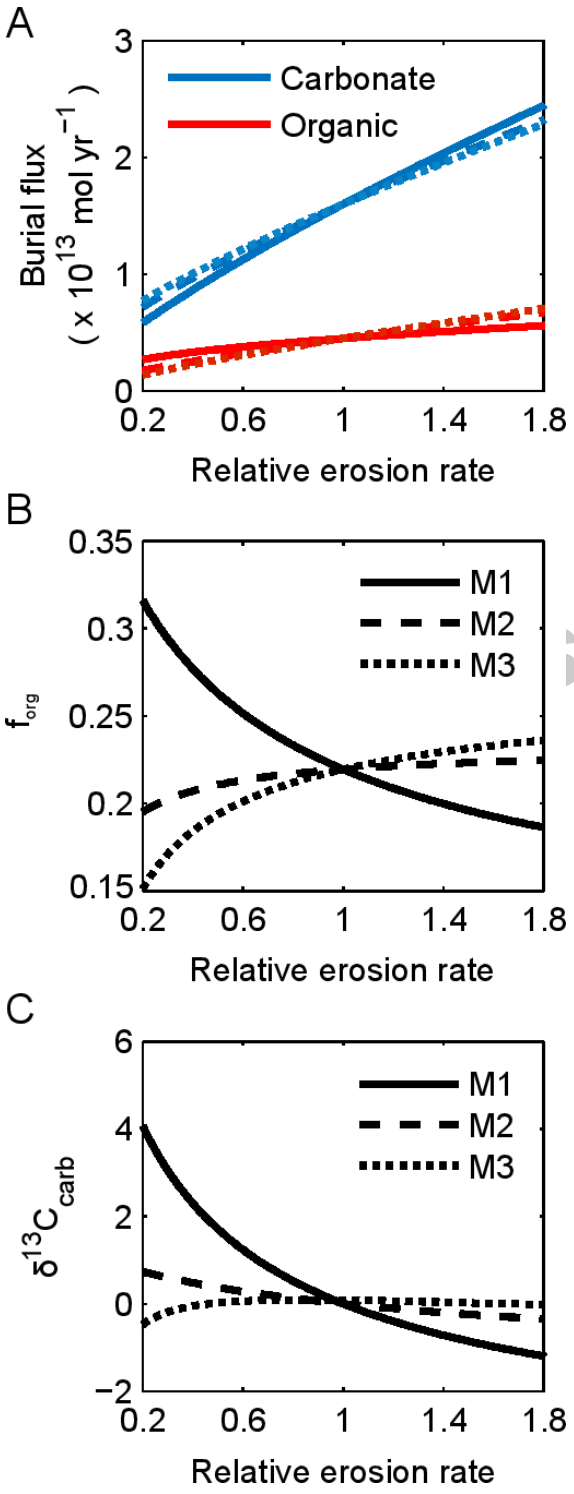

Fig. 3. Steady states of the long-term carbon cycle model. The system shown in Figure 2 is run to steady state for different values of the relative global uplift/erosion rate. Bold lines (M1) show results when silicate weathering delivers around 58% of ocean phosphate (29, see SI), dashed lines (M2)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

carbonate weathering – deposition cycle is CO_2 neutral on time scales relevant to the C-isotope mass balance, increasing the carbonate weathering (and deposition) rates acts to decrease f_{org} without impacting the net carbon fluxes responsible for driving climate. Although this is not the first study to link changes in carbonate weathering to $\delta^{13}C$, for example, it has been shown that a transient increase in carbonate weathering rates would drive an increase in $\delta^{13}C_{in}$ (23), our proposition differs from previous work by highlighting how sustained changes in carbonate deposition rates can alter f_{org} directly.

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

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

$$\delta^{13}C_{carb} = (F_{bg} \times \Delta B)/F_{total} + \delta^{13}C_{in} \quad (3)$$

Taking average values from the literature for carbon fluxes ($F_{wg} = 7.75\times10^{12}$ mol/yr, $F_{wc} = 24\times10^{12}$ mol/yr, $F_{mg} = 1.25\times10^{12}$ mol/yr, $F_{mc} = 8\times10^{12}$ mol/yr, $F_{bg} = 9\times10^{12}$ mol/yr; $F_{total} = F_{wc} + F_{mc} + F_{wg} + F_{mg} = 41\times10^{12}$ mol/yr (19, 27), equation (3) suggests that trends in the long-term $\delta^{13}C$ average of ~-1‰ to ~+5‰ can be explained by varying the carbonate weathering flux between 1.5 times and 0.2 times the present day rate, respectively, without requiring any change in the rate of organic carbon burial. Such changes are within the limits of published estimates based on the Sr isotope record and/or sedimentation rates (see SI). Note that this mechanism does not require changes in $\delta^{13}C_{in}$.

Modelling the carbon isotope mass balance

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

An important consideration in this work is that changes in erosion rate also alter the rate of organic carbon burial via changes to the phosphorus cycle. To explore this further we link the rate of organic carbon burial in the model to the availability of phosphorus (22, 6). Phosphorus enters the surface system via the weathering of silicate, carbonate and organic C-bearing rocks, and the strength of the relationship between erosion and organic C burial depends on the P delivery from the weathering of each individual rock type.

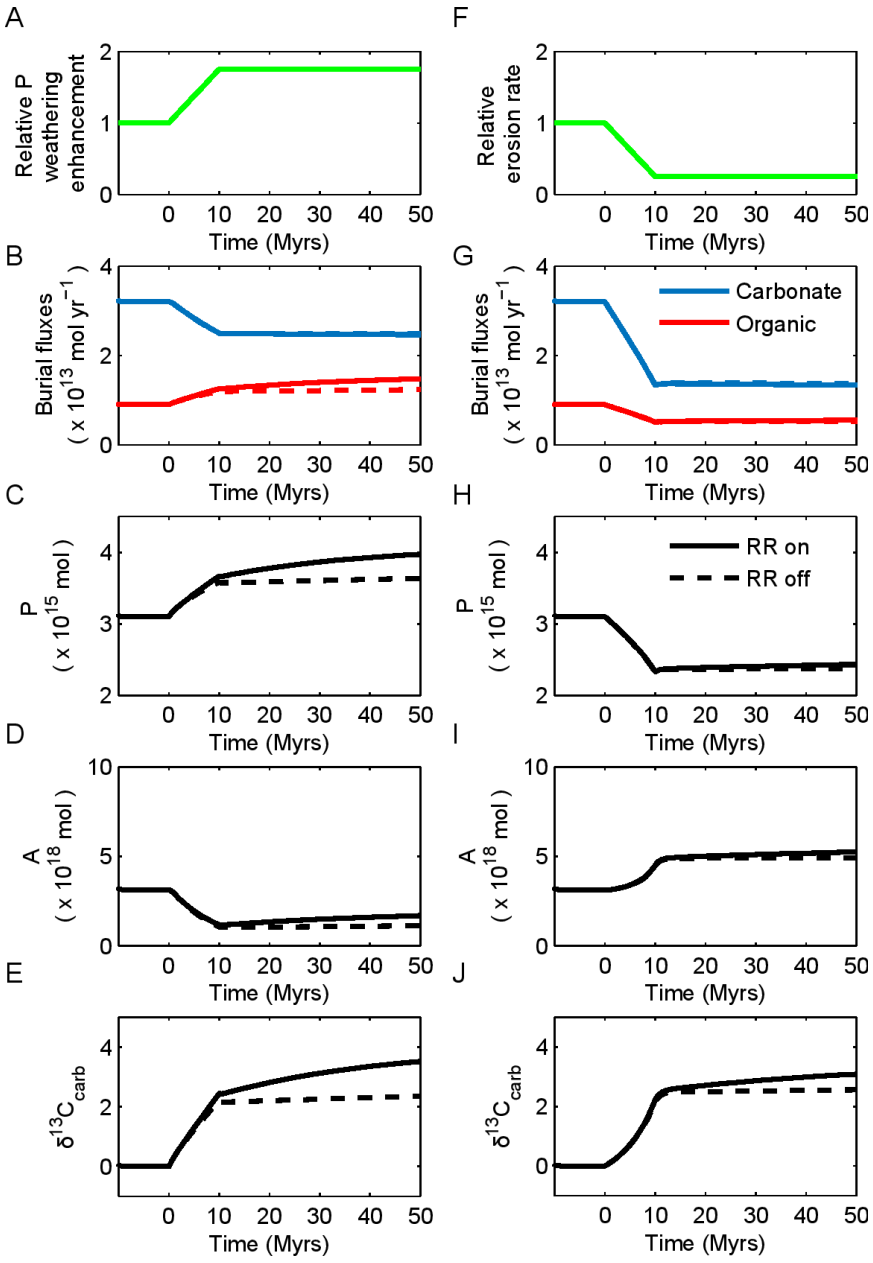

Fig. 4. Comparison of positive $\delta^{13}C$ excursions driven by burial and erosion events.Panels show A: Relative model forcing factor. B, Burial fluxes for carbonate (F_{bc}, blue) and organic carbon (F_{bg}, red). C, Ocean phosphate. D, Atmosphere and ocean carbon. E, $\delta^{13}C$ of atmosphere/ocean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

Recent studies of P delivery from different rock types (29, 30) suggest that silicates play the major role, delivering more than 50% of riverine P (see SI). The model run showing this setup (M1) is shown in bold in figure 3. When the weathering of silicates is chiefly responsible for P delivery, an increase in erosion will not greatly affect the steady state P delivery or organic C burial, because the global silicate weathering rate is tightly controlled at steady state by the rate of CO_2 release (which remains constant in the model), and by any imbalance in the organic C cycle.

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

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

We acknowledge that the long-term effects of erosion on global P delivery and organic carbon burial are still poorly constrained. Uncertainties exist in the various temperature and erosion effects on individual chemical weathering fluxes, the degree of preferential chemical weathering of accessory apatite minerals, and the possibility that changes in sedimentation rate may impact organic carbon burial differently to the burial of carbonates. In particular, it has been proposed that increased rates of sedimen-

tation will enhance the preservation of buried organic carbon and phosphorus (5). Our model calculates the rate of organic carbon burial based on a relationship between ocean phosphate, new production and sedimentation rate (31), but we have also run an alternative model setup to further explore this idea, wherein we strengthen this relationship by giving the burial rates of organic carbon and phosphorus an additional linear dependence on the global erosion rate. The model results for ocean phosphate concentration are altered under these assumptions, but the steady-state burial rates of carbon and phosphorus are not affected, as they are ultimately constrained by the supply flux of P from weathering (see SI for more details).

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

Figure 4 shows a series of time-dependent model runs where a +3‰ positive excursion in $\delta^{13}C$ is caused by either increasing organic carbon burial (via increased P delivery), or decreasing the erosion rate. Increasing $\delta^{13}C$ via an organic C burial event (Figure 4. A-E) results in a decrease in the atmosphere/ocean carbon reservoir, i.e. a decrease in atmospheric pCO_2, and global cooling. Driving a similar positive excursion via a reduction in erosion rates (Figure 4. F-J) causes a warming event due to the weakening of silicate weathering. Importantly, we show that a positive $\delta^{13}C$ excursion may be coincident with either an increase, or decrease in the rate of organic carbon burial. This should be a serious consideration for work aiming to tie the C isotope record to global biogeochemical events.

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

The isotopic composition of carbon inputs ($\delta^{13}C_{in}$) is not fixed in our model, but responds to the changing composition of the crustal reservoirs. Although changes to $\delta^{13}C_{in}$ (e.g. due to preferential weathering of high-$\delta^{13}C$ lithologies) have been shown to drive C isotope excursions (20, 23), the mechanism explored in this paper does not depend on variations in $\delta^{13}C_{in}$. As an example we run the model with this parameter fixed (Figure S7), which shows the same qualitative results.

Interrogating carbon isotope excursions

A positive carbon isotope excursion caused by changes to the inorganic carbon cycle has different climatic effects from one caused by increasing the burial rate of organics: notably an increase in CO_2 and surface temperature, rather than a decrease. Such testable distinctions allow us to constrain the causes of specific carbon isotope events, and suggest that major, but short-lived $\delta^{13}C$ events, which coincide with global cooling, such as the late Ordovician Hirnantian event, could potentially relate to excess organic burial. The longer Permo-Carboniferous glaciations also occurred at a time of generally high $\delta^{13}C$, and are thus consistent with an elevated organic burial flux, perhaps associated with the evolution of a modern land biota (32). However, relatively low erosion rates throughout this period imply that rates of organic C burial need not have been as high as previously thought – potentially resolving conflicts over the prediction of hyperambient O_2 levels (5). By contrast, glaciation during the Cenozoic is associated with decreasing $\delta^{13}C$, and so appears to be more consistent with the notion that the erosional forcing of carbonate deposition outweighed that of organic burial.

Some times of elevated $\delta^{13}C$ do not coincide with glaciation, and this is the case for the post-glacial Lomagundi Event of exceptionally high $\delta^{13}C$ during the Palaeoproterozoic . Such high $\delta^{13}C$ values may result from a hugely increased oxidative weathering flux (21), following the Great Oxidation Event, which could have been self-sustained by oxygenic siderite (iron carbonate) weathering (22). Although not related to decreased erosion rates, the Lomagundi Event can still be viewed as a time of proportionately higher net carbon flux relative to gross carbon throughput, in the same way as we argue for other times of high baseline $\delta^{13}C$, such as during the Tonian Period of supercontinent peneplanation. Note that in none of these cases does high $\delta^{13}C$ imply net oxygenation. Previously, these well-established $\delta^{13}C$ events were first-order determinants in our understanding of Earth's oxygenation history.

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

Conclusions

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

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