Bioturbation and directionality in Earth’s carbon isotope record across the Neoproterozoic–Cambrian transition

R. A. Boyle1,2 | T. W. Dahl3 | C. J. Bjerrum4 | D. E. Canfield2

1Danish Institute for Advanced Study, University of Southern Denmark, Odense M, Denmark
2Nordic Centre for Earth Evolution and Institute of Biology, University of Southern Denmark, Odense M, Denmark
3Natural History Museum of Denmark, University of Copenhagen, København K, Denmark
4Department of Geosciences and Natural Resource Management, University of Copenhagen, København K, Denmark

Correspondence
R. A. Boyle, Danish Institute for Advanced Study, University of Southern Denmark, Odense M, Denmark. Email: richboyleacademic@gmail.com

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Abstract
Mixing of sediments by moving animals becomes apparent in the trace fossil record from about 550 million years ago (Ma), loosely overlapping with the tail end of the extreme carbonate carbon isotope $\delta^{13}C_{\text{carbonate}}$ fluctuations that qualitatively distinguish the Proterozoic geochemical record from that of the Phanerozoic. These Precambrian-scale fluctuations in $\delta^{13}C_{\text{carbonate}}$ (PSF-$\delta^{13}C_{\text{carbonate}}$) remain enigmatic, due to their high amplitude and inclusion of global-scale negative $\delta^{13}C_{\text{carbonate}}$ values, below anything attributable to mantle input. Here, we note that different biogeochemical-model scenarios plausibly explaining globally synchronous PSF-$\delta^{13}C_{\text{carbonate}}$ converge: via mechanistic requirements for extensive anoxia in marine sediments to support sedimentary build-up of $^{13}$C-depleted carbon. We hypothesize that bioturbation qualitatively reduced marine sediment anoxia by exposing sediments to oxygenated overlying waters, which ultimately contributed to decreasing the carbon cycle’s subsequent susceptibility to PSF-$\delta^{13}C_{\text{carbonate}}$. Bioturbation may also have reduced the quantity of (isotopically light) organic-derived carbon available to contribute to PSF-$\delta^{13}C_{\text{carbonate}}$ via ocean crust carbonatization at depth. We conduct a comparative modelling exercise in which we introduce bioturbation to existing model scenarios for PSF- $\delta^{13}C_{\text{carbonate}}$ expressing both the anoxic proportion of marine sediments, and the global organic carbon burial efficiency, as a decreasing function of bioturbation. We find that bioturbation’s oxygenating impact on sediments has the capacity to prevent PSF- $\delta^{13}C_{\text{carbonate}}$ caused by authigenic carbonate precipitation or methanogenesis. Bioturbation’s impact on the $f$-ratio via remineralization is partially offset by liberation of organic phosphate, some of which feeds back into new production. We emphasize that this study is semi-quantitative, exploratory and intended merely to provide a qualitative theoretical framework within which bioturbation’s impact on long-term, first-order $\delta^{13}C_{\text{carbonate}}$ can be assessed (and it is hoped quantified in more detail by future work). With this proviso, we conclude that it is entirely plausible that bioturbation made a decisive contribution to the enigmatic directionality in the $\delta^{13}C_{\text{carbonate}}$ record, from the Neoproterozoic–Cambrian boundary onwards.

KEYWORDS
biogeochemistry, bioturbation, cambrian substrate revolution, carbon isotope record, evoluión, Neoproterozoic
1 | INTRODUCTION

The visionary Soviet geochemist Vladimir Vernadsky described life as "the only variable part of the thermodynamic field of the biosphere" (Vernadsky, 1998, 1926), implying that what we now refer to as the "Earth system" exhibits a directionality in time that qualitatively distinguishes it from comparable lifeless planets. A tangible example of such biologically generated qualitative geochemical change is bioturbation; the reworking and mixing of soils and sediments by life (most importantly the burrowing and physiological activities of moving animals). The idea that bioturbation can be expected to have driven unique changes in Earth system function sits easily with the long-anticipated significance of animal-driven sediment homogenization within contemporary environments (e.g., Meysmann, Middelberg, & Heip, 2006) and has historical note as an area of personal interest and enthusiasm for Charles Darwin (e.g., Feller, Brown, Blanchart, Deleporte, & Chernyanski, 2003). It is also consistent with the long-term impact that bioturbation has been postulated to have had on Earth's sulphur (Canfield & Farquhar, 2009) and phosphorus (Boyle et al., 2014) cycles. But when animals disrupt sediments, it is generally in connection with foraging for food; meaning that the carbon cycle is where the earliest geochemical evidence for the activity of moving animals might logically be expected. From this point of view, it is informative to explore the potential relevance to activities within the "Cambrian substrate revolution" (e.g., Bottjer, Hagadorn, & Dornbos, 2000).

Within the contemporary marine sediment environments likely of closest relevance to the earliest moving animals, the biogeochemical impact of bioturbation is to disrupt horizontal stratification, and to increase chemical reaction between sediments and the water column. Mechanistically, this covers a range of processes that can be categorized as either (i) particle reworking, that is mixing, breakup of solids, "diffusor" versus "conveyor belt" movement of sediment or (ii) burrow ventilation; that is flushing of sediments with water, otherwise known as "bioirrigation" (e.g., Kristensen et al., 2012). Furthermore, bioturbation is a fundamental factor in the control of the movement of oxygen from the overlying water column into sediments, because the volume of oxygenated sediment associated with burrow walls often vastly exceeds that of the sediment surface, driving a significant proportion of sedimentary oxygen consumption (Kristensen, 2000). Even periodic bioturbation-mediated redox oscillation is sufficient to increase remineralization of organic matter to levels comparable to continuously oxygenated conditions (e.g., Aller, 1994).

The above considerations illustrate how bioturbation leads to a degree of decoupling between marine oxygen levels, and the impact that these oxygen levels have on sedimentary composition and organic carbon dynamics, which is potentially biogeochemically significant. The marine shelf sediments inhabited by bioturbating fauna are thought to be responsible for about 80%-90% of total marine sedimentary remineralization (Middleburg, Soetaert, & Herman, 1997). Thus, although over geologic timescales the quantitative contribution of bioturbation to the balance between remineralization and burial is non-trivial to calculate (we attempt a "first pass" at such a calculation here), it is presumably highly significant. From a long timescale "Earth system" perspective, the general premise that we seek to explore is that the rise of bioturbation must necessarily have been associated with increased oxygen exposure and organic carbon remineralization in marine sediments.

1.1 | Bioturbation and the fossil record

The relatively sudden appearance and diversification of animals are perhaps the most striking change observable in the fossil record, and bioturbation is of conceptual importance in that it constitutes the earliest example of animal-induced "niche construction" (Odling-Smee, Laland, & Feldman, 1996). However, the initial morphological diversification of animals is somewhat decoupled from the emergence of the "infaunal ecospace" in marine sediments (Erwin et al., 2011; Mangano & Buatois, 2014), quantitative details of which are still being determined. As early as 565 Ma, apparent burrow-like structures associated with a "meniscate" lining have been proposed as the first evidence for bioturbation (Rogov et al., 2012). The biogenic nature of these specimens has been questioned (Brasier, McLroy, Liu, Antcliffe, & Menon, 2013), but alternative trace fossils are indicative of some form of movement through sediment during roughly the same time period (Liu, McLroy, & Brasier, 2009). There is evidence for shallow burrows from about 560 Ma (Menon, McLroy, & Brasier, 2013), followed by an observable increase in burrow size, and their appearance in more shoreward environments from about 540 Ma (Droser & Bottjer, 1988; McLroy & Logan, 1999).

The "Cambrian substrate revolution" refers to a transition between "Ediacaran Matground" environments, within which marine sediments are inferred to have been predominantly covered by microbial mats (Bottjer, 2005), to a more complex and dynamic sedimentary environment (Bottjer et al., 2000). By extrapolation from modern environments, this change goes hand in hand with (i) bioturbation, (ii) bioirrigation (enhanced exchange between sediment pore water and the overlying water column, due to burrow flushing and animal movement), (iii) exploitation of sedimentary organic matter as a food source and (iv) more extensive oxygenation and aerobic respiration of sedimentary organic matter, ultimately due to increased available reactive surface area for any given chemical exchange between sediments and the water column (e.g., Meysmann et al., 2006).

Two key stages within the Cambrian substrate revolution can be identified, the Fortunian (541–529 Ma) biodiversification event and the Cambrian stage 2 (529–521) "agronomic revolution." The former event involves a qualitative increase in the architectural complexity of animal body plans and trace fossils (coupled mainly to sediment "bulldozing" and increased sediment-water column exchange). The latter interval saw an extension of the vertical depth of bioturbation and introduced the ventilated, advection-dominated sediment macroecology characteristic of the Phanerozoic (Seilacher, 1999).

The extent of bioturbation in marine sediments is estimated using the bioturbation index (BI) (Taylor & Goldring, 1993), which provides...
an estimate of the proportion of primary bedding fabric disrupted by the activity of bioturbation. The maximum observable bioturbation index in preserved sediments increases from 0 to 1 (1%–4% bioturbation) at around 550 Ma, to 3 (5%–30%) by about 540 Ma, and up to 6 (100%) from about 530 Ma onwards. The mean bioturbation index increases through values of 0.1, 0.5 and 2.4, respectively, within these same time intervals. Additionally, between 540 and 529 Ma maximum observable burrow depth rose to approach modern levels of almost a metre. On the basis of these and similar metrics, it has generally been argued that bioturbation had begun to increase towards levels comparable with the later Phanerozoic by around 530–520 Ma (Mangan & Buatois, 2014). Importantly, however, the rate, scale and degree of continuity versus discontinuity within this "substrate revolution" have recently been subject to re-evaluation.

Epistemological concerns arise surrounding "scaling up" from a relatively small number of fossils in the preserved rock record to global-scale, quantitative measures of biogeochemical activity. More recent research has argued that a sizable proportion of the shelf remained unmixxed until at least 120 million years after the Precambrian–Cambrian transition (Tarhan & Droser, 2014; Tarhan, Droser, Planavsky, & Johnston, 2015). This "delayed mixing" scenario builds on earlier studies (e.g., Droser & Bottjer, 1988; McIlroy & Logan, 1999) arguing for the persistence of unmixed sections of the continental shelf much later than assumed within the "substrate revolution" narrative. This is justified on the basis of methods attempting to contextualize trace fossil samples to their sedimentary environment in an appropriately temporally extensive and continuous way. An implication of the delayed mixing model is that the alternative, relatively sudden "revolution" scenario (reviewed in Mangan & Buatois, 2016) is based on an unjustified extrapolation from the morphology of a relatively small number of specimens, taken out of sedimentary context.

This debate, we argue, raises interesting philosophical questions as to how best to frame deep time hypotheses. Specifically, when dealing with an ancient and quantitatively incomplete biogeochemical record, the qualitative presence/absence of a given process (bioturbation being present, in at least some sections, from a given date) is much easier to reconstruct than the quantitative value of a flux or property (the specific proportion of continental shelf sediments, or indeed a given biogeochemical flux, subjected to bioturbation). This is because the latter, quantitative category of evidence will always be more sensitive to incomplete preservation, unknowable details such as precise continental areas, relief and hypsography, and will become increasingly sensitive to such details the further back one moves in time. In this context, we stress that our focus here is to provide a qualitative, theoretical exposition of the likely feedbacks involved; focusing primarily on the immediate Neoproterozoic–Cambrian boundary (with the hope that future work may reveal changes in the quantitative strength of bioturbation’s subsequent impact).

The delayed mixing scenario is gaining increasing recognition and is arguably more consistent with widespread anoxia in the early Cambrian, or at least some form of protracted trajectory scenario, by which oxygen reached modern levels well after the Neoproterozoic–Cambrian transition (e.g., Dahl et al., 2010, 2014; Gill et al., 2011), or a scenario within which deep waters were only transiently oxygenated (Cheng et al., 2017). In theory, low-oxygen levels could connect to the spread of early bioturbating fauna, through a negative feedback by which low-oxygen levels limit the spread of moving animals, potentially even stabilizing biogeochemical dynamics at a new steady state (Boyle et al., 2014). However, the precise timing at which any such feedbacks may have come into operation is still being determined. We therefore set this distinction between the “delayed mixing” and “sudden revolution” scenarios outside the scope of this work and attempt to examine the processes on a theoretical basis, with the caveat that the time at which bioturbation’s geochemical effects become most significant may be subject to future revision. On a practical note, it is nevertheless worth emphasizing that but both sets of researchers agree that the mean bioturbation index for shelf sediments was in the region of 2–3 after about 540 Ma.

1.2 The Neoproterozoic–Cambrian boundary and the carbonate carbon isotope \(\delta^{13}C_{\text{carbonate}}\) record

Positive and negative perturbations in the carbonate carbon isotope \(\delta^{13}C_{\text{carbonate}}\) record are, respectively, due to the preferential deposition of either relatively heavy \(\delta^{13}C\)-enriched or relatively light \(\delta^{13}C\)-depleted carbon to the preserved carbonate rock record, ultimately caused by changes in the relative magnitude of different carbon fluxes with different isotopic compositions. (This is assuming that at least some first-order features of the \(\delta^{13}C_{\text{carbonate}}\) record are genuinely connected to the global carbon cycle, as opposed to being derived from diageneric or contact with meteoric groundwater—an assumption which we consider the most parsimonious interpretation, see below). Carbonate carbon precipitates from, and over geologic time-scales is assumed to be at isotopic equilibrium with, the contemporaneous dissolved inorganic carbon (DIC) pool in seawater, the isotopic composition of which reflects the relative influence of various carbon fluxes. The \(\delta^{13}C_{\text{carbonate}}\) of a given sample records its \(\Delta^{13}C_{\text{DIC}}\) ratio,

\[
R_{\text{sample}} = R_{\text{std}} = 0.0112372 \quad \text{(Libbes, 1992)};
\]

\[
\delta^{13}C_{\text{sample}} = \left(\frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}}\right) \cdot 1000
\]  

(1)

Rubisco, the enzyme responsible for photosynthetic carbon fixation, kinetically favours \(\Delta^{13}C\), meaning that organic carbon is significantly depleted in \(\Delta^{13}C\) in comparison with the carbon pool from which it is fixed (Craig, 1953). From a biogeochemical perspective, this leads to the inference that the more marine organic matter is buried, the more \(\Delta^{13}C\)-enriched the DIC pool becomes. Consequently, global positive \(\delta^{13}C_{\text{carbonate}}\) values have classically tended to be interpreted as indicating high-organic carbon burial; that is relatively enhanced removal of \(\Delta^{13}C\)-depleted organic carbon from the DIC pool (e.g., Hayes, Strauss, & Kauffman, 1999; Kump & Arthur, 1999). The organic fraction of total (i.e., organic and inorganic carbonate) carbon burial in the
is, at steady state (see Appendix 1), generally assumed to be related to the \( \delta^{13}C_{\text{carbonate}} \) record via:

\[
\delta_{\text{org}} = \frac{\delta_c - \delta_{\text{in}}}{\epsilon_p},
\]

where \( \delta_c \) is the isotopic composition of the carbonate carbon (i.e., \( \delta_c \equiv \delta^{13}C_{\text{carbonate}} \)), \( \delta_{\text{in}} \) is the averaged isotopic composition of carbon input to the ocean-atmosphere system from weathering and the mantle combined, and \( \epsilon_p \) is the fractionation factor by which organic matter differs from carbonate carbon \( \epsilon_p = \delta_c - \delta_{\text{org}} \approx 25\% \) (e.g., Freeman & Hayes, 1992; Kump & Arthur, 1999).

Because organic carbon burial is a source of atmospheric oxygen over geologic timescales (Betts & Holland, 1991; Holland, 1984), it has conventionally been expected that positive \( \delta^{13}C_{\text{carbonate}} \) values should go hand in hand with elevated oxygen input to the Earth's atmosphere-ocean system. A narrative has consequently emerged in which positive \( \delta^{13}C_{\text{carbonate}} \) values are interpreted as indicating increases in marine organic carbon burial, thus increases in the size of the global ocean-atmosphere oxygen reservoir.

Assuming that the global synchronous \( \delta^{13}C_{\text{carbonate}} \) curve over time is accurately temporally resolved, and that changes are genuinely representative of changes in the organic burial fraction \( f_{\text{org}} \) then any long-term excursions should be recorded in both the carbonate \( \delta^{13}C_{\text{carbonate}} \) and organic \( \delta^{13}C_{\text{organic}} \) carbon records (i.e., because organic carbon fractionates from the dissolved inorganic carbon (DIC) pool by a consistent factor of \( \epsilon_p \)). An additional set of hypotheses attributes local \( \delta^{13}C_{\text{carbonate}} \) excursions to the variable input of an isotopically light (i.e., \( ^{13}C \)-depleted) carbon pool, via weathering of organic matter or organic-rich mudstones on the land surface, affecting a coastal microcosm isotopically decoupled from the wider carbon cycle (Johnston, MacDonald, Gill, Hoffman, & Schrag, 2012). More significantly, the lack, in some Neoproterozoic sections, of isotopic covariance between carbonate \( \delta^{13}C_{\text{carbonate}} \) and organic \( \delta^{13}C_{\text{organic}} \) carbon has caused some researchers to attribute isotopic excursions to local phenomena such as changes in contact with isotopically lighter meteoric water (Allan & Matthews, 1982; Knauth & Kennedy, 2009) or diagenesis (Derry, 2010). Some of these alternative interpretations could even, in theory, lead to globally synchronous \( \delta^{13}C_{\text{carbonate}} \) changes. For instance, global sea level changes driven by glacial-interglacial cycles could drive differential mixing between DIC-equilibrated and meteoric-derived carbon, during transgressive flooding events, leading to a coupling between \( \delta^{13}C_{\text{carbonate}} \) and \( \delta^{18}O \) (Immenhauser, Della Porta, Kenter, & Bahamonde, 2003; Oehlerl & Swart, 2014). By contrast, some studies propose that the lowest point of the Shuram excursion coincides with a maximum flooding surface—the opposite of what would be expected if the anomaly was related to subaerial exposure of shallow marine environments during a glaciation (e.g., Young, 2015). On the other hand, other arguments focus on the fact that diagenesis need not be confined to sequence boundaries and may impart a signature below the exposure surface (Swart, 2015). The scale of the effect of diagenetic alteration on the \( \delta^{13}C_{\text{carbonate}} \) record is a subtle question outside the scope of this work.

Nevertheless, the first-order features of the Neoproterozoic-Cambrian \( \delta^{13}C_{\text{carbonate}} \) are broadly synchronous across multiple different data sets, and in general, first-order global changes in \( \delta^{13}C_{\text{carbonate}} \) do, broadly, covary with \( \delta^{13}C_{\text{organic}} \) (e.g., Krissansen-Totton, Buick, & Catling, 2015). Thus, these complicating factors do not negate the interpretation of the \( \delta^{13}C_{\text{carbonate}} \) as indicative of global-scale carbon cycle changes, legitimizing the question as to the cause of the large-scale fluctuations in \( \delta^{13}C_{\text{carbonate}} \) over Earth history. The most productive insights towards an answer have been gained from noting that the interpretation necessary to derive (2) assumes a carbon cycle in steady state.

Rothman, Hayes, and Summons (2003) provided a key insight by noting that Neoproterozoic data sets generate a slope of \( f_{\text{org}} = \) 1 on a graph of \( \delta_c \) against \( \epsilon_p \), meaning that the Neoproterozoic \( \delta^{13}C_{\text{carbonate}} \) record, and the extreme fluctuations that it features, would require an implausibly large organic carbon burial fraction in order for (2) to hold. On this basis, it was reasoned that the Neoproterozoic carbon cycle could not be described as one source and two sinks at steady state. Rothman’s initial hypothesis was that the Proterozoic ocean contained an exceptionally large dissolved organic carbon (DOC) pool, of the order of 100 times larger than that of the present system. This “Rothman ocean” scenario attributed negative \( \delta^{13}C_{\text{carbonate}} \) excursions to bursts of remineralization from this exceptionally large DOC reservoir (injecting \( ^{13}C \)-depleted carbon into the DIC pool and therefore the preserved carbonate record). But later work noted that rapid, large bursts of remineralization would probably impose electron acceptor demands that approached quantitative depletion of the \( \text{O}_2, \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) pools (Bristow & Kennedy, 2008), which is impossible to reconcile with the wider geochemical record.

Importantly, however, Rothman’s model provided the conceptual framework theme upon which subsequent Precambrian carbon isotope models have been based: There is a need for either non-steady state explanations to produce the short-term negative \( \delta^{13}C_{\text{carbonate}} \) excursions, or non-traditional explanations involving a neglected, isotopically light carbon flux that can explain negative excursions without violating the assumption of steady state within the inorganic carbon budget. An additional isotopically light carbon flux (i.e., other than organic carbon burial) could preferentially remove \( ^{13}C \)-depleted carbon from the DIC-carbonate record, leading to positive \( \delta^{13}C_{\text{carbonate}} \) (i.e., because the remaining DIC pool would be correspondingly \( ^{12}C \)-enriched), without invoking unrealistic values for the organic carbon burial fraction \( f_{\text{org}} \). Theoretically, negative \( \delta^{13}C_{\text{carbonate}} \) excursions could be explained by \( ^{12}C \)-depleted carbon being occasionally transferred from this additional flux into the DIC-carbonate pool and ultimately thus preserved (perhaps due to topographic changes or other temporarily irregular forcings). Two such fluxes that are mechanistically plausible in this regard are (i) the precipitation of \( ^{12}C \)-depleted carbonate carbon during hydrothermal alteration of the seafloor (Bjerrum & Canfield, 2004), and (ii) direct (i.e., authigenic) carbonate precipitation within highly alkaline anoxic microenvironments.
in sedimentary pore fluids (Schrag, Higgins, MacDonald, & Johnston, 2013).

In contrast to these steady state models, dynamical scenarios explain negative δ13C_{carbonate} excursions via a transient injection of 13C-depleted carbon into the preserved record. Most relevantly, a climatic feedback loop (see methods) has been postulated, involving methanogenic oxidation of sedimentary dissolved organic carbon (DOC), decreasing atmospheric hydroxyl levels and leading to a positive feedback involving further methane release, global-scale temperature and isotopic fractionation changes, and ultimately the injection of isotopically light carbon into the preserved record (Bjerrum & Canfield, 2011).

The key conclusion from the Neoproterozoic δ13C_{carbonate} literature is the existence of a fundamental unresolved uncertainty: any mechanistic explanation as to why extreme isotopic excursions occurred during the Neoproterozoic era must also contain an in-built explanation as to why these excursions tailed off, and eventually stopped, from approximately the Neoproterozoic–Cambrian boundary onwards. In this vein, a key observation guiding this work is that the final and most extreme negative δ13C_{carbonate} excursion, the Shuram anomaly, which ended at ~550 million years ago (Ma), broadly overlaps with the first signs of bioturbation in Earth’s history (Grotzinger, Fike, & Fischer, 2011; Lee et al., 2013). Our purpose here is to examine the plausibility of any causal connection between these two observations. Our methodology is an exploratory modelling exercise in which the purpose of the mathematics is primarily to focus and clarify the assumptions, and we are explicit about the uncertainties involved. We argue that this semiquantitative approach is consistent with the simplicity of the basic question we explore here: to what extent might the origin and spread of the earliest bioturbating fauna have altered fluctuation in the δ13C_{carbonate} across the Neoproterozoic–Cambrian boundary?

2 | SUMMARY OF METHODS

Our approach involves the rederivation and modification of several different existing model studies, which makes the description of our methods unavoidably lengthy. We therefore restrict ourselves to a short summary here. A detailed, quantitative description of each of the models used, and full derivation of our bioturbation formulation in each case, is given in the Appendix 1 at the end of paper, and the key model formulations referred to in the results, and the equations from which they are taken, are summarized in Table 1.

We write a carbon cycle formulation expressing both (i) the balance between marine production, remineralization and burial and (ii) the anoxic fraction of shelf sediments, as a function of bioturbation, and then introduce this formulation to various existing models of δ13C_{carbonate}. We put both remineralization and sediment oxygenation as a function of a key variable, f_{biot}, defined as the fraction of the global organic carbon burial flux that occurs in bioturbated sediments. Specifically, we proceed as follows:

1. We calculate the global organic carbon burial efficiency ζ using two end member cases, which differ by whether or not they include the contribution of bioturbation to remineralization of organic carbon in marine sediments. We calculate a high burial efficiency term, representing a non-bioturbated system prior to the evolution of moving animals (ζ_{prebiot}), and low burial efficiency term representing full bioturbation ζ_{biot}. We use f_{biot} to apportion between these two limiting-case burial efficiency terms to calculate the overall organic carbon burial efficiency ζ = ζ_{biot}f_{biot} + ζ_{prebiot}(1 - f_{biot}) used in the rest of the model (see equation [10], Appendix 1). In other words, bioturbation varies continuously according to f_{biot} within bounds dictated by the difference between ζ_{biot} and ζ_{prebiot}. Although simplistic, we argue that this linear formulation is the most parsimonious and tractable way in which to begin to guess at the long-term impact of bioturbation on organic carbon burial efficiency.

2. We express the anoxic fraction of marine sediments anox_{sed} = f_{anox_{sed}}f_{biot} as a decreasing function of bioturbation (and an increasing function of the wider global ocean anoxic fraction). These anoxia terms plug into both carbon isotope model formulations and global biogeochemical burial fluxes. If bioturbation is below present level, the anoxic

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Model formulations</th>
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<tbody>
<tr>
<td>Formulation</td>
<td>Equation used for δ13C_{carbonate} results</td>
</tr>
<tr>
<td>f-ratio (Kump &amp; Arthur, 1999)</td>
<td>(23)</td>
</tr>
<tr>
<td>Authigenic carbonate precipitation (Schrag et al., 2013)</td>
<td>(27)</td>
</tr>
<tr>
<td>Ocean crust carbonatization (Bjerrum &amp; Canfield, 2004)</td>
<td>(31)</td>
</tr>
<tr>
<td>Methanogenesis-driven climate feedback loop (Bjerrum &amp; Canfield, 2011)</td>
<td>(56)</td>
</tr>
<tr>
<td>Exogenous terrestrial carbon source (Johnston et al., 2012)</td>
<td>(59)</td>
</tr>
</tbody>
</table>
fraction of marine sediments can be greater than the anoxic fraction of the ocean floor as a whole; in keeping with our general hypothesis that bioturbation leads to a decoupling between oxygen levels in the water column, and sedimentary exposure to those oxygen levels. The sedimentary anoxia term is defined as the fraction of sediment (by mass) deposited under anoxic conditions—not by (e.g.) molar fraction of total carbon buried. The \( \text{anox}_{\text{sed}} \) factor is a catch-all, semiquantitative term for total sediment anoxic fraction, insofar as this fraction influences redox-sensitive burial fluxes (see Appendix 1 for more details).

3. We couple this bioturbation-linked carbon cycle formulation to a dynamical model of the marine phosphorus cycle (and its connection to the atmosphere-ocean oxygen reservoir), so as to predict the marine phosphate concentration, which then feeds into marine productivity, and therefore dictates the magnitude of the marine organic carbon burial flux (Table 2).

4. We use the marine organic carbon burial flux to derive a final value for the organic carbon burial fraction \( f_{\text{org}} \). We then use \( f_{\text{org}} \) to calculate steady state \( \delta^{13} \text{C}_{\text{Carbonate}} \) within various different model formulations (each of which are discussed in more detail in the subsequent sections):

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Modified Redfield Revisited model (Lenton &amp; Watson, 2000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>Baseline value (zero subscript denotes present day, fluxes in moles per year)</td>
</tr>
<tr>
<td>( O_{20} )</td>
<td>( O_{20} = 3.7 \times 10^{19} ) mol</td>
</tr>
<tr>
<td>( P_{0} )</td>
<td>( P_{0} = 3.1 \times 10^{15} ) mol</td>
</tr>
<tr>
<td>( B_{\text{org}} )</td>
<td>( B_{\text{org,0}} = 3.75 \times 10^{12} ) mol/year</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>( \zeta = 0.03 ) (sensitivity analysis to ( \zeta = 0.25 ))</td>
</tr>
<tr>
<td>( f_{\text{biot}} )</td>
<td>( f_{\text{biot}} = 0.6 )</td>
</tr>
<tr>
<td>( \text{anox} )</td>
<td>( \text{anox}_{\text{0}} = 0.14 )</td>
</tr>
<tr>
<td>( \text{anox}_{\text{sed}} )</td>
<td>Normalized to present</td>
</tr>
<tr>
<td>( W_{\text{ox}} )</td>
<td>( W_{\text{ox,0}} = 3.75 \times 10^{12} ) mol/year</td>
</tr>
<tr>
<td>( \text{EP} )</td>
<td>( \text{EP}_{0} = 2.25 \times 10^{15} ) molC/year</td>
</tr>
<tr>
<td>( \text{phosw} )</td>
<td>( \text{phosw}_{0} = 3.675 \times 10^{10} ) molP/year</td>
</tr>
<tr>
<td>( \text{mopb} )</td>
<td>( \text{mopb}_{0} = 1.5 \times 10^{15} ) molP/year</td>
</tr>
<tr>
<td>( \text{capb} )</td>
<td>( \text{capb}_{0} = 1.5 \times 10^{10} ) molP/year</td>
</tr>
<tr>
<td>( \text{fepb} )</td>
<td>( \text{fepb}_{0} = 0.6 \times 10^{10} ) molP/year</td>
</tr>
</tbody>
</table>
TABLE 3  Fluxes and corresponding isotopic weighting factors from Bjerrum and Canfield’s methane-feedback model

<table>
<thead>
<tr>
<th>Flux</th>
<th>Isotopic weighting factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboyante weathering influx carbw</td>
<td>$\delta_{\text{carbw}} = \delta_w = 2%_o$</td>
</tr>
<tr>
<td>$\text{carbw} = 0.81(1 + 0.087(T - T_0)) (\sqrt{\frac{M_{\text{DIC},0}}{M_{\text{DIC}}}})_{\text{carbw}}$</td>
<td></td>
</tr>
<tr>
<td>$T_0 = 15^\circ C \equiv 288.15^\circ K$, $\text{carbw}<em>0 = 13.35 \times 10^{12} \text{ mol/year, } M</em>{\text{CO}_2,0} = 7.64 \times 10^{16}$ mol</td>
<td></td>
</tr>
<tr>
<td>$\text{mccb} = \frac{M_{\text{DIC}}}{M_{\text{DIC},0}}$, where $M_{\text{DIC},0} = 192 \times 10^{16} \text{ mol and mccb}<em>0 = \text{B}</em>{\text{carbw}0}$</td>
<td></td>
</tr>
<tr>
<td>$\delta_{\text{carbw}} = \delta_{\text{DIC}} + 1 - \Delta_c$, where $\Delta_c = 1.2%_o$</td>
<td></td>
</tr>
<tr>
<td>Export production EP</td>
<td>$\delta_{\text{carbw}} = \delta_{\text{DIC}} - \epsilon_p - \Delta_{\text{DIC-CO}_2}$</td>
</tr>
<tr>
<td>$\text{EP} = \text{EP}_0 \left( \frac{P}{P_0} \right)$</td>
<td></td>
</tr>
<tr>
<td>where $\text{EP}_0 = 1.824 \times 10^{17}$ and $P_0 = 0.1 \mu\text{mol/kg}$</td>
<td></td>
</tr>
<tr>
<td>Marine organic carbon burial mccb</td>
<td>$\delta_{\text{mccb}} = \delta_{\text{DIC}} - \epsilon_p$</td>
</tr>
<tr>
<td>Modified to mccb given by (4), (5) and (6)</td>
<td></td>
</tr>
<tr>
<td>Aerobic $R_{\text{meth}} = \text{EP}(1 - \gamma)(1 - \text{anox}<em>{\text{ocean}})$ anaerobic non-methanogenic $R</em>{\text{anox}} = \text{EP}(1 - \gamma)(1 - f_{\text{ac}})$ and methanogenic $R_{\text{meth}}' = \text{EP}(1 - \gamma) \cdot \text{anox}<em>{\text{sed}}$ $f</em>{\text{ac}}(1 - \gamma)$ remineralization of dissolved organic carbon and methanogenic fraction $f_{\text{ac}} = 1 - \frac{\Delta_{\text{CH}_4}}{\epsilon_p}$ and $\gamma = 0.5$ is the CH$_4$:CO$<em>2$ ratio for methanogenesis, and anox$</em>{\text{sed}}$ is given by (8)</td>
<td></td>
</tr>
</tbody>
</table>

(a). We consider a "conventional" $f$-ratio formulation (in which positive isotopic excursions in the carbonate carbon pool result from removal of $^{13}$C-depleted carbon through the organic burial flux), and use this formulation to calculate the final $\delta^{13}$C-carbonate value. The $f$-ratio formulation is used:

i. In isolation, within a conventional carbon cycle model formulation (e.g., Kump & Arthur, 1999), in which $\delta^{13}$C-carbonate varies due to changes in the organic burial fraction $f_{\text{org}}$ only $\delta = \delta_{\text{in}} + \epsilon_p f_{\text{org}}$ (where $\delta_{\text{in}}$ is the isotopic composition of the combined input from weathering and degassing, and $\epsilon_p$ is the photosynthetic fractionation factor, see Appendix 1, equation (23)).

ii. In combination with a substantial authigenic carbonate carbon sink, such that $\delta^{13}$C-carbonate varies with both $f_{\text{org}}$ and the fraction $f_{\text{ac}}$ of authigenic carbonate burial with a $^{13}$C-depleted isotopic signature (Schrag et al., 2013). The latter fraction $f_{\text{ac}}$ is either parameterized or is a function of bioturbation through sediment anoxia $f_{\text{ac}} = \text{anox}_{\text{sed}} = \text{MAX}[\text{anox}_{\text{ocean}} \cdot 1 - \frac{\Delta_{\text{CH}_4}}{\epsilon_p}]$ (where MAX denotes "the maximum value of" and $f_{\text{biot}}$ is the normalization value necessary to balance modern day fluxes, see Appendix 1 equation (28)), and within the authigenic formulation this sediment-specific anoxia contributes to the system's susceptibility to authigenic carbonate precipitation. This semiquantitative parameterization of $f_{\text{ac}}$ does admittedly introduce a degree of error, but the real value of this term is uncertain in any case, and a range of values around the ballpark of $f_{\text{ac}} = 0.3-0.5$ are compatible with slight positive values of $\delta^{13}$C-carbonate depending on the organic burial fraction and other model parameters. The key point is that, a higher value for $f_{\text{ac}}$ corresponds, at steady state, to more $^{13}$C-depleted carbon being removed from the system (see Appendix 1 for more details).

iii. In combination with an ocean crust carbonation (OCC) scenario (Bjerrum & Canfield, 2004), in which $\delta^{13}$C-carbonate varies with $f_{\text{org}}$ and with the fraction $\lambda$ of inorganic carbon burial accounted for by the OCC process (and also carrying a $^{13}$C-depleted signature). The focus for this formulation is the isotopic difference $\Delta_{\text{CH}_4}$ between OCC-derived carbonates and the DIC-equilibrated marine carbonate precipitated closer to sea level. This difference is thought to be an increasing function of degradation of organic carbon at depth, based on the premise that the DIC that feeds into OCC is $^{13}$C-depleted because it is organic in origin and derives from such degradation. Here, we hypothesize that bioturbation qualitatively increased the proportional contribution of the shelf to total marine remineralization of organic matter, reducing the contribution from remineralization at depth, thus reducing $\Delta_{\text{CH}_4}$. We tentatively speculate that the modern circumstances in which very little shelf-derived organic carbon reaches the deep ocean (Martin, Knauer, Karl, & Broenkow, 1987; Wakeham, Lee, Hedges, Hernes, & Peterson, 1997) need not have been applicable prior to the existence of bioturbation's dramatic increasing impact (Reimers & Suess, 1982) on organic carbon remineralization in shelf sediments (discussed further below). We therefore write: $\Delta_{\text{CH}_4} = \Delta_{\text{CH}_4}^{\text{early}} + (\Delta_{\text{CH}_4}^{\text{late}} - \Delta_{\text{CH}_4}^{\text{early}}) \cdot \frac{f_{\text{org}}}{f_{\text{sed}}}$ where $\Delta_{\text{CH}_4}^{\text{late}}$, $\Delta_{\text{CH}_4}^{\text{early}}$ are threshold values from the original model, expressing how the isotopic difference between sea level and crustal-precipitated carbonates has decreased over Earth's history. (See equations [30] and [31]).

5. We derive an approximation to a dynamical model of a methane greenhouse induced climatic feedback sequence that leads to a transient, negative $\delta^{13}$C-carbonate excursion (Bjerrum & Canfield, 2011). This formulation centres on the idea that the reduction in sediment anoxia by bioturbation reduces the baseline level of methanogenesis on which this feedback sequence depends. We approximate this model analytically, and define a quasi-steady
state situation, at the inflection point characterizing the peak of the climate perturbation’s impact on the carbon cycle (see Appendix 1). The δ13C_{carbonate} excursion that results is sensitive to bioturbation via remineralization and sediment anoxia, (1) and (2) above, (see equations [55] and [56]) Table 3.

6. We include δ13C_{carbonate} results both in the presence and absence of a bioturbation-induced organic phosphorus sink hypothesized (Boyle et al., 2014) in previous work. In the presence of this feedback, marine organic phosphorus burial mopb is an increasing function of both bioturbation and marine organic carbon burial \( B_{org} \cdot mopb = F(B_{org} \cdot f_{biot}) \). In the absence of bioturbation, the organic phosphorus burial flux scales by a fixed constant with the organic carbon burial flux \( mopb = F(B_{org}) \). (Note that inclusion of this feedback is not essential to our main arguments about δ13C_{carbonate}).

7. We derive an analytic approximation of a mixed local microcosm scenario, which attributes aspects of δ13C_{carbonate} negative excursions to the influx of a 13C-depleted carbon source derived from weathering of organic matter on the land surface (Johnston et al., 2012). In this formulation, local δ13C_{carbonate} is impacted upon by remineralization of organic material, both from this exogenous source and from “normal” (i.e., endogenous) sedimentary organic carbon. In our modification of this scenario, the fraction of remineralization that is derived from the exogenous source is proportional to \( f_{biot} \) because we argue that this exogenous source will necessarily be more resistant to degradation than sedimentary carbon, therefore more likely to remain present in the microcosm for a sufficient time to influence local δ13C_{carbonate} (see equation [59] and associated discussion). (This final formulation is peripheral to our general arguments about the global carbon cycle, but we include it because such models are an important conceptual category within discussion about the Precambrian–Cambrian boundary δ13C_{carbonate} literature).

8. We conduct a wavelet analysis of compiled δ13C_{carbonate} data from the literature, by which we derive the most appropriate fit for the period and wavelength of the observed isotopic fluctuations (see equation [62]). This provides empirical grounding for our general premise that the amplitude and period of fluctuation in δ13C_{carbonate} declines from roughly the Neoproterozoic–Cambrian boundary onwards.

We emphasize that because we are comparing multiple separate model formulations, each with their own set of uncertainties in terms of unconstrained parameters, our aim is a semiquantitative characterization of the potential impact of bioturbation on long-term trends in the δ13C_{carbonate} record. We make no claim to rigorously reproduce a quantitatively accurate dynamical picture of bioturbation and δ13C_{carbonate} and their coevolution over time. Rather, we attempt a systematic conceptual analysis of how bioturbation might be expected to have modified the carbon isotope record, under different hypothetical assumptions about its underlying dynamics.

3 | RESULTS

Figure 1 plots compiled δ13C_{carbonate} data from several published papers (see Appendix 1) for the interval from 900 Ma to present, against a wavelet power spectrum fit, which we used to explore the data for periodicity (see Appendix 1). The wavelet analysis illustrates a clear qualitative decline in both amplitude and period of δ13C_{carbonate}.

![Figure 1](image-url)
excursions after about the Precambrian–Cambrian boundary. The Neoproterozoic $\delta^{13}C_{\text{carbonate}}$ record exhibits higher amplitude, longer period fluctuations than that of the Cambrian, and a damping in this happens from about 550 Ma onwards. The general principle of a dampening in carbon isotope variation from the Cambrian is consistent with the first-order trends, and other more comprehensive statistical analyses (e.g., Krissansen-Totton et al., 2015).

### 3.1 Steady state results

Figure 2 shows steady state results illustrating the relationship between $f_{\text{biot}}$ and $\delta^{13}C_{\text{carbonate}}$ This relationship is compared for various different model scenarios, prescribed values for the modern day organic carbon burial efficiency, and in the presence and absence of a dynamical marine phosphorus cycle limiting new production. Positive steady state $\delta^{13}C_{\text{carbonate}}$ values result from the preferential burial of $^{13}C$-depleted carbon by marine organic carbon burial either in isolation ($f$-ratio scenario, left) or in combination with authigenic carbonate precipitation (middle) or carbonatization of the ocean floor (right). We discuss preliminary cases and caveats before dealing with the main results.

#### 3.1.1 Bioturbation and remineralization of organic carbon

Increased $f_{\text{biot}}$ translates into lower net organic carbon burial efficiency $\zeta$ (by equation [10], i.e., the impact of bioturbation on remineralization) for a given level of export production. When bioturbation affects only remineralization, and hence organic carbon burial efficiency (dashed
Bioturbation begins to have a significant impact on burial efficiency, thus $\delta^{13}C_{\text{carbonate}}$ at a lower value of $f_{\text{biot}}$, when the prescribed modern day burial efficiency $\zeta_0$ is lower (compare the blue and red dashed line in Figure 2a and c). This is because the presumed modern day organic carbon burial efficiency is used to calculate the modern export production flux (equation [9]) and therefore the pre-bioturbation organic carbon burial efficiency $\zeta_{\text{prebiot}}$ (equation [8]). Both of these quantities are very difficult to constrain for deep time, so to some extent, the difference between the blue (lower limit modern organic carbon burial efficiency $\zeta_0 = 0.003$) and red (extreme upper limit modern organic carbon burial efficiency $\zeta_0 = 0.25$) can be considered an artefact of the simplistic way in which we have balanced the organic carbon fluxes. But the key point is that the qualitative relationship between $\delta^{13}C_{\text{carbonate}}$ (discussed in detail below) and $f_{\text{biot}}$ is not altered by this parameter choice, although it does alter the specific $\delta^{13}C_{\text{carbonate}}$ value that the model predicts.

### 3.1.2 Bioturbation and marine organic phosphorus burial

A bioturbation-induced phosphate sink leads to a decrease in marine phosphate concentration, which decreases production, thus organic carbon burial, and thus finally steady state $\delta^{13}C_{\text{carbonate}}$. As we have discussed elsewhere, the premise behind this hypothesized bioturbation-induced organic phosphate sink is that bioturbation exposes sediments to oxygen in the overlying waters and is therefore arguably a more direct control on many redox-sensitive sedimentary processes than oxygen levels per se. The basic empirical justification...
for this idea is the observation that bioturbated shales retain more phosphorus relative to carbon than do laminated ones (Anderson, Delaney, & Faul, 2001; Ingall, Bustin, & Van Cappellen, 1993). The idea that the physical activity of bioturbating fauna moves remineralized organic phosphate into the sediment where it is captured by microbial polyphosphate sequestration in a net sink is supported by spatially resolved diagenetic modelling (Dale, Boyle, Lent, Ingall, & Wallman, 2016). Nevertheless, the bioturbation-induced phosphate sink is not essential for the carbon-isotopic results that are our focus here.

Increased organic phosphorus burial leads, at steady state, to decreased marine phosphate concentration, therefore decreased marine organic carbon burial, therefore decreased oxygen (Betts & Holland, 1991; Holland, 1984; Lent & Watson, 2000). Decreased oxygen leads to increased ocean anoxia, which in turn reduces Fe-adsorbed phosphate burial, leading to a secondary increase in marine phosphate concentration in a net negative feedback (Ingall & Van Cappellen, 1990; Lent & Watson, 2000). This works in the opposite direction as the first-order impact of the bioturbation-induced phosphate sink, with a compensating impact on marine phosphate concentrations. The overall consequence is that the biogeochemical impact of a bioturbation-induced organic phosphorus burial sink is likely to have been a strong decrease in ocean-atmosphere oxygen levels, but only a weak decrease in marine phosphate concentrations (Boyle et al., 2014).

These feedbacks are illustrated by a comparison between the upper and lower rows in Figure 3. This figure depicts the global ocean-atmosphere oxygen and marine phosphate reservoirs, magnitude of relevant fluxes, and the $\delta^{13}C_{\text{carbonate}}$ values predicted. The increase in marine organic phosphorus burial associated with introduction of the bioturbation-induced organic phosphorus sink (lower row) triggers a substantial decrease in ocean-atmosphere oxygen and ocean phosphate. The subsequent stabilization of phosphate concentrations is due to a balancing decline in the other inorganic phosphorus burial fluxes (lower right panel, i.e., Figure 3b4). When bioturbation affects remineralization and sediment anoxia, but does not affect marine organic phosphorus burial, bioturbation actually causes a slight increase in marine phosphate concentrations (3A4, top right). This is because the oxygen consumption by bioturbation-induced remineralization increases ocean anoxia, decreasing Fe-adsorbed phosphate burial.

Crucially in terms of our focus here, the strength of bioturbation’s decreasing impact on $\delta^{13}C_{\text{carbonate}}$ is substantially enhanced by including a bioturbation-induced organic phosphorus sink, only in the $f$-ratio scenario, not the authigenic or carbonatization scenarios. This is because the latter two scenarios do not require changes in production or marine organic carbon burial to produce positive $\delta^{13}C_{\text{carbonate}}$ values, and instead depend upon sediment anoxia.

### 3.1.3 | Bioturbation, sediment anoxia and authigenic carbonate precipitation

In the authigenic scenario, more positive steady state $\delta^{13}C_{\text{carbonate}}$ values occur when the magnitude of the authigenic carbonate precipitation flux is greater, because this flux removes $^{13}C$-depleted carbon from the preserved record, leaving DIC-equilibrated marine carbonate proportionally $^{13}C$-enriched. Figure 2b shows how bioturbation reduces marine sediment anoxia, which decreases the authigenic carbonate flux (see equations [12], [27] and [28]), reducing the steady state $\delta^{13}C_{\text{carbonate}}$ value. This basic relationship is robust to parameter changes, and does not depend on whether or not the carbon fluxes are coupled to marine phosphate dynamics. The only exception to this general relationship occurs at very high levels of bioturbation $f_\text{biot} \rightarrow 1$, at which the oxygen decline caused by increased remineralization leads to a secondary increase in overall ocean anoxia, sediment anoxia and the final $\delta^{13}C_{\text{carbonate}}$ value. (The strength of this secondary effect is increased by including full oxygen and phosphate dynamics, compare the gradient of the solid and dashed lines on Figure 2b). Other $\delta^{13}C_{\text{carbonate}}$ values may result from our choice of parameters, particularly the authigenic fractionation factor $\epsilon_{\text{ac}} = 15$; for which other values are plausible (Schrag et al., 2013), but again the qualitative result is unaffected. The conceptual explanation of this result is simple; the authigenic flux depends on the build-up of carbonate alkalinity in anoxic sediments, the abundance of which bioturbation would qualitatively decrease.

### 3.1.4 | Bioturbation and ocean crust carbonatization

Figure 2c plots the relationship between $f_\text{biot}$ and steady state $\delta^{13}C_{\text{carbonate}}$ in the ocean crust carbonatization (OCC) scenario. The result is analogous to the authigenic scenario; increasing $f_\text{biot}$ decreases the steady state $\delta^{13}C_{\text{carbonate}}$ value across all parameter choices. Positive $\delta^{13}C_{\text{carbonate}}$ values, as in the authigenic scenario, result from increased removal of $^{13}C$-depleted carbon at increased levels of the OCC flux. Bioturbation decreases the isotopic difference between this flux and “normal” (DIC-equilibrated) carbonate (equations [31] and [32]), thus reduces the magnitude of the positive $\delta^{13}C_{\text{carbonate}}$ that the OCC flux causes. As with the other scenarios, as $f_\text{biot} \rightarrow 1, \delta^{13}C_{\text{carbonate}} \rightarrow 0$, with the curve of this relationship dictated by the choice of burial efficiency terms and the presence/absence of a bioturbation-induced organic phosphate sink. Again, the qualitative relationship is robust to parameter changes.

To reiterate, this formulation is based on two arguments; that carbonate derived from the OCC process is relatively $^{13}C$-depleted compared to surficial/DIC-equilibrated carbonates $|\Delta f| > 0$, and that bioturbation’s impact on remineralization may have contributed to a decline in this vertical isotopic difference over geologic time. OCC-derived rocks from the Archean (Veizer, Hoeffs, Lowe, & Thurston, 1989) exhibit a more negative $\delta^{13}C_{\text{carbonate}}$ than those deposited closer to the present, probably as a result of the accumulation of oxidation products at depth (Bjerrum & Canfield, 2004; Broecker & Peng, 1982; Smittenberg, Pancost, Hopmans, Paetzel, & Sinninghe Damsté, 2004). We stress that this formulation in particular is intended in a semiquantitative and exploratory spirit: The vertical isotopic gradient on which the OCC hypothesis depends is not observed in all sections (Fischer et al., 2009), and in the modern ocean, a very small proportion of the POC produced in the photic zone ends up on the ocean floor (Martin et al., 1987; Wakeham et al., 1997). Our key (speculative)
argument here is that the vertical isotopic gradient $\Delta_z$ was likely an increasing function of the proportion of total organic carbon remineralization occurring at depth, and by implication a decreasing function of the proportion occurring on the shelf, the latter being increased by bioturbation’s rise. Today, the small component of POC that does reach the ocean floor does so over a timescale of a few months (Deuser & Ross, 1980; Honjo, 1982), that is, relatively rapidly in comparison with the marine residence time of DOC of the order of ~4000-6,000 years (Bauer, Williams, & Druffel, 1992; Williams & Druffel, 1987). Furthermore, there is some evidence that deep ocean transfer of POC feeds into a locally highly concentrated pool of semi-labile DOC (Follet, Repeta, Rothman, Xu, & Santinelli, 2014). Consequently, we suggest that transfer of carbon from sea level to the vicinity of crustal spreading zones was conceivably more efficient in the ancient ocean than the modern one, prior to the onset of a significant bioturbation-driven remineralization sink in shelf sediments. We further note that the outstanding uncertainties as to the cause of the observed difference between $(\Delta_{s_{\text{late}}})$ and $(\Delta_{s_{\text{early}}})$ (i.e., an explanation as to why carbonatized rocks from the Archean (Veizer et al., 1989) exhibit a more negative $\delta^{13}C_{\text{carbonate}}$ than those deposited closer to the present) are not unique to this work.

3.2 | Approximation to a dynamical model: Bioturbation and a methanogenesis-driven feedback loop

As described above, we formulate a simple (zero dimensional, analytic) approximation to the various steps in the feedback sequence (equation [33], and as described above), in which sediment anoxia is a decreasing function of bioturbation $f_{\text{biot}}$ (equation [12]). The basis of the feedback loop (i.e., in the original model, aside from any effect of bioturbation) is summarized by the original authors as “photooxidation of DOC results in a high flux of CO to the atmosphere, which lowers the concentration of the hydroxyl radical $\cdot OH$, which in turn increases the residence time of methane in the atmosphere. This increase in methane residence time is greater than would be accomplished by just an increase in the methane flux. The end result is higher atmospheric methane concentrations. Greenhouse warming from the methane increases surface temperature and melts glacial ice, which combine to produce a negative $^{18}O$ anomaly in precipitated carbonates. The higher temperatures also accelerate the weathering of continental rocks, drawing down atmospheric CO$_2$. Lower CO$_2$, in turn, reduces the isotopic fractionation between DIC and organic carbon during primary production, while the $\delta^{13}C$ composition of organic carbon is buffered by the large DOC reservoir.” (Bjerrum & Canfield, 2011). The crucial (again qualitative) “tweak” that we propose may be relevant to this feedback sequence is that methanogenic oxidation of organic matter depends on sediment anoxia and is therefore likely to be a decreasing function of bioturbation. Again, quoting the original authors “the extent to which organic carbon oxidation proceeds by methanogenesis should be related to the volume of anoxic waters and sediments, which is a function of atmospheric oxygen concentration and other factors.” Our suggestion here is that bioturbation was a crucial such additional factor.

Figure 4 shows a compilation of results expressing the magnitude of $\delta^{13}C_{\text{carbonate}}$ excursion triggered by the feedback loop.
against $f_{\text{biot}}$, for different prescribed magnitudes (see legend) of the initial perturbation (a decline in atmospheric -OH radicals, see methods). For larger parameterized initial magnitudes of the perturbation (-OH decrease) and resultant atmospheric CH$_4$ increase, the sensitivity to bioturbation is greater (i.e., the gradients of the lines are steeper). This is due to the multiplicative nature of the feedbacks involved. Increasing bioturbation reduces the capacity of sediments to produce CH$_4$ because it leads to increased sediment oxygenation. The magnitude of the increase in atmospheric CH$_4$ concentration and residence time that is associated with this feedback sequence is a function of sedimentary methanogenesis. The ultimate effect of this CH$_4$ increase on the final (negative) $\delta^{13}$C$_{\text{carbonate}}$ excursion is significant, because this increase occurs early in the feedback sequence and alters the magnitude of each of the subsequent stages (see Appendix 1). Again, despite quantitative uncertainties in the actual $\delta^{13}$C$_{\text{carbonate}}$ change produced, the key result is simple; increased bioturbation reduces the magnitude of the negative $\delta^{13}$C$_{\text{carbonate}}$ excursion caused by this feedback loop.

### 3.3 Local isotopic microcosm model: Bioturbation and an exogenous, terrestrial organic carbon source

The final set of results, Figure 5, refer to a localized shallow shelf microcosm scenario involving input of terrestrial, organic-derived, $^{13}$C-depleted carbon (Johnston et al., 2012). This scenario is qualitatively different from the others described, because it refers to the $\delta^{13}$C$_{\text{carbonate}}$ of a local site, rather than the global DIC-equilibrated average. Although it is peripheral to our main arguments, we include this scenario so as to represent the category of Neoproterozoic $\delta^{13}$C$_{\text{carbonate}}$ models that attribute negative $\delta^{13}$C$_{\text{carbonate}}$ values to such local phenomena (based on the lack of isotopic covariance

**FIGURE 5** The impact of bioturbation on the local isotopic composition of a mixed carbon pool, impacted upon by a $^{13}$C-depleted pool derived from the land surface. The isotopic composition of this pool is parameterized (legend). Remineralization from this organic carbon impacts the DIC pool (Y-axis), and the relative impact of the exogenous pool increases with increasing bioturbation (X-axis) because bioturbation increases remineralization of endogenous carbon.
between $\delta^{13}C_{carbonate}$ and $\delta^{13}C_{organic}$ in some sections exhibiting negative isotopic excursions, see Appendix 1). We formulate this hypothesis in terms of bioturbation on the basis of two key arguments. First, increasing bioturbation increases organic carbon remineralization in the focal microcosm. Second, the exogenous terrestrial organic carbon pool is more resistant to remineralization than "normal" endogenous sedimentary organic carbon (equations [59] and [60]); therefore, bioturbation's effect on endogenous organic matter may be stronger. For organic material to trigger negative $\delta^{13}C_{carbonate}$ excursions in the microcosm, it must be sufficiently resistant to degradation to concentrate within it, but not so recalcitrant that it is not broken down, and is thus unable to impact upon $\delta^{13}C_{carbonate}$. We argue that bioturbation, by enhancing remineralization of endogenous organic material, would have enhanced the concentration of such an exogenous source of organic carbon.

Figure 5 depicts the local $\delta^{13}C_{carbonate}$ within this scenario, which is impacted upon by remineralization of both endogenous, DIC-equilibrated organic carbon, and exogenous $^{13}$C-depleted, organic carbon. The total organic proportion of the microcosm is set by $f_{org}$, three different values of which are depicted (note this local organic fraction is distinct from the global $f$-ratio discussed above). Increased remineralization of organic matter leads to an input of $^{13}$C-depleted carbon to the DIC pool, lowering $\delta^{13}C_{carbonate}$. Some of this remineralization is made up by breakdown of the exogenous $^{13}$C-depleted organic pool derived from terrestrial input, which significantly lowers $\delta^{13}C_{carbonate}$. The specific isotopic composition of this exogenous input is parameterized (legends) such that the proportion of remineralization that is derived from the exogenous (highly $^{13}$C-depleted) carbon pool increases with increasing bioturbation $f_{biot}$ (equations [59] and [60]). As a result, larger $f_{biot}$ values result in more negative local $\delta^{13}C_{carbonate}$ values. To reiterate, this result is a consequence of our assumption (above) that bioturbation-induced remineralization will have a stronger impact on endogenous than exogenous $^{13}$C-depleted organic carbon (because the latter must necessarily be resistant to degradation in order to survive the weathering process). Crucially, in this scenario, bioturbation's effect would be to enhance the susceptibility to (in this case, local, negative) isotopic excursions—in direct contrast to the other results.

4 | DISCUSSION

Our results provide a broad-brush survey of how the evolution of bioturbation may have impacted upon the $\delta^{13}C_{carbonate}$ record, for various different existing models seeking to explain large Precambrian isotopic fluctuations. Into each of these models, we have incorporated a semiquantitative formulation of how (we propose) bioturbation can be assumed to have altered the marine carbon cycle. Bioturbation potentially causes (i) increased total organic carbon remineralization, (ii) increased oxygenation of marine sediments, (iii) a decline in the isotopic difference between marine DIC-carbonate and carbonate derived from the OCC process. We have not specifically focused on either negative or positive $\delta^{13}C_{carbonate}$ excursions, but rather on the mechanisms driving fluxes containing a disproportionate amount of $^{13}$C-depleted carbon, which can be preferentially removed from the preserved record, leading to positive $\delta^{13}C_{carbonate}$ values, or periodically included within it, leading to negative $\delta^{13}C_{carbonate}$. In general, our aim has been to examine the extent to which each model scenario can, in combination with bioturbation, explain the observed dampening of $\delta^{13}C_{carbonate}$ variability (Figure 1) across the Neoproterozoic–Cambrian boundary.

Our results are, at their core, semiquantitative and comparative. Thus, it would be inappropriate to claim that our results accurately predict a specific, unique $\delta^{13}C_{carbonate}$ value for a given level of bioturbation. Furthermore, the categorical nature of the bioturbation index data and the inherent incompleteness of the sedimentary record makes a global quantitative representation of bioturbation against time an unrealistic aim. With these provisos stated, however, we argue that our results strongly support the plausibility of the following conclusions:

1. The exposure of sediments to oxygenated waters by bioturbation could have reduced the susceptibility to $\delta^{13}C_{carbonate}$ excursions caused by mechanisms reliant upon sediment anoxia (e.g., authigenic carbonate precipitation, methanogenic DOC remineralization).

2. If bioturbation increased the proportion of organic carbon remineralization occurring on the shallow shelf, and if this ultimately lead to less organic matter breakdown in the deep oceans, it could conceivably have caused less $^{13}$C-depleted carbon to be available for incorporation into ocean crust carbonatization. Consequently, the evolution of bioturbation may have reduced the isotopic difference between OCC-derived carbonates and those from shallower environments, therefore decreased susceptibility to $\delta^{13}C_{carbonate}$ excursions associated with the OCC process.

3. The impact of bioturbation on remineralization of organic carbon could plausibly have had a negative impact on the organic carbon burial ratio $f_{org}$ but this is unlikely to have had a significant impact on the long-term $\delta^{13}C_{carbonate}$ record. This is because simultaneous balancing of carbon, oxygen and phosphorus budgets necessitates that at least some of the phosphate liberated by bioturbation-induced remineralization of organic matter feeds back into export production. If the previous hypothesis concerning a bioturbation-enhanced remineralization of organic matter feeds back into export production.

4. The core idea, that is, that bioturbation reduced susceptibility to subsequent $\delta^{13}C_{carbonate}$ excursions, sits most easily with the authigenic carbonate and/or methanogenic feedback loop hypotheses. This is because these scenarios depend upon sediment anoxia, and bioturbation-driven ventilation of sediments appears to be a robust way in which to explain the dampening in
δ¹³C_carbonate fluctuation observed from the Cambrian onwards, relative to the Neoproterozoic.

5. We find the idea that local, negative δ¹³C_carbonate excursions were caused by input from weathering of an exogenous, isotopically light, organic carbon source difficult to reconcile with our arguments. The fact that such a source must necessarily have been more resistant to remineralization than endogenous marine sediment organic carbon, implies that, if anything, bioturbation would enhance any local δ¹³C_carbonate excursions associated with it. This is inconsistent with the fact that such excursions become less frequent after the rise of bioturbation.

The relatively rapid quantitative spread of bioturbation after the appearance of the first trace fossils (reviewed by, e.g., Mangano & Buatois, 2014) is fully compatible with the hypotheses we present here and with the δ¹³C_carbonate record. The “delayed mixing” scenario (Tarhan et al., 2015) would necessitate a period in which bioturbation was limited relative to modern intensities, but Neoproterozoic-scale δ¹³C_carbonate fluctuations, incorporating negative values, nevertheless did not occur, due to carbon cycle changes unconnected to bioturbation (which is also entirely plausible). The key argument we make here is of a bioturbation-driven reduction in susceptibility to Precambrian-scale δ¹³C_carbonate fluctuations, across the immediate Neoproterozoic–Cambrian boundary. We do not propose that the rise of bioturbation acted as a “magic bullet” that suddenly rendered such fluctuation impossible. The strength of bioturbation’s influence likely increased over time, to an extent that will be revealed by future high-resolution constraints on bioturbation’s quantitative spread.

We think it may be productive to test a prediction that follows from our arguments: that there will exist a systematic and global-scale negative correlation between the quantitative extent to which marine sediments are bioturbated, and the amplitude and period of fluctuation in δ¹³C_carbonate. We argue that the presence of such a correlation is already supported by existing data, (albeit at a coarse level), and hope that this contribution may motivate the experimental community to conduct such across-referencing exercise.

We tentatively argue that either the methane-feedback loop (Bjerrum & Canfield, 2011) and/or the authigenic carbonate scenario (Schrag et al., 2013) are probably the most plausible explanations for the unique trends in the late Precambrian δ¹³C_carbonate record. Furthermore, although the authigenic carbonate scenario refers to steady state and the methanogenesis-feedback to a dynamical instability in climate, strictly speaking these two mechanisms may have both operated at different times. However, to some extent, the reliance of these scenarios on biogeochemical processes that have been relatively invariant over Earth’s history means that they do not easily lend themselves to an explanation of directional change in δ¹³C_carbonate. The authigenic scenario explicitly attributes the decline in excursions to biological irrigation of sediments, and the methane-scenario entails a decline in the occurrence of the feedback loop as the oxygen and sulphate reservoirs increased in size. It is clear that bioturbation could provide a direct mechanism by which the irrigation of sediments could occur and could introduce oxygen (and sulphate) directly to the site of ¹³C-depleted carbon build-up. Thus, perhaps it was ultimately evolutionary innovation that introduced any directionality.

There is a natural convergence between our arguments and those of a study (published during the final stages of this manuscript’s preparation), attributing the decline in δ¹³C_carbonate perturbation amplitude to a change in the typical depth/aerial extent of oxygen minimum zones during Earth history (Bachan et al., 2017). This work proposed that large, shallow oxygen minimum zones (OMZs) effectively render anoxia-driven feedbacks on marine phosphate cycling (Van Cappellen & Ingall, 1994) more sensitive to sea level changes. Shallow OMZs (with less areal impact on sedimentary burial due to the nature of the hypsographic curve) potentially cause a given sea level change to have increased impact on marine shelf anoxia, with impact on both organic matter and marine phosphate burial fluxes. This ultimately means that shallow OMZs lead to high amplitude/duration δ¹³C-carbonate fluctuation for a given weathering-derived nutrient input to the ocean (Bachan et al., 2017; Lau et al., 2016). This line of reasoning attributes the decline in δ¹³C_carbonate fluctuation amplitude to a movement over Earth history of typical OMZ position into deeper waters. We propose that the spread of bioturbing fauna caused a directly analogous deepening of the position of non-ventilated sediments, by oxygenating the shallow sediments they inhabited.

The single most striking directional trend in the δ¹³C_carbonate record is not a change in the global average, but the dampening of fluctuation in the Phanerozoic geochemical record relative to the Proterozoic. In the broadest sense therefore, perhaps Darwin’s seemingly mundane observation about earthworms, and the “astonishing number of half-decayed leaves which they draw into their burrows to a depth of 2 or 3 in” (Feller et al., 2003) anticipated important effects that scale all the way up the global carbon cycle, exerting a qualitative geochemical change of the sort that Vernadsky might have regarded as uniquely biological.

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AUTHOR CONTRIBUTIONS

RB designed and performed research and wrote the manuscript with significant help and input from all co-authors. TWD performed wavelet analysis and data compilation for Figure 1.


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APPENDIX 1

A1 | FULL METHODS AND MODEL DERIVATIONS

In this section we discuss the details of each carbon isotope model scenario, and present a hypothesis for how bioturbation could have reduced the system’s predisposition to isotopic excursions in each case.

A1.1 | Quantifying the impact of bioturbation on the remineralization of organic carbon

The earliest bioturbating animals must have inhabited the sediments of the shallow continental shelf, which in the modern ocean support 89% of the remineralization and 91% of the burial of particulate organic carbon (Dunne & Sarmiento, 2005). The globally integrated shelf sediment organic carbon remineralization flux can be bracketed between (Sarmiento & Gruber, 2006).

\[ 1.0 \times 10^{14} \leq R_{\text{sed}} \leq 2.66 \times 10^{14} \text{molCyr}^{-1} \]  

Different numbers for the above estimates are also in the literature (e.g., Dunne, Sarmiento, & Granadesikan, 2007), but do not qualitatively alter our results. Various estimates of the proportion \( \varepsilon_r \) of this respiration flux attributable to bioturbation range between 0.44 \( \leq \varepsilon_r \leq 0.9 \) (Ingall & Van Cappellen, 1990; Reimers & Suess, 1982). Multiplying \( R_{\text{sed}} \varepsilon_r \) gives a “ballpark” estimate of the bioturbation-associated sedimentary organic carbon remineralization flux as between:

\[ 4.4 \times 10^{13} \leq R_{\text{bikurb}} \leq 1.95 \times 10^{14} \text{molCyr}^{-1} \]  

The balance between remineralization, export production and organic carbon burial in the global marine carbon cycle can be represented as:

\[ \text{EP} \cdot \zeta = B_{\text{org}} \]  

Where EP is the export production flux leaving the photic zone (i.e., the difference between net primary production and photic zone respiration), \( B_{\text{org}} \) is the global organic carbon burial flux (both of
which are in units of moles carbon per year), and $\zeta$ is the global organic carbon burial efficiency. Estimates of the present day value of this burial efficiency term from global mass balances are between (Betts & Holland, 1991; Holland, 1984):

$$0.002 \leq \zeta_0 \leq 0.003$$  \hspace{1cm} (6)

But much higher values, in the region of $0.05 \leq \zeta_0 \leq 0.1$ are observable in some non-euxinic marine sediments (Canfield, 1993) and it is entirely plausible that the organic burial efficiency may have varied substantially over the Precambrian-Cambrian boundary (perhaps more than at any other period of Earth history), in particular if oxygen levels were significantly lower than present day. Consequently, in our numerical simulations, we examine the sensitivity of the results to two extreme limiting case values $\zeta_0 = 0.003$ and $\zeta_0 = 0.25$ (although the former, lower value is likely far more representative of the global average). We estimate a ballpark figure for the organic carbon burial efficiency prior to the rise of bioturbation, by taking numbers from the modern system for a hypothetical case, in which all of the bioturbation-induced remineralization $R_{\text{bioturb}}$ is instead lumped into the burial flux, so that the pre-bioturbation organic carbon burial efficiency is:

$$\zeta_{\text{prebiot}} = \frac{B_{\text{org},0} + R_{\text{bioturb}}}{\text{EP}_0}$$  \hspace{1cm} (7)

Where the zero subscript denotes present day value for marine organic carbon burial $B_{\text{org},0} = 6.65 \times 10^{12}$ molC yr$^{-1}$ (Lasaga & Ohmoto, 2002) and export production flux for steady state:

$$\text{EP}_0 = \frac{B_{\text{sed}}}{\zeta_0} = 2.22 \times 10^{15}$ molC yr$^{-1}$  \hspace{1cm} (8)

Note that when we give results for different values of the modern day organic carbon burial efficiency $\zeta_0$ (see below), this merely acts as a scaling factor that, in effect, sets the export production flux (8) and pre-bioturbation burial efficiency (7), but does not alter the underlying dynamics (or the qualitative results, see Discussion in main text). This gives a rough estimate for the pre-bioturbation burial efficiency in the range $0.023 \leq \zeta_{\text{prebiot}} \leq 0.091$. Alternatively, if we take some empirical (Dunne & Sarmiento, 2005; Sarmiento & Gruber, 2006) estimates giving larger values for the export production fluxes $\text{EP}_0 = 5.42 \times 10^{14}$ molC yr$^{-1}$ and $B_{\text{org},0} = 2.167 \times 10^{13}$ molC yr$^{-1}$, we get the much larger range $0.121 \leq \zeta_{\text{prebiot}} \leq 0.399$. Clearly, there is a huge range in this global, pre-bioturbation burial efficiency and it is impossible to constrain the parameter with reliability over these timescales. We select (admittedly somewhat arbitrarily) the average of these second two values $\zeta_{\text{prebiot}} = 0.2605$ for the upper limit baseline burial efficiency value, so as to examine the maximum impact of a high burial efficiency, pre-bioturbation ocean. The overall organic carbon burial efficiency used in the model is:

$$\zeta = \zeta_{\text{prebiot}} \cdot (1 - f_{\text{biot}}) + \zeta_{\text{biot}} \cdot f_{\text{biot}}$$  \hspace{1cm} (9)

Where, as mentioned above, $f_{\text{biot}}$ is the proportion of the global organic carbon burial flux that occurs in bioturbated sediments. We constrain the post-bioturbation burial efficiency $\zeta_{\text{biot}}$ to be less than or equal to the baseline modern day burial efficiency $\zeta_{\text{biot}} \leq \zeta_0$, with $\alpha = .9$ (and $\zeta_0 = 0.003$) unless otherwise stated, so as to be consistent with (9) equal to $\zeta_0$ (i.e., for present day mass balance) creates the requirement that:

$$f_{\text{biot},0} = \frac{\zeta_0 - \zeta_{\text{prebiot}}}{\zeta_{\text{biot}} - \zeta_{\text{prebiot}}}$$  \hspace{1cm} (10)

for modern day organic carbon burial mass balance. This provides one constraint on the modern day bioturbated fraction $f_{\text{biot},0}$ (i.e the constraints imposed by as calculated by the organic carbon burial efficiency). Another constraint on $f_{\text{biot},0}$ is provided by the need to balance the modern day phosphorus burial fluxes (see below). Finally, it is worth remembering that even if global remineralization was much lower (organic burial efficiency much higher) prior to the evolution of bioturbation, its upper limit is constrained by the ratio of phosphate (which limits production) to carbonate alkalinity (thus potential carbonate burial magnitude) in crustal rock (Junge et al., 1975). We cap the $f_{\text{ratio}}$ at $f_{\text{org,max}} \leq 0.3$, which is a generous overestimate of the $f_{\text{org,max}} \leq 0.125 \pm 0.06$ invoked by this crustal ratio (Saltzman & Thomas, 2012).

### A1.2 The impact of bioturbation on sediment anoxia

We argue in general, building on previous work (Boyle et al., 2015) that model feedbacks linking burial fluxes to marine redox state, were qualitatively strengthened by the rise of bioturbation; because it is bioturbation that actively exposed the sediments in which these burial fluxes occur to the oxygen levels of ambient seawater. Although global oxygen levels in themselves are also relevant, an undisturbed sediment below an oxygenated body of water will go anoxic within less than a centimeter of the boundary layer (Gundersen & Jorgensen, 1993), whereas bioturbation and bio-irrigation can introduce oxygenated water to at least 6–8cm (Pischedda et al., 2007; Rippey et al., 2007; Weissberge et al., 2009). Qualitatively speaking, after the rise of bioturbation, the uppermost marine sediments of the continental shelf must have experienced a qualitative increase in the degree of exposure to the overlying water. Assuming (merely) that the first bioturbating animals required oxygen this amounts to the qualitative proposition that sediments were systematically oxygenated. We express this by writing the anoxic fraction of shallow shelf sediments relative to present day:

$$\text{anox}_{\text{sed}} = \text{MAX} \left[ \text{anox}_{\text{ocean}}, 1 - \frac{f_{\text{biot}}}{f_{\text{biot},0}} \right]$$  \hspace{1cm} (11)

Where $\text{anox}_{\text{ocean}}$ is the fraction of the global ocean floor that is anoxic (calculated as a function of oxygen reservoir size and global remineralization demand, see below), and $f_{\text{biot},0}$ is, as above, the value
of $f_{biot}$ necessary for consistency between the present day marine organic carbon and marine organic phosphorus burial fluxes, $B_{org}$ and mopb, respectively (see below) and “MAX” obviously denotes the maximum of these two. Equation (11) shows that the global scale extent of shelf sediment anoxia cannot be less than that of the ocean as a whole (an oxygenated body of sediment below a completely anoxic water column is obviously ruled out), but it can be greater (sediments can be less well oxygenated than the overlying water column if bioturbation is less than the present level).

### A1.3 | Bioturbation, marine phosphate dynamics and constraining the modern day bioturbated fraction $f_{biot0}$

Marine organic phosphorus burial scales with marine organic carbon burial, divided by the net C:P stoichiometry of organic matter (Van Capellen & Ingall, 1994; Lenton & Watson, 2000). In previous work, we argued that this C:P stoichiometry is a function of bioturbation, due primarily to redox changes in microbial polyphosphate sequestration after the ventilation of sediments (Boyle et al., 2014). The premise behind this hypothesized bioturbation-induced organic phosphate sink is that bioturbation exposes sediments to oxygen in the overlying waters, and is therefore arguably a more direct control on many redox-sensitive sedimentary processes than oxygen levels per se. The basic empirical justification for this idea is the observation that bioturbated shales retain more phosphorus relative to carbon than do laminated ones (Anderson & Delaney, 2001; Inglal et al., 1993). The idea that the physical activity of bioturbating fauna moves remineralized organic phosphate into the sediment where it is captured by microbial polyphosphate sequestration in a net sink, is supported by spatially resolved diagenetic modelling (Dale et al., 2016). Nevertheless, the bioturbation-induced phosphate sink is not essential for the carbon-isotopic results that are our focus here.

Here, we include some simulations both with and without this bioturbation-induced organic phosphorus sink. In simulations with bioturbation-sensitive marine organic phosphorus mopb burial, this flux is a function of marine organic carbon burial $B_{org}$ via the carbon to phosphorus ratios for bioturbated $CP_{biot}$ and laminated $CP_{lam}$ sediments, the bioturbated fraction $f_{biot}$ and a phosphorus specific retention factor $\beta$:

$$mopb = B_{org} \left( f_{biot} \cdot \beta + \frac{1 - f_{biot} \cdot \beta}{CP_{lam}} \right)$$  \hfill (12)

In simulations without this feedback, mopb scales with $B_{org}$ by a fixed constant (see Table 2). Setting all the burial fluxes to their present-day values (denoted by the zero subscript, see Table 2; Lenton & Watson 2000), inserting (10) and solving for $\beta$:

$$\beta = \left( \frac{f_{biot} - f_{prebiot}}{f_{biot} - f_{prebiot}} \right) \cdot \left( \frac{mopb}{B_{org0}} \right) \cdot \left( \frac{CP_{lam} - CP_{biot}}{CP_{lam} \cdot CP_{biot}} \right)$$  \hfill (13)

$\beta$ thus represents the difference between the relative impact of bioturbation on the phosphorus and carbon burial fluxes, for steady state at present day. For $CP_{biot}$, $CP_{lam}$ taking values between 150, 3,900, or 700, 200, or 500, 250 respectively (Algeo & Ingall, 2007; Anderson et al., 2001; Ingall & Jahnke, 1994; Van Capellen & Ingall, 1994) works out as:

$$0.1283 \leq \beta \leq 0.313$$  \hfill (14)

Thus we formulate bioturbation’s impact on remineralization (10) and C:P burial stoichiometry (8), so as to be consistent with each other with present day fluxes. We select a value that is consistent with both these (independent) constraints and set $\beta = 0.23$, then use $f_{biot0} = 0.6$ as a normalization factor in (11). Thus, within model formulations in which bioturbation is less than this value, then sediments are increasingly anoxic.

In order to produce meaningful estimates of limiting nutrient concentrations, we use a box model of the coupled oxygen and phosphorus cycles (Lenton & Watson, 2000, also see Van Capellen & Ingall, 1994). The full model is described in the original papers, we simply list the equations and function definitions here. The time derivatives of the global marine phosphorus and atmosphere-ocean oxygen reservoirs (in moles), are, respectively:

$$\frac{dO_d}{dt} = B_{org} - W_{ox}$$  \hfill (15)

$$\frac{dp}{dt} = W_0 - mopb - capb - fepb$$  \hfill (16)

(See Table 2 and the original papers contain detailed flux definitions). The model was initialized at a fixed steady state, then numerically integrated by a Runge Kutta method in MATLAB. Note that in some simulations the phosphorus and oxygen cycles were held constant as a reference point, i.e., with (15) and (16) set to zero and the export production and organic carbon burial fluxes held constant at their present values (Table 1), so that only the carbon cycle equations (given below) affect the results.

### A1.4 | Steady state models of $\delta^{13}$C Carbonate

#### A1.4.1 | Organic carbon burial and the “f-ratio” (Kump & Arthur, 1999)

The removal of $^{13}$C-depleted carbon can be attributed to changes in the relative magnitude of the organic carbon burial flux (Kump & Arthur, 1999). Consider the total mass $M_C$ of dissolved inorganic carbon in Earth’s ocean-atmosphere $CO_2$ system, and assume that this pool (and the carbonate carbon that precipitates from it) has global average isotopic composition $\delta$. The time derivative of the isotopically weighted inorganic carbon pool is:
\[
\frac{d}{dt}(M_C \cdot \delta_C) = \delta_C \cdot \frac{dM_C}{dt} + M_C \cdot \frac{d\delta_C}{dt}
\]  
(17)

The time derivative \(\frac{dM_C}{dt}\) of the reservoir's mass is:

\[
\frac{dM_C}{dt} = F_{IN} - B_{carb} - B_{org}
\]  
(18)

Where \(F_{IN}\) is the combined input to the ocean DIC pool from the flux of gaseous CO\(_2\) from tectonic outgassing and aqueous CO\(_2\) from weathering of carbonate rock on the land surface, \(B_{carb}\) is the burial flux of carbonate carbon following the precipitation of calcium and magnesium carbonates in the ocean, and \(B_{org}\) is, as above, the burial flux of organic carbon. If the input, carbonate burial, and organic carbon burial fluxes have respective isotopic compositions of \(\delta_{IN}\), \(\delta_C\), and \(\delta_{org}\) (where \(\epsilon_P > 0\) is the isotopic difference between organic and carbonate carbon), then it is possible to write (17) with each flux weighted by its isotopic composition:

\[
\frac{d}{dt}(M_C \cdot \delta_C) = \delta_{IN} \cdot F_{IN} - \delta_C \cdot B_{carb} - (\delta_C - \delta_{org}) \cdot B_{org}
\]  
(19)

Substituting (18) into (17), then equating (17) and (19), and solving for \(\frac{d\delta_C}{dt} = 0\):

\[
\frac{d\delta_C}{dt} = \frac{1}{M_C} \cdot (\delta_{IN} - \delta_C) F_{IN} + \epsilon_P \cdot B_{org} = 0
\]  
(20)

Multiplying through by \(\frac{M_C}{F_{IN}}\), and noting that if the mass as a whole is at steady state \(\frac{dM_C}{dt} = 0\) then (by (18)), this means that the influx balances the combined burial fluxes, i.e., \(F_{IN} = B_{carb} + B_{org}\), which in turn means that \(\frac{\delta_{IN}}{\epsilon_P} = \frac{\delta_C}{\epsilon_P + \delta_{org}} = f_{org}\) (where \(f_{org}\) is the organic fraction of total carbon burial), which finally gives:

\[
\epsilon_P \cdot f_{org} = \delta_C - \delta_{IN}
\]  
(21)

This is one way of expressing the carbonate "lever rule", which describes the relationship between the organic burial fraction and the fractionation difference between organic and carbonate carbon (Kump & Arthur, 1999). An important implication of this relationship is that if the system is at steady state, then a graph of the isotopic composition of carbonate carbon \(\delta_C\), plotted against the organic fractionation factor \(\epsilon_P = \delta_C - \delta_{org}\) (i.e., the isotopic difference between organic and carbonate carbon), should have a slope given by the organic burial fraction \(f_{org}\), a premise that is relevant to diagnosing the unique behavior of the carbon isotope record during the Neoproterozoic (see text). From (18), the final steady state isotopic composition is:

\[
\delta_C = \delta_{IN} + \epsilon_P \cdot f_{org}
\]  
(22)

Where the fractionation factor is in the range:

\[
17 \leq \epsilon_P \leq 32.5
\]  
(23)

And the mantle input is about \(\delta_{IN} = -5\%\) (Freeman & Hayes, 1992; Krissansen-Totton et al., 2015; Kump & Arthur, 1999). Unless otherwise stated, we use the middle of these two limiting values \(\epsilon_P = 24.5\). The assumption of steady state carbonate carbon means that the carbonate carbon burial flux must balance that influx of carbonate from weathering of silicate and carbonate rocks on the land surface:

\[
B_{carb} = W_{sol} + W_{carb}
\]  
(24)

Which, using \(W_{sol} = 6.65 \times 10^{12}\) molyr\(^{-1}\) and \(W_{carb} = 13.35 \times 10^{12}\) molyr\(^{-1}\) gives \(B_{carb,0} = 2.0 \times 10^{13}\) molyr\(^{-1}\).

### A1.4.2 | Authigenic carbonate carbon precipitation
(Schrag et al., 2013)

The previously hypothesized \(^{13}\)C-depleted authigenic carbonate burial flux, discussed in key papers (Higgins et al., 2009; Schrag et al., 2013) prompted serious debate (Canfield & Kump, 2013) as to whether the impact on \(^{13}\)C(carbonate) from the organic carbon burial flux, and by implication the expected connection between increases in \(^{13}\)C(carbonate) and oxygen, has been over-estimated. These authors followed previous work (Bjerrum & Canfield, 2004) in postulating a conceptually neglected isotopically light carbon sink, other than the burial of organic matter. Authigenic carbonates are isotopically light (i.e., \(^{13}\)C-depleted) and form in anoxic microenvironments within sedimentary pore waters (as a result of alkalinity build via iron and sulphate reduction, e.g., through anaerobic oxidation of methane). Schrag et al. reasoned that because the formation of such microenvironments is inhibited by the presence of oxygen, then authigenic carbonate precipitation over Earth history was (a) more isotopically influential within the Precambrian's less oxygenated Earth system, and (b) that authigenic carbonate precipitation was (is) systematically biased to deeper shelf-slope sediments, relative to "normal" marine carbonate, in favor of "slope or deep base sections that are typically consumed or highly deformed during subduction" (Schrag et al., 2013). The same authors propose that formation of carbonate platforms was more likely in the anoxic oceans of the past, in which carbonate saturation was relatively homogeneous between the surface ocean and the deep (by contrast, in the oxygenated contemporary ocean, carbonate tends to precipitate near the surface but dissolve at depth as saturation declines).

Following the original authors, we define three specific isotopic fractionation factors. First, that associated with precipitation of marine carbonate carbon (assumed isotopically continuous with the dissolved inorganic carbon reservoir):

\[
\delta_{IN} = 2.0 \times 10^{13}\text{ molyr}^{-1}
\]
Second, the fractionation associated with photosynthesis $\varepsilon_p$ (as above), and third, the fractionation associated with authigenic carbonate precipitation, (set as a positive number that is subtracted from the isotopic composition of carbonate/DIC) $15 \leq \varepsilon_{ac} \leq 20$. We set $\varepsilon_{ac} = 15$ unless otherwise stated, then write an isotopically weighted mass balance (i.e., $\delta^{13}C_{in}$: $F_{in} = \delta^{13}C_{org} \cdot B_{org} + \delta^{13}C_{carb} \cdot B_{carb}$), assuming steady state ($F_{in} = B_{org} + B_{carb}$), therefore $F_{org} = \frac{F_{in} \cdot B_{org}}{B_{carb}}$, and dividing by $F_{in}$ we get $\delta^{13}C_{in} = \delta^{13}C_{org} \cdot f_{org} + \delta^{13}C_{carb} \cdot (1 - f_{org})$, exactly as described in the f-ratio scenario above. We follow the original authors in including the additional parameter $f_{sc}$, the fraction of the total inorganic carbonate burial flux that is authigenic carbonate precipitation, which means this mass balance becomes:

$$\delta^{13}C_{in} = (\delta_{c} - \varepsilon_{p}) \cdot f_{org} + (1 - f_{org}) \cdot ((\delta_{c} - \varepsilon_{mc}) \cdot f_{sc} + (\delta_{c} - \varepsilon_{mc}) \cdot (1 - f_{sc}))$$

Solving for the steady state $\delta^{13}C_{carbonate} = \delta_{c}$:

$$\delta^{13}C_{in} = \delta_{c} \cdot f_{org} - \varepsilon_{p} \cdot f_{org} + (1 - f_{org}) \cdot ((\delta_{c} \cdot f_{sc} - \varepsilon_{mc} \cdot f_{sc} + \delta_{c} \cdot (1 - f_{sc}) - \varepsilon_{mc} \cdot (1 - f_{sc}))$$

which gives: $\delta_{c} = \delta^{13}C_{in} + (\varepsilon_{p} \cdot f_{org} + (1 - f_{org}) \cdot (\varepsilon_{mc} \cdot f_{sc} + \varepsilon_{mc} \cdot (1 - f_{sc}))$

which (assuming (25) does indeed hold), gives simply:

$$\delta_{c}^{authigenic} = \delta^{13}C_{in} + \varepsilon_{p} \cdot f_{org} + (1 - f_{org}) \cdot \varepsilon_{mc} \cdot f_{sc}$$  (26)

(Where, obviously, the subscript “authigenic” refers to this model scenario as a whole, i.e., $\delta_{c}^{authigenic}$ is the global average $\delta^{13}C_{carbonate}$ when impacted upon by authigenic carbonate precipitation).

Although there is a dearth of evidence for systematic, geologically influential authigenic carbonates, and as such, the jury remains out on the validity of the hypothesis the relevance of hypsographic and diageneric factors would be consistent with an apparent lack of directionality in the average $\delta^{13}C_{carbonate}$ value over time. Importantly as regards to bioturbation, the authigenic scenario implicitly relies on a systematic oxygenation (or other loss) of the microenvironments conducive to authigenic carbonate precipitation after roughly 550 Ma (if it is to provide an explanation the cessation of isotopic fluctuations as well as its occurrence). As Schrag et al. state “fluctuations in the authigenic carbonate sink might have resulted from modest variations in surface redox, or evolutionary leaps such as the biological irrigation of sediments”. Here we hypothesize that the evolution of animal bioturbation provided this central evolutionary leap (and that the general principle of a qualitative change through animal-induced sediment oxygenation applies beyond the authigenic carbonate scenario specifically). We argue that the authigenic fraction of inorganic carbonate carbon burial $f_{sc}$, can be qualitatively approximated by the anoxic fraction of continental shelf marine sediments $f_{anox}$, and thus as a function of bioturbation, as defined above:

$$f_{sc} = f_{anox}$$

$$f_{anox} = \text{MAX} \left[ 0, \frac{\delta^{13}C_{anox} - \delta^{13}C_{DIC}}{\delta^{13}C_{DIC} - \delta_{anox}} \right]$$  (27)

In other words, if bioturbation is below present level, the sediments can potentially be more anoxic than the ocean floor as a whole, and within the authigenic formulation this sediment-specific anoxia contributes to the system’s susceptibility to authigenic carbonate precipitation.

A1.4.3 | Ocean crust carbonatization (Bjerrum & Canfield, 2004)

Ocean crust carbonatization (OCC) results from hydrothermal alteration of the ocean floor, leading to the precipitation of calcium carbonate in which the $\mathrm{CO}_2$ anion is ultimately derived from DIC. In Precambrian (but not more recent) rocks there is a difference between the isotopic composition of DIC-equilibrated carbonates deposited from surface waters on the shallow shelf, $\delta^{13}C_{carbonate} = 0$ and those resulting from OCC (and derived from the precipitation of deep ocean bicarbonate) $-5 \leq \delta^{13}C_{carbonate}^{OCC} \leq -3$, a vertical isotopic difference that persists to a lesser extent today (Broecker & Peng, 1982). Again, disproportionate removal and preservation of this light carbon sink could in theory contribute to positive and negative global preserved $\delta^{13}C_{carbonate}$ values respectively.

Following the original authors (Bjerrum & Canfield, 2004). We weight the carbonate carbon isotopic composition using the fraction $\lambda$ of inorganic carbon that is comprised by the OCC sink, and assume that this carbon deviates isotopically from the marine DIC pool via:

$$\delta_{OCC} = \delta_{C} + \Delta_{S}$$  (28)

Where $\Delta_{S}$ is a negative number expressing the magnitude by which OCC derived carbonate is isotopically lighter than DIC-derived carbonate. Otherwise using the same fractionation terms as above, and the mass balance becomes:

$$\delta^{13}C_{in} = (\delta_{c} - \varepsilon_{p}) \cdot f_{org} + (1 - f_{org}) \cdot (\delta_{c} \cdot (1 - \lambda) + \lambda \cdot (\delta_{c} + \Delta_{S}))$$  (29)

This gives a final steady state solution for $\delta^{13}C_{carbonate}^{OCC}$:

$$\delta_{c}^{OCC} = \delta^{13}C_{in} + \varepsilon_{p} \cdot f_{org} - (1 - f_{org}) \cdot \lambda \cdot \Delta_{S}$$  (30)

Crucial as regards to the connection to bioturbation is the vertical isotopic difference $\Delta_{S}$. The relative $^{13}C$-depletion of OCC derived carbonates is thought to result from the fact that the carbonate/bicarbonate anions incorporated into the crust ultimately derived from the breakdown of organic matter, meaning that OCC-induced carbonate precipitation could be impacted upon by the amount of organic matter that reaches the deep ocean. We hypothesize that the rise of bioturbation caused the proportion of global remineralization...
occurring on the shelf, in close proximity to surface waters, to qualitatively increase. We suggest that in so doing, bioturbation caused the isotopic impact of organic-carbon remineralization on OCC derived carbonates to qualitatively decrease, because less organic-derived carbon made it into the proximity of seafloor spreading zones as remineralization became more intense in shallow shelf sediments, via bioturbation-induced remineralization. This is consistent with the fact that the continental shelves, only a small fraction of the total ocean area, may account for up to 48% of the global organic carbon flux to the ocean floor (Dunne et al., 2007). Thus ultimate effect of bioturbation was, we hypothesize, was to lessen the isotopic gradient between the shallow and deep ocean. We write:

$$\Delta_s = \langle \Delta_s \rangle_{\text{early}} + \langle \Delta_s \rangle_{\text{late}} - \langle \Delta_s \rangle_{\text{early}} \cdot f_{\text{biot,0}}$$

(31)

Where we set $\langle \Delta_s \rangle_{\text{early}} = -5$ and $\langle \Delta_s \rangle_{\text{late}} = -2$ (see Bjerrum & Canfield, 2004). Thus, we hypothesize that the magnitude of the isotopic difference between crustal and surficial carbonates declines as bioturbation increases to its current value.

A1.5 | Non-steady state and local scenarios

A1.5.1 | Dynamical scenario: An approximation of the methane-climate feedback loop (Bjerrum & Canfield, 2011)

The transient nature of negative $\delta^{13}C_{\text{carbonate}}$ excursions was attributed to a dynamical feedback loop involving the release of methane from sedimentary DOC oxidation, and a resultant climatic feedback sequence leading to transient enrichment with $^{13}C$ in the preserved record (Bjerrum & Canfield, 2011). In our modification of this scenario we explore the hypothesis that bioturbation-driven sediment oxygenation was crucial in reducing susceptibility to this methane driven feedback sequence. Occurrence of this feedback loop presupposes a DOC rich ocean approximately 30 times larger than the modern reservoir, something that is proposed to be more realistic than the ~100 times larger DOC reservoir invoked by the original Rothman ocean (Rothman et al., 2003). As mentioned in the main text, the feedback sequence invoked by the original authors attributes photo-oxidation of DOC to its high marine concentrations, as a result of which "photo-oxidation of DOC results in a high flux of CO to the atmosphere, which lowers the concentration of the hydroxyl radical -OH, which in turn increases the residence time of methane in the atmosphere. This increase in methane residence time is greater than would be accomplished by just an increase in the methane flux. The end result is higher atmospheric methane concentrations. Greenhouse warming from the methane increases surface temperature and melts glacial ice, which combine to produce a negative $^{18}O$ anomaly in precipitated carbonates. The higher temperatures also accelerate the weathering of continental rocks, drawing down atmospheric CO$_2$. Lower CO$_2$, in turn, reduces the isotopic fractionation between DIC and organic carbon during primary production, while the $\delta^{13}C$ composition of organic carbon is buffered by the large DOC reservoir." (Bjerrum & Canfield, 2011).

To reiterate the core sequence of events, there exists, by hypothesis (and implicitly as a consequence of the DOC rich ocean), a decline in the size of the atmospheric hydroxyl radical pool $\exists \Delta M_{\text{OH}, \Delta M_{\text{OH}} < 0}$, which induces a decrease in the methane oxidation rate. This causes an increase in the mass and residence time of the atmospheric methane pool $\exists \Delta M_{\text{CH}_4, \Delta M_{\text{CH}_4} > 0}$. This, in turn increases temperature $\Delta T$, $\Delta T > 0$, increasing silicate and carbonate weathering $\exists \Delta W, \Delta W > 0$, which leads to the drawdown of CO$_2$ from the atmosphere, leading to an influx of aqueous carbonate anions to the ocean (and in the case of silicate weathering constituting a permanent CO$_2$ sink), $\exists \Delta C_{\text{O}_2}, \Delta C_{\text{O}_2} < 0$. This leads to a transient change in the atmospheric CO$_2$ content, decreasing the magnitude of the (CO$_2$-sensitive) photosynthetic fractionation factor $\epsilon_{\text{p}}$. This contributes to ultimately reducing the DIC-carbonate isotopic composition $\exists \Delta \delta^{13}C, \Delta \delta^{13}C > 0$.

Using "$\Delta M_X$" to denote a perturbation in the mass $M$ of the reservoir of variable $X$, and $\rightarrow$ to denote a causal connection, the whole feedback sequence postulated by the original authors can be labelled as:

$$\Delta M_{\text{OH}} \rightarrow \Delta M_{\text{CH}_4} \rightarrow \Delta T \rightarrow \Delta W \rightarrow \Delta C_{\text{O}_2} \rightarrow \Delta e \rightarrow \Delta \delta^{13}C$$

(32)

We define the relative magnitude of each of the above stages of the feedback sequence via a simplified analytic approximation to the original model, which incorporates the impact of bioturbation on sediment oxygenation. Define the mass $M_{\text{OH}}$ of the hydroxyl radical reservoir, with baseline size $M_{\text{OH}} = 0.29 \times 10^6$ mol (Prather, 2007), and using the subscript "pre" and "post" denoting the reservoir’s size before and after the perturbation, we can parameterize the initial magnitude of the decrease in the amount of -OH in the atmospheric reservoir, using the perturbation magnitude parameter $\phi$:

$$M_{\text{OH, POST}} = M_{\text{OH, PRE}} - |\Delta M_{\text{OH}}| = M_{\text{OH, PRE}} \cdot (1 - \phi_{\text{OH}})$$

(33)

This reduces the oxidative reaction of atmospheric methane with hydroxyl radicals, leading to a transient increase in the size of the atmospheric methane reservoir, which ultimately drives the rest of the feedback sequence.

We make a quasi-steady-state approximation to the maximal atmospheric methane concentration, at the inflexion point defining the maximum size of the perturbation (i.e., the maximum value that the atmospheric methane reservoir $M_{\text{CH}_4}$ takes before it starts to decline back to steady state).

Thus the time derivative of the atmospheric methane reservoir is:

$$\frac{dM_{\text{CH}_4}}{dt} = F_{\text{CH}_4, \text{INV}} - F_{\text{OX,CH}_4, 0} \cdot M_{\text{CH}_4} \cdot M_{\text{OH}} - F_{\text{Phot,CH}_4} \cdot M_{\text{CH}_4}$$

(34)
The first term, the methane influx to the atmosphere, must conform to:

\[ F_{\text{CH}_4,\text{IN}} = D_{\text{CH}_4,\text{HYDRATE}} + R_{\text{DOC,CH}_4} + R_{\text{DOC,CH}_4,\text{in}} \] (35)

Where the input to the atmosphere via degassing \( D_{\text{CH}_4,\text{HYDRATE}} \) is the product of baseline degassing rate, a time dependent forcing factor, and the size of the methane hydrate pool, which works out as: \( D_{\text{CH}_4,\text{HYDRATE}} = 4.032 \times 10^{14} \text{ molyr}^{-1} \) (although in the original model the flux may fall below this baseline value by a factor of ten due to the time dependent perturbation forcing). The baseline rate of methanogenesis can be calculated using a baseline (constant) oxygen insensitive background flux \( R_{\text{DOC,CH}_4} = 1.45 \times 10^{13} \text{ molyr}^{-1} \) and an anoxia-sensitive flux, the latter of which we write as:

\[ R_{\text{DOC,CH}_4,\text{ox}} = (R_{\text{DOC,CH}_4,\text{ox}})_0 \cdot \text{anox}_\text{sed} \] (36)

Where \((R_{\text{DOC,CH}_4,\text{ox}})_0 = 1.71 \times 10^{14} \text{ molyr}^{-1}\) and \(\text{anox}_\text{sed} \) is, as defined above, the anoxic fraction of marine shelf sediments (and a decreasing function of \( f_{\text{biot}} \)). The baseline scaling factor for the hydroxyl-independent photo-oxidation of methane in the atmosphere \( F_{\text{phot,CH}_4} = 2.03 \times 10^{-8} \text{ yr}^{-1} \) is multiplied by the size of the atmospheric reservoir \( M_{\text{CH}_4} \), to produce the final value for the flux. By (34), define the pre-perturbation steady state as:

\[ (M_{\text{CH}_4})_{\text{pre}} = \frac{F_{\text{CH}_4,\text{IN}}}{F_{\text{OXCH}_4,0} \cdot (M_{\text{CH}_4})_{\text{pre}} + (F_{\text{phot,CH}_4})_0} \] (37)

Where \((M_{\text{CH}_4})_{\text{pre}} = 0.299 \times 10^6 \text{ mol} \) and \( F_{\text{OXCH}_4,0} = 7.067 \times 10^{12} \text{ mol} \). Define the perturbation by:

\[ (M_{\text{CH}_4})_{\text{post}} = (M_{\text{CH}_4})_{\text{pre}} \cdot (1 + \Phi_{\text{CH}_4}) \]

\[ = \frac{F_{\text{OXCH}_4,0} \cdot (M_{\text{CH}_4})_{\text{pre}} + (F_{\text{phot,CH}_4})_0}{(1 + \Phi_{\text{CH}_4}) \cdot (M_{\text{CH}_4})_{\text{pre}}} \] (38)

Substituting (35) into (36) and solving for \( \Phi_{\text{CH}_4} \) we get:

\[ -\Phi_{\text{CH}_4} = \Phi_{\text{CH}_4} \left( 1 - \frac{(F_{\text{phot,CH}_4})_0}{F_{\text{OXCH}_4,0} \cdot (M_{\text{CH}_4})_{\text{pre}}} \right) \approx \Phi_{\text{CH}_4} \] (39)

On the basis of which we assume a 1:1 ratio between the magnitudes of the perturbations in the atmospheric hydroxyl and methane reservoirs. In accordance with the results of the original model, we initially parameterize a methane increase in the region of \( \Phi_{\text{CH}_4} \approx 300 \), but the results in the main text are essentially a sensitivity analysis to this parameter.

The impact of this methane increase on climate occurs via the resultant temperature increase. In the original model the temperature function is the sum of a radiative energy balance component, a time dependent solar insolation component, and a greenhouse warming component \( T \) which is of the form \( T = \Gamma \cdot \ln \left( \frac{M_{\text{CO}_2,\text{pre}} + M_{\text{CH}_4}}{M_{\text{CO}_2,\text{pre}} + M_{\text{CH}_4}} \right) \).

Because the rest of the temperature function is unaffected by the perturbation, we define a baseline starting temperature \( T_0 = 15^\circ \text{C} \equiv 288.15^\circ \text{K} \), to which we add the methane induced temperature perturbation to calculate the temperature post methane-induced warming, i.e.:

\[ \Delta T = \Gamma \cdot \ln \left( \frac{M_{\text{CO}_2,\text{post}} + M_{\text{CH}_4}}{M_{\text{CO}_2,\text{pre}} + M_{\text{CH}_4}} \right) - \Gamma \cdot \ln \left( \frac{M_{\text{CO}_2,\text{pre}} + M_{\text{CH}_4}}{M_{\text{CO}_2,\text{pre}} + M_{\text{CH}_4}} \right) \] (40)

\[ T_{\text{post}} = T_0 + \Delta T \] (41)

Where \( \Gamma = 6^\circ \text{C} \) is a methane sensitive greenhouse warming parameter (Beerling et al., 2002), \( M_{\text{CO}_2,\text{pre}} = 7.64 \times 10^{16} \text{ mol} \), \( \lambda_{\text{CH}_4} = 6.4 \) is the ratio between the greenhouse response to methane and that to carbon dioxide, and \( M_{\text{CH}_4,\text{pre}} = 2.2 \times 10^{15} \text{ mol} \) and \( (M_{\text{CH}_4})_{\text{pre}} \) is calculated as above. We simplify the effect on weathering of this temperature perturbation, by incorporating silicate and carbonate weathering functions from Bergman’s COPSE model (Bergman, Lenton, & Watson, 2004), into which we incorporate the temperature perturbation, calculating the change \( \Delta \text{silw} \) induced in the silicate weathering flux:

\[ \Delta \text{silw} = \text{silw}_0 \sqrt{0.35 \cdot ((1 + 0.025 \cdot T_{\text{pre}}^{0.65} e^{0.09 T_{\text{pre}}}) - (1 + 0.025 \cdot T_{\text{pre}}^{0.65} e^{0.09 T_{\text{pre}}}))} \] (42)

Similarly the warming induced variation in the carbonate weathering flux is:

\[ \Delta \text{carbw} = \text{carbw}_0 \cdot 0.87 \cdot (T_{\text{post}} - T_{\text{pre}}) \] (43)

Where \( \text{silw}_0 = 6.65 \times 10^{12} \text{ molyr}^{-1} \) and \( \text{carbw}_0 = 13.35 \times 10^{12} \text{ molyr}^{-1} \), and the difference between the weathering fluxes is calculated holding all factors other than temperature as constant. We hold CO\(_2\) constant prior to the weathering increase, then use the latter change in order to calculate the subsequent CO\(_2\) drawdown induced by this weathering change. The stoichiometry of silicate weathering leads to a net CO\(_2\) drawdown:

\[ \text{Ca(Mg)SiO}_3\text{land} + 2\text{CO}_2\text{atmos} \rightarrow \text{Ca(Mg)CO}_3\text{seafloor} + \text{CO}_3\text{aq} + \text{SiO}_2\text{aq} \]

whereas that of carbonate weathering only leads to a transient carbonate ion influx to the ocean, without a net change in the overall ocean-atmosphere reservoir size (Ca/Mg

\[ \text{CO}_3\text{land} + \text{CO}_2\text{atmos} + \text{H}_2\text{O} \rightarrow \text{Ca(Mg)CO}_3\text{seafloor} + \text{H}_2\text{CO}_3\text{aq} \]

(Walker et al., 1981).

However, increased carbonate weathering can lead to a transient change in carbonate alkalinity that potentially influences atmosphere-ocean apportioning of CO\(_2\) relevant to the transient perturbation being considered here, and we therefore consider the effect of the perturbation on the latter flux.
Approximating the global derivative for the atmosphere-ocean CO₂ reservoir as \( \frac{d\text{DIC}}{dt} = -\text{silw} \) with degassing D constant, then using the silicate weathering formulation from COPSE (Bergman et al., 2004) \( \text{silw} = \text{silw} \cdot \sqrt{K_{\text{DIC}}} \cdot \sqrt{0.35 \cdot ((1 + 0.025 \cdot (T_{\text{pre}} - T_0)^{0.65})e^{0.09(T_{\text{pre}} - T_0)})} \), with \( T_0 = 15°C \) then for steady state, CO₂ reservoir sizes before and after the temperature perturbation are:

\[
M_{\text{CO}_2,\text{pre}} = \frac{M_{\text{CO}_2,\text{post}}}{0.35 \cdot ((1 + 0.025 \cdot (T_{\text{pre}} - T_0)^{0.65})e^{0.09(T_{\text{pre}} - T_0)})^2}
\]

\[
M_{\text{CO}_2,\text{post}} = \frac{M_{\text{CO}_2,\text{pre}}}{0.35 \cdot ((1 + 0.025 \cdot (T_{\text{post}} - T_0)^{0.65})e^{0.09(T_{\text{post}} - T_0)})^2}
\]

And if \( T_0 = T_{\text{pre}} \) then the difference between the two simplifies to:

\[
\Delta M_{\text{CO}_2} = M_{\text{CO}_2,\text{post}} - M_{\text{CO}_2,\text{pre}} = \frac{M_{\text{CO}_2,\text{pre}}}{0.35 \cdot ((1 + 0.025 \cdot (T_{\text{pre}} - T_0)^{0.65})e^{0.09(T_{\text{pre}} - T_0)})^2 (1 - 1)}
\]

\[
\Delta M_{\text{CO}_2} = \frac{M_{\text{CO}_2,\text{pre}}}{0.35 \cdot ((1 + 0.025 \cdot (T_{\text{pre}} - T_0)^{0.65})e^{0.09(T_{\text{pre}} - T_0)})^2 (1 - 1)}
\]

i.e., \( \Delta M_{\text{CO}_2} < 0 \) is the net CO₂ drawdown, as given by (44).

The temperature increase also leads to a net (negative) change in the solubility of CO₂ in the ocean, with implications for the photosynthetic isotopic fractionation factor. CO₂ in surface ocean waters is equilibrated with the atmosphere according to the solubility \( K_0 \) and fugacity \( f(CO_2) \):

\[
CO_{2(aq)} = K_0 \cdot f(CO_2)
\]

Where \( K_0 \) is in units of moles per kilogram per part per million CO₂, and the fugacity is given by:

\[
f(CO_2) = \frac{M_{\text{CO}_2} \cdot \psi}{\text{mol atm} \cdot 1 \times 10^{-6}}.
\]

Where \( \psi = 0.0164 \) is an estimate (Bergman et al., 2004) of the pre-industrial atmospheric fraction of the total CO₂ reservoir, which we hold constant. The solubility constant is given by:

\[
\ln (K_0) = -60.2409 + 93.4157 \cdot \left( \frac{100}{T_e} \right) + 23.3585 \cdot \ln \left( \frac{T_e}{100} \right) + 0.022351 - 0.02356 \cdot \frac{S_0}{100} + 0.0047306 \cdot \left( \frac{T_e}{100} \right)^2
\]

(49)

Where the temperature is in Kelvin \( T_e = T + 237.16 \) and the salinity is held constant at the modern salinity \( S_0 = 34.72 \text{gNaClkg}^{-1} \). We approximate the change in the concentration of CO₂ dissolved in surface ocean waters, and \( CO_{2(aq)} \) is in units of moles per kilogram seawater. Because we do not explicitly calculate all carbonate alkalinity speciation, we approximate dissolved CO₂ by (44) and (45) and simply write:

\[
\Delta CO_{2(aq)} = CO_{2(aq)}(M_{\text{CO}_2,\text{post}}, T_{\text{post}}) - CO_{2(aq)}(M_{\text{CO}_2,\text{pre}}, T_{\text{pre}})
\]

(50)

(Obviously a more realistic model would explicitly calculate carbonate alkalinity speciation, but for our purposes we consider this simplification acceptable). Thus we have an approximation of the maximum temperature and CO₂ change induced by the methane perturbation at its peak. We now use a difference approximation of the time derivative for the DIC reservoir used in the original paper, in order to derive an approximate, upper bound estimate of the change in isotopic composition of that reservoir (as accurately as can be achieved without resolving the detailed equilibration dynamics in the DIC pool). We write a difference formulation for the isotopically weighted derivative for the DIC reservoir as (by the product rule):

\[
\Delta (M_{\text{DIC}}) = \Delta M_{\text{DIC}} = \frac{\Delta M_{\text{DIC}}}{M_{\text{DIC}}} \cdot \Delta M_{\text{DIC}} + \Delta M_{\text{DIC}} \cdot \Delta M_{\text{DIC}}
\]

(51)

The difference formulation of the derivative of the carbonate carbon pool is taken from the original model \( \frac{dM_{\text{DIC}}}{dt} \) term:

\[
\Delta M_{\text{DIC}} = \text{carbw} - \text{mccb} - EP - \text{mocb} + R_{\text{ox}} + R_{\text{anox}} + R_{\text{meth}} (1 - \gamma)
\]

(52)

For each flux in the above equation, we separately consider the impact of the perturbation on the magnitude of the flux itself, i.e., \( \text{flux}_{\text{pre}} + \Delta \text{flux} \), and the impact upon the isotopic composition of that flux (i.e., \( \delta_{\text{flux,pre}} + \Delta \delta_{\text{flux}} \)), with the pre-perturbation value being calculated using \( T = T_{\text{pre}} \), \( M_{\text{CO}_2} = M_{\text{CO}_2,\text{pre}} \) thus:

\[
\Delta (M_{\text{DIC}}) = \sum (\text{flux}_{\text{pre}} + \Delta \text{flux}) \cdot \delta_{\text{flux,pre}} + \Delta \delta_{\text{flux}}
\]

(53)

Where for each of the specific fluxes (i.e., carbonate weathering carbw, marine carbonate burial mccb, and so on) in (52), the perturbation-induced change in the magnitude of each flux is of the form:

\[
\Delta \text{flux} = \text{flux}_{\text{post}} - \text{flux}_{\text{pre}} = \text{flux}_{\text{pre}}(T_{\text{post}}, M_{\text{CO}_2,\text{post}}, M_{\text{CH}_4,\text{post}}) - \text{flux}_{\text{pre}}(T_{\text{pre}}, M_{\text{CO}_2,\text{pre}}, M_{\text{CH}_4,\text{pre}})
\]

Similarly, the change in the isotopic composition of each specific flux is:

\[
\Delta \delta_{\text{flux}} = (T_{\text{post}}, M_{\text{CO}_2,\text{post}}, M_{\text{CH}_4,\text{post}}) - (T_{\text{pre}}, M_{\text{CO}_2,\text{pre}}, M_{\text{CH}_4,\text{pre}})
\]

(55)

The formulation of each of the specific fluxes and the isotopic composition by which these fluxes are weighted is taken from the original model and given in table 3. We proceed by using these formulations in order to calculate the perturbation induced change in each flux (by (54)) and each flux-specific isotopic composition (by (55), which we then substitute into (52), ending up with an explicit version of (53). Then, as above, we put \( \delta_{\text{DIC}} = \delta_{\text{DIC,pre}} - 2\%M_{\text{DIC}} = M_{\text{DIC,pre}} \) in the right hand side of (51), put \( \Delta M_{\text{DIC}} \) equal to (52), and solve for \( \Delta \delta_{\text{DIC}} \).
\[ \Delta \delta_{\text{DIC}} = \frac{1}{M_{\text{DIC}}} \left( \sum \left( \text{flux}_{\text{pre}} \cdot \Delta \delta_{\text{flux}} + \Delta \delta_{\text{flux}} \right) \right) + \Delta \delta_{\text{DIC,0}} \Delta M_{\text{DIC}} \]  

This provides an estimate of the change in isotopic composition of marine DIC directly attributable to the feedback loop above.

In terms of the potential impact of bioturbation, the authors (Bjerrum & Canfield, 2011) also state that “While the form of our parameterization of DOC decomposition pathways and the choice of absolute values is unconstrained, the extent to which organic carbon oxidation proceeds by methanogenesis should be related to the volume of anoxic waters and sediments, which is a function of atmospheric oxygen concentration and other factors.” We suggest here that inbuilt into this scenario is a potential shut-down of the feedback loop by the ventilation of sediments through bioturbation. We use the \( f_{\text{biot}} \) term defined above to approximate the methanogenic fraction of anaerobic remineralization of DOC:

\[ f_m = 1 - f_{\text{biot}} \]  

This expresses the idea that methanogenesis (being inhibited by the presence of both oxygen and sulphate) would have been particularly inhibited by the presence of bioturbation, even relative to other anaerobic processes for oxidizing carbon. As well as incorporating the perturbations in temperature, the authors of the original paper formulate the composition of this mixture using two distinct mass fraction terms, but in order to simplify the idea, we define two key free parameters: \( \varphi \), the fraction of the organic carbon in the microcosm of interest that is comprised by the terrestrial-derived pool, and \( f_{\text{rem}} \), the fraction of inorganic matter that is isotopically impacted upon by the remineralization of organic matter, and thereby impacts upon the isotopic composition of DIC in that microcosm. The isotopic composition of inorganic carbon, impacted upon by remineralization of contemporaneous organic matter, can thus be written as:

\[ (\delta^{13}C_{\text{DIC, mixture}}) = f_{\text{rem}} \cdot (1 - \varphi) \cdot (\delta^{13}C_{\text{DIC}} - \varepsilon_p) + \varphi \cdot (\delta^{13}C_{\text{org, EQ}}) + (1 - f_{\text{rem}}) \cdot \delta^{13}C_{\text{DIC}} \]  

We set \( \delta^{13}C_{\text{DIC}} = -1\% \) (i.e., assuming there is no other process responsible for negative isotopic enrichment at the global scale), and treat both the isotopic composition of the terrestrial carbon \(-50 \leq \delta^{13}C_{\text{org, EQ}} \leq -10\), and the “remineralization-influenced fraction” \% \leq f_{\text{rem}} \leq 5\% as parameters. Importantly, in terms of the role of bioturbation, we suggest that because the exogenous terrestrial carbon must necessarily be qualitatively more resistant to remineralization, and because bioturbation will enhance remineralization of “normal” organic carbon in sediments, we can meaningfully write:

\[ \varphi = f_{\text{biot}} \]  

In other words, in the fraction of “normal” organic matter (i.e., organic matter that is isotopically equilibrated with the DIC pool) in the
microcosm, will decline with increasing bioturbation, because bioturbation will promote the breakdown of this organic matter more than it will the recalcitrant exogenous pool.

A1.6 | Wavelet analysis of $\delta^{13}C$ data

The data used in figure 1 is a compilation of that taken from previous compilations (Halverson et al., 2010; Saltzman et al., 2012). A wavelet power spectrum was used to determine the period of oscillations within this compilation (a wavelet is a brief oscillation beginning at zero, with a defined amplitude and length). Periodograms of wavelet transforms (Torrence & Compo, 1998) were produced from the smoothed $\delta^{13}C_{\text{carbonate}}$. The datapoint density was standardized using a smoothing spline from within the "csaps" function in MATLAB, which has a single tunable variable determining the degree of fit between the data and the curve. This approach differs from binning the data into time intervals in that the curve implicitly takes into account the number of datapoints supporting a given interpolation path. A wavelet power spectrum was obtained using the wavelet toolbox in MATLAB, using a 1-dimensional continuous wavelet transform with the Morlet wavelet (Morlet, Arehs, Fourgeau, & Giard, 1982) as the mother function. As discussed in the main text, we find a qualitative decline in the amplitude and wavelength of oscillations in the Paleozoic in comparison to the Neoproterozoic. The Morlet wavelet $\psi$ is a sinusoid with period $a$ modulated at time $t$ by a Gaussian of width $b$:

$$\psi_{a,b}(t) = \pi^{-\frac{1}{4}}(a/l)\cdot \frac{1}{2} \cdot e^{\frac{-2a}{\pi} (t-b)^2} \cdot (\frac{2}{\pi})^{\frac{1}{2}}$$

(62)

Where the parameter $l$ modifies wavelet transform bandwidth resolution either in favour of time or in favour of frequency, according to the uncertainty principle. The bandwidth resolution for wavelet transform varies with $\Delta a = a \cdot \frac{l^{\frac{3}{2}}}{4l}$ and the location resolution $\Delta b = \frac{al}{\sqrt{2}}$ and parameter $l = 10$ are chosen so as to give sufficiently precise resolution in depth and frequency respectively.