Nutrient enriched waters, oxygenation and climate change during the Tonian-Cambrian interval of biological innovation

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Abstract: The Tonian-Cambrian interval (~0.9 to ~0.5 Ga) witnessed major tectonic, climatic and chemical changes to the Earth system, and culminated in the Ediacaran-Cambrian radiation of animals. Negative carbon isotope ($\delta^{13}C$) excursions of extraordinary magnitude form the backdrop to all these events and are consistent with the presence of a vast, marine organic carbon reservoir that changed its size due to periodic imbalances between organic production (as an oxidant source) and terrestrial oxidant sinks. Prior to both Cryogenian glaciations, this pool of long-lived organic carbon became substantially depleted, leading to a weakening of climate and oxygen regulation. The late Ediacaran 'Shuram' anomaly likely represents a third depletion event, followed by oxygenation and the Ediacaran-Cambrian radiation. The evolutionary diversification of animals shortened the ocean residence time of organic carbon and introduced new carbon cycle feedbacks that together helped to mould the modern Earth system.

The Precambrian-Cambrian boundary (c.540 Ma) traditionally marks the first incontrovertible fossil evidence for animal life in the form of mineralized skeletons or associated traces (Brasier *et al.* 1994; Briggs 2015). However, plausible animal fossils have now been found in much older Ediacaran strata, implying a cryptic pre-history of evolutionary diversification that possibly began over 200 Myr earlier (Erwin, 2015). The 'Cambrian explosion' of skeletal forms is now viewed as the last of several pulses of biological diversification that occurred against a backdrop of climatic, tectonic and environmental changes, which span approximately the same time interval. The role of nutrients, for example, in the Cambrian radiation has long been debated (Brasier 1992, Tucker 1992, Peters & Gaines 2013), and is tightly coupled to tectonic upheavals because nutrient (P, N) and micronutrient (e.g. Fe, Mo) fluxes are governed by weathering and erosion, as well as redox conditions. Oxygenation is another widely cited trigger for the Cambrian radiation (Cloud 1968; Squire *et al.* 2006, Campbell & Squire 2010), although its relative importance is strongly contested (Butterfield 2009, Sperling *et al.* 2015). Recently, a more nuanced synthesis of the Cambrian radiation has emerged, in which changes to nutrient and oxygen availability are considered to have been both a cause and effect of biological innovations (McIlroy & Logan 1999; Shields-Zhou & Zhu 2013; Knoll & Sperling 2014; Lenton *et al.* 2014). The present study seeks to contribute to this more nuanced account of the Proterozoic-Phanerozoic transition.

The dominant tectonic 'event' of the Tonian-Cambrian interval, starting from ~0.85 Ga, was arguably the break-up of Rodinia (Li *et al.* 2004, Li *et al.* 2008), latter stages of which have been implicated in the onset of global 'Snowball Earth' glaciations between 717 and 635 Ma (Donnadieu *et al.* 2004, Rooney *et al.* 2014, Horton 2015, Cox *et al.* 2016). The subsequent reamalgamation of rifted Rodinian blocks during the formation of Gondwanaland led to exceptional mountain building (Pan-African orogeny) during the Ediacaran and Cambrian periods (Brasier & Lindsay 2001, Meert & Lieberman 2008). The Cambrian radiation is commonly viewed as an expansion of animal forms and traits into new ecological niches made available through a series of sea-level rises (Brasier 1982, Dalziel 2014) that eroded uplifted cratonic interiors, producing the so-called 'Great Unconformity' of the western USA (Peters & Gaines 2013), and elsewhere (Brasier & Lindsay 2001; He *et al.,* this issue). Several authors have linked this series of tectonic events from break-up to collision to exceptionally high nutrient flux, oxygenation and eukaryotic diversification (Campbell & Squire 2010; Planavsky *et al.* 2010; Horton 2015; Gernon *et al.* 2016).

Although some form of Neoproterozoic Oxygenation Event (NOE) is widely accepted (Shields-Zhou & Och 2011), it is ambiguously recorded in geochemical data because the most established redox proxies relate to the marine environment only. It is therefore challenging, on the basis of sparsely sampled, often ambiguous data, to distinguish whether ocean oxygenation events were the trigger for biological expansion or whether they were an effect of biological innovations (filter feeding, suspension feeding, faecal pellets, etc.), which reduced the residence time of organic carbon in seawater (Logan *et al.* 1995, Butterfield 2009, Lenton *et al.* 2014). Trace metal (V, Mo, U) concentrations and isotopic (Mo, Se) data show how the spatial extent of anoxic bottom waters decreased markedly during the Ediacaran-Cambrian interval, possibly in stages (Scott *et al.* 2008, Sahoo *et al.* 2012, Chen *et al.* 2015). Ocean oxygenation episodes also seem to have followed glaciations (Canfield *et al.* 2007, Sahoo *et al.* 2012) during periods of excessive weathering (Shields *et al.* 1997, Kasemann *et al.* 2014). A final expansion of oxygenated waters may have accompanied the 'Cambrian explosion', reaching near modern distribution of oxic seafloor by ~520 Ma (Chen *et al.* 2015), but this is challenged by a recent statistical analysis of Fe-speciation data (Sperling *et al.* 2015). Because Fe speciation relates to local redox conditions in the shallow marine realm (although sedimentologically characterized as 'deep'), whereas trace metal redox proxies reflect the global flux and distribution of redox-controlled sources and sinks, these apparently opposing views are not necessarily contradictory.

Carbon isotopes are undoubtedly the most widely studied of sedimentary geochemical proxies, and have the advantage that ocean $\delta^{13}C$ relates directly to the major net source of all atmospheric oxygen: organic carbon burial. However, the $\delta^{13}C$ record turns out to be a fickle proxy for oxygenation. Both positive and negative $\delta^{13}C$ anomalies have been interpreted as oxidation events (Knoll *et al.* 1986; Rothman *et al.* 2013), while neither short-lived anomalies nor long-term baseline or mean trends in $\delta^{13}C$ are sufficiently understood (Schrag *et al.* 2013). The late Tonian to early Cambrian interval is especially puzzling in this regard, with decreasing $\delta^{13}C$ towards the Cambrian, counter-intuitively suggesting lowered rates of organic burial (Brasier & McIlroy 1998, Brasier & Lindsay 2001), and extraordinary, negative $\delta^{13}C$ excursions, which consistently defy explanation using conventional mass balance approaches (Rothman *et al.* 2003, Bjerrum & Canfield 2011, Tziperman *et al.* 2011, Grotzinger *et al.* 2011). Although the progressive oxidation of a vast reservoir of organic carbon in the lower oceans has been proposed to explain these carbon isotope perturbations (Rothman *et al.* 2003), the required oxidant demand is generally considered to be implausibly high (Bristow & Kennedy 2008), leading many to favour non-global or diagenetic explanations (Derry 2010, Grotzinger *et al.* 2011).

Notwithstanding these prior arguments, it is worth exploring whether recalcitrant dissolved organic carbon did indeed have a longer residence time in the Proterozoic ocean than its current ~330 years (Hansell 2013) and what consequences this might have had for climate regulation and biological evolution, keeping in mind the otherwise surprising coincidence that extreme negative $\delta^{13}C$ excursions between ~730 and ~520 Ma brackets precisely the late Tonian to early Cambrian interval of exceptional climatic and biological upheaval. In this review, I will attempt to synthesize the most recent evidence for exceptionally high rates of erosion and nutrient input during the Ediacaran and Cambrian periods. This evidence confirms that the collisional formation of Gondwanaland was accompanied by exceptionally high rates of erosion, consistent with other evidence for abundant nutrients in the Ediacaran-Cambrian oceans. The case is then developed that prolonged periods of unusually low $\delta^{13}C$ values can only plausibly be explained by the existence of a vast pool of organic carbon in the lower oceans. The possible implications of this organic carbon pool are then explored, informed by the temporal relationship between $\delta^{13}C$ perturbations, and Tonian to Cambrian climatic and biological events. A firmer understanding of these genuinely unique $\delta^{13}C$ anomalies would greatly assist us in solving the mysteries of early animal evolution.

Increasing erosion rates from the Tonian to the Cambrian

High erosion rates have frequently been implicated as a driver of the Ediacaran-Cambrian radiations. A global overview of relevant evidence (Brasier & Lindsay 2001) confirmed that "*increasing rates of subsidence and uplift accompanied the dramatic radiation of animal life through the Neoproterozoic-Cambrian interval*". Quantifying paleo-erosion flux is difficult, however, and each method has its own caveats. Seawater $^{87}Sr/^{86}Sr$, for example, is controlled by the age and type of materials undergoing weathering, and thus only indirectly by erosion rates (Berner & Rye 1992). Similarly, the observed abundances of sedimentary rocks are subject to preservation and sampling biases (Hay *et al.* 2006). Despite such uncertainties, it is accepted that the ~3-5 x10^8 year supercontinent cycle of formation and break-up led to a prolonged period of mountain uplift during the Late Precambrian and early Paleozoic (Squire *et al.* 2006, Bradley 2011, Peters & Gaines 2013), followed by a time of cratonic stability and low erosion rates during the late Paleozoic and Early Mesozoic (e.g. Spencer *et al.* 2014). This long-term dynamic is independently evidenced by records of orogenies, collisions and paleogeographies (e.g. Condie 2004), and has recently been elucidated further by the study of zircon hafnium and oxygen isotope compositions. Zircon εHf and $\delta^{18}O$ values (Spencer *et al.* 2013, Spencer *et al.* 2014) highlight the Ediacaran-Cambrian interval of low carbonate $\delta^{13}C$ as a time of exceptional uplift (unroofing) of deep crustal roots and of tectonic sediment reworking, respectively, providing independent and quantitative support for the supercontinent cycle dynamic (Figure 1). The earlier Tonian interval of exceptionally high $\delta^{13}C$ (Des Marais 1994, Krissansen-Totton *et al.* 2015) is interpreted, by contrast, as a time of relative orogenic quiescence (Cawood *et al.* 2013), which occurred after formation of Rodinia, but before its total break-up.

Although the tectonic backdrop to the Cambrian radiation seems to be increasingly substantiated, authors have emphasized different consequences of this rise in erosion rates. Brasier and Lindsay (2001) considered that increased erosion led to eutrophication of the shallow marine environment and the spread of nutrient enriched waters (NEW) during the

Cambrian transgressions. However, they were careful to highlight the taphonomic effects of the spread of anoxic waters (see also Brasier 1992) rather than any evolutionary ones. Although it is difficult to make direct connections between nutrient flux and biodiversification, some authors make an indirect case via oxygenation. For example, Campbell & Allen (2008) consider that the nutrients released during orogenesis led to both higher productivity and increased organic burial due to higher rates of sediment deposition. Other connections have been made between erosion and the Cambrian explosion, but these relate only to aspects of the event, such as biomineralization, which has been linked to increased weathering flux caused by the Ediacaran-Cambrian rise in sea-level (e.g. Peters & Gaines, 2013). Increased oxygenation of the surface environment remains the most widely invoked physical causation mechanism used to explain the Ediacaran-Cambrian radiations.

The carbon isotope record for the Precambrian-Cambrian interval has long remained a puzzle. Brasier and Lindsay (2001) summed it up thus: "*increasing rates of sediment accumulation through this time … might be expected to have increased the global rates of carbon burial… The long-term trend for carbon burial, however, is falling* [$\delta^{13}C$] *values through the Neoproterozoic-Cambrian. This means that increases in carbon burial due to raised rates of sediment accumulation must have been offset by raised rates of organic carbon oxidation*". The decreasing trend to which they are referring is obvious in Figure 1A, but any effect of oxidative weathering on $\delta^{13}C$ would normally be offset by an equivalent increase in carbonate weathering (Schrag *et al.* 2002). Several authors have noted that the Cambrian Period, in particular, was a time of maximal carbonate sedimentation (e.g. Peters & Gaines, 2013), which would be consistent with elevated rates of uplift and erosion as carbonate rocks are weathered quantitatively, unlike other rock types. Taking this into account, it seems more likely that low $\delta^{13}C$ during the Ediacaran-Cambrian interval (Fig. 2) was related to high rates of erosion because subsequent increased carbonate deposition would lead to lower proportional organic carbon burial (low f_{org}). This is because organic burial, unlike carbonate burial, is ultimately limited by outgassing rates (Berner 1991). In other words, high erosion rates can lead to greater nutrient flux and therefore to greater organic burial, but this will not necessarily lead to higher $\delta^{13}C$ values.

The excess phosphorus hypothesis can be tested using nitrogen isotopes. The Ediacaran-Cambrian transition interval exhibits decreasing $\delta^{15}N$ values (Ader *et al.* 2014), which are consistent with domination by N-fixers and local nitrate starvation at eutrophic ocean margins during the Cambrian radiation (Cremonese *et al.* 2014). Nutrient enriched marine waters would have fuelled organic production, leading at times to the spread of mid-shelf anoxia, anaerobic remineralization, bacterial sulphate reduction and early diagenetic phosphogenesis near key redox transitions (Brasier 1992). In the absence of other negative feedbacks, phosphogenesis may provide a key mechanism by which nutrient overload and resultant oxygenation has been regulated in the Earth system, especially since the evolution of animals (Boyle *et al.* 2014).

Negative $\delta^{13}C$ excursions during the Tonian-Cambrian interval

Carbonate carbon isotope excursions to values at or below the canonical mantle value of about -5‰ or -6‰ are characteristic features of the interval from about 0.9 Ga to 0.5 Ga (Halverson *et al.* 2010) (Figs. 2,3). Negative carbon isotope excursions of the Neoproterozoic were first reported in a pioneering study (Knoll *et al.* 1986), and shown to both precede and succeed Cryogenian glacial events many times subsequently (Kaufman *et al.* 1991, Kaufman *et al.* 1997, McKirdy *et al.* 2001, Halverson *et al.* 2005, Rose *et al.* 2012, Macdonald *et al.* 2013a). Negative δ^{13}C anomalies of extreme magnitude occur in upper Tonian and upper Cryogenian pre-glacial successions across the world, but are now known to recover to more normal values before onset of worldwide glaciation (Fig. 3), e.g. the 'Islay anomaly' (Brasier & Shields 2000, Rooney *et al.* 2014) and the pre-Marinoan 'Trezona anomaly' (Walter *et al.* 2000, Rose *et al.* 2012). Post-glacial δ^{13}C anomalies characterize transgressive strata overlying both of the main Cryogenian glacial phases (Kennedy *et al.* 1998).

A mid-Ediacaran anomaly has been associated with the more regional ~580 Ma Gaskiers glaciation, which was followed by the global 'Shuram' anomaly (Macdonald *et al.* 2013b). The late Ediacaran 'Shuram' event was first reported from Oman (Burns & Matter 1993, Burns *et al.* 1994) and then Australia (Calver 2000), but has subsequently been recognized in correlative strata all over the world (Lu *et al.* 2013). Many studies have demonstrated that the Shuram excursion is stratigraphically correlative, both regionally and globally (Lu *et al.* 2013), while there is increasing agreement that it cannot be explained by diagenetic alteration (Burns & Matter 1993, Le Guerroué 2010, Lu *et al.* 2013, Husson *et al.* 2015, Lee *et al.* 2015), notwithstanding several alternative, diagenetic explanations (Knauth & Kennedy 2009, Bristow & Kennedy 2008, Derry 2010, Oehlert & Swart 2014).

Negative excursions of the lower Cambrian were also identified early on (Magaritz *et al.* 1986), and initially assigned to a mass extinction event that took place before the final phase of the Ediacaran-Cambrian radiation: the traditional 'Cambrian explosion' (Hsu *et al.* 1985, Kimura & Watanabe 2001). Although the lower Cambrian anomalies are not obviously associated with major climate change, regional glaciations have been reported from the Ediacaran-Cambrian transition interval (Chumakov 2009). Despite the obvious temporal overlap between extreme perturbations to the global carbon cycle, evidenced from both climate change and carbon isotopes, linking these two phenomena within a parsimonious synthesis has proven to be challenging.

The long duration of many of these excursions, especially the late Ediacaran Shuram excursion, which seems likely to have lasted at least 10 million years (Macdonald *et al.* 2013b), means that the conventional isotope mass balance can be applied:

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

Standard calculations assume that the average isotopic composition of carbon input ($\delta^{13}C_{in}$) from weathering and outgassing is constant and approximately equal to $\delta^{13}C_{mantle}$ or about -6‰ (±1‰). Rearranging equation (1) then allows the proportion of carbon buried as organic matter (f_{org}) to be read directly from the carbonate C isotope record (Fig. 4):

$$f_{org} = (\delta^{13}C_{carb} - \delta^{13}C_{in}) / (\delta^{13}C_{carb} - \delta^{13}C_{org}) \qquad (2)$$

Knowledge of f_{org}, and the total input (≈ output) rate of carbon, F_{total}, then allows the rate of organic carbon burial, and hence oxygen production to be estimated (Broecker 1970).

It is generally considered that extremely negative carbon isotope excursions below the canonical mantle value of -5‰ or -6‰ "*cannot be explained by conventional mass balance scenarios*" (e.g. Lee *et al.* 2013). However, the long time-scales involved in many of these global and primary excursions necessitates agreement with global mass and isotope-mass balance, in which case the only plausible explanation for them must invoke a decrease in $\delta^{13}C_{input}$ to below the measured values in marine carbonate successions. This was concluded already in earlier studies (Rothman *et al.* 2003, Melezhik *et al.* 2005), with the most commonly cited reason for lower $\delta^{13}C_{input}$ being the repeated oxidation of a huge dissolved organic carbon (DOC) reservoir during the Neoproterozoic (Rothman *et al.* 2003). No other plausible mechanism has been proposed to explain how a low $\delta^{13}C$ ocean can be sustained for millions of years.

Assessing the 'Rothman' model of DOC oxidation

The DOC reservoir explanation for negative excursions (Rothman *et al.*, 2003) is believed to be problematic for two main reasons, as outlined by Grotzinger *et al.* (2011). Firstly, the model predicts that the isotopic composition of sedimentary organic carbon would be buffered by the isotopic composition of the DOC reservoir, and so remain unchanged during negative excursions. It is not clear why a DOC pool would need to affect the isotopic composition of all sedimentary (particulate) organic carbon, but in any case, recent studies show that the lack of co-variation between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values is more apparent than real, and caused by admixture of exotic (non-primary) particulate organic carbon (POC) in organic-poor samples (Johnston *et al.* 2012). Although the source of this extraneous POC was presumed to be terrestrial, i.e. detrital, this remains to be demonstrated and it may instead derive from microbial reworking of the DOC pool (Lee *et al.* 2015). The presence or absence of co-variation is not a test of the DOC hypothesis, while cases of demonstrable co-variation (Shields *et al.* 2002, Swanson-Hysell *et al.* 2010, Johnston *et al.* 2012) cement the case for a primary origin for the negative excursions.

Secondly, it has been argued that oxidation of a vast organic carbon pool would lead to an implausibly high oxidant demand, exceeding that provided by all the oxygen in the present atmosphere many times over (Bristow & Kennedy 2008). This problem raises the thorny issue of how such huge amounts of free oxygen could be kept separate from the reduced organic carbon reservoir in the lower ocean for millions of years (Grotzinger *et al.* 2011). However, this reading of the isotope record assumes that DOC oxidation was an additional oxygen sink that kicked in only during isotope excursions. It would be more realistic to view the DOC pool as an inherent part of the normal Proterozoic carbon cycle, helping to maintain mass balance via dynamic changes to the net DOC oxidation flux. In other words, the long-lived negative isotopic excursions of the Tonian to Cambrian interval could represent a system at steady state, albeit an evolving steady state, with respect to carbon and oxygen. This interpretation seems to be supported by the gradual onset, gradual ending and static baseline to, for example, the DOUNCE (Shuram) $\delta^{13}C$ anomaly (Lu *et al.,* 2013). Because of the long time scales involved, the plausibility of the DOC oxidation model relies more on the size of the oxidant flux than on the required size of the oxidant reservoirs. To pick this apart further, let us consider the carbon and oxidant fluxes in the modern carbon cycle:

Carbon enters the atmosphere/ocean system via four routes: oxidative weathering of fossil carbon (F_{wg}), carbonate weathering (F_{wc}) and metamorphic degassing of sedimentary organic carbon (F_{mg}) and carbonates (F_{mc}). Although this ignores volcanic outgassing of primary CO_2, the addition of this relatively poorly constrained flux would not change the overall analysis below. Carbon leaves the surface pool via burial of organic carbon (F_{bg}) and inorganic carbonates (F_{bc}), with the fraction leaving via the organic route denoted f_{org}. Taking average values from the literature (Berner 1991, Kasting 2013), modern carbon flux are: $F_{wg} = 7.75\times10^{12}$ mol C/yr; $F_{wc} = 24\times10^{12}$ mol/yr; $F_{mg} = 1.25\times10^{12}$ mol C/yr; $F_{mc} = 8\times10^{12}$ mol C/yr; $F_{bg} = 9\times10^{12}$ mol C/yr. The total flux of carbon into and out of the exogenic Earth system equals approximately 41×10^{12} mol C/yr, and equates to the total carbon throughput, comprising the combined carbonate weathering and outgassing flux (= silicate weathering + carbonate weathering + organic carbon burial flux) at steady state:

$$F_{total} = F_{wc} + F_{mc} + F_{wg} + F_{mg}$$

It is generally argued that the carbon isotopic composition of F_{total} would equal the mantle composition at approximately -6‰. This is because the integrated $\delta^{13}C$ value of the sedimentary weathering flux (organic and carbonate carbon) should average the same as the isotopic composition of the burial flux, while both would approximately equal that of metamorphic / volcanic outgassing. Assuming the existence of an additional carbon source, i.e. DOC oxidation, then the total source (= sink) flux would now equal:

$$F_{total} = F_{wc} + F_{mc} + F_{wg} + F_{mg} + F_{DOC}$$

, whereby F_{DOC} equals the carbon flux from DOC oxidation. Clearly $\delta^{13}C_{input}$ would be changed if any net imbalance occurred between DOC oxidation and DOC formation, as any extra ^{12}C-depleted carbon would not be balanced by a compensating ^{12}C-enriched source. To quantify this effect, for $\delta^{13}C_{input}$ to decrease to -12‰, partial oxidation of a pool of DOC ($\delta^{13}C$ = -30‰) would need to input an extra ~20% of the total carbon throughput, or net f_{DOC} = 0.2:

$$\delta^{13}C\,(F_{total}) = (1-f_{DOC}).\delta^{13}C\,(F_{wc} + F_{mc} + F_{wg} + F_{mg}) + (f_{DOC}).\delta^{13}C\,(F_{DOC})$$

Assuming modern carbon flux rates, this would be equivalent to ~10 $\times10^{12}$ mol C/yr. Taking the conventional carbon isotopic mass balance (1), and this new -12‰ value for $\delta^{13}C_{input}$, the steady-state $\delta^{13}C$ value for the ocean/atmosphere system works out at -8‰ for a proportional organic burial rate (f_{org}) of ~0.13 (Fig. 4), i.e. about the same as that for the late Cambrian / early Ordovician (Krissansen-Totton *et al.* 2015; Fig. 1).

The size of the DOC reservoir can be estimated from the duration and magnitude of the excursion, whereby for a duration of 10 million years, throughout which an ocean's $\delta^{13}C$ value was -8‰, a size 10^7 times higher than the annual flux rate would be required, i.e. about 1×10^{20} moles of carbon. For the sake of comparison, this is approximately 30 times larger than the modern ocean's inorganic carbon (DIC) reservoir. A similar magnitude (1.6×10^{21} grams, or 1.3×10^{20} moles of carbon) was estimated in a recent study (Ridgwell & Arndt 2015), which considered that the DOC pool needed to be ~10x larger than the contemporaneous total inorganic carbon (DIC + atmospheric pCO_2) inventory (Bristow & Kennedy 2008). For such long time-scales ($>10^5$ years), the size of the IC pool will determine the response time to the oxidation event, but not the magnitude or duration of the isotopic excursion, which is instead determined by the size of the relevant flux. Response times could have been similar to today (~10^5 years) and in any case less than an order of magnitude longer (<~10^6 years) during the Ediacaran-Cambrian transition interval because although the Ediacaran IC inventory was likely 4-5 times larger than at present (Ridgwell & Arndt 2015), the high rates of isotopic change (Maloof *et al.* 2010) and high rates of erosion (see above) indicate that flux rates were also relatively high.

Oxidation of the DOC pool at steady state requires that the annual supply of oxidant matched the total demand from terrestrial weathering and outgassing plus the increased net F_{DOC} flux. The oxidative weathering flux and the theoretical F_{DOC} flux above are of a similar order of magnitude, and so an approximate doubling of oxidant generation would need to be achieved through excess organic carbon burial, pyrite burial and iron reduction, equivalent to about 10×10^{12} mol O_2/yr for the duration of the negative excursion. By comparison, the present atmosphere contains about 36.6 $x10^{18}$ mol O_2, while the oceans contain an additional, substantial amount of oxidizing power in the form of sulphate ions. The necessary fluxes are six orders of magnitude smaller than the reservoir size, and of a similar magnitude to the modern organic burial rate at steady state, and so are not an insurmountable challenge to the world's oxidant budget. Far from depleting Earth's surface oxidant budget, an evolving steady state scenario does not need to imply any change in atmospheric pO_2 at all, although O_2 and CO_2 fluxes, and presumably pCO_2 would all see an increase from their previous levels during the isotope excursion.

Mechanisms of DOC oxidation imbalance

The prime contender for oxidation of the sub-pycnocline ocean would be organic carbon burial and/or pyrite burial, driven by increased rates of nutrient supply. In earlier papers, this was considered unlikely because organic carbon burial would tend to increase $\delta^{13}C$, and so counteract the effect of the DOC oxidation (Bristow & Kennedy 2008, Peltier et al. 2007, Ridgwell & Arndt 2015). However, as argued above, higher erosion rates are equally (Kaufman *et al.* 1993), or arguably more (*ibid*) consistent with a decrease in the proportional rate of organic carbon relative to carbonate burial (f_{org}), which is the major factor controlling mean $\delta^{13}C$ at equilibrium. Because increased erosion would expose more sedimentary organic matter and pyrite to oxidation, for DOC oxidation to proceed, an increased oxidant supply via organic production must have overwhelmed terrestrial oxygen sinks during negative excursions. During positive excursions, the opposite would have been the case, i.e. the terrestrial oxidant sink would have outweighed the marine oxidant source, leading to growth in the marine DOC reservoir. DOC oxidation is therefore consistent with the notion that nutrient flux from weathering was boosted at times during the Tonian to Cambrian interval (Kennedy *et al.* 2006) and/or that oxygen sinks were lowered (Kump 2014), following the evolution of soil biota. According to this latter scenario, the introduction of a significant upper soil layer would have decreased the delivery of oxygen to the weathering environment, resulting in a less efficient sink for oxygen on the continents.

In recent years, it has become increasingly popular to invoke the rise of animals as the cause, at least in part, of ocean oxygenation (Lenton *et al.* 2014) either through their actions to parcel organic matter into larger, denser packages such as fecal matter that sinks faster (Logan *et al.* 1995), or through the filter feeding habits of early sponges (Sperling *et al.* 2007). Butterfield (Butterfield 2009) considered the co-evolutionary impact of animal grazing on increasing the optimal size of phytoplankton, concluding that a perpetually turbid Precambrian ocean gave way to a clearer, and better oxygenated Phanerozoic one as a result. Once the dominance of cyanobacterial picoplankton in the Proterozoic oceans gave way to larger eukaryotic forms, an irreversible shift in the biological pump towards greater sinking rates seems plausible. Although all of these ideas have considerable merit, biologically induced DOC oxidation (as with climatically or oceanographically induced DOC oxidation) is fundamentally self-limiting in the absence of excess oxygen production.

In the case of greater sinking rates, presumably due to a combination of larger cell sizes, greater tendency to aggregate, and increased ballasting from tests and scales, oxygen demand would spread out over a greater depth of the water column, weakening peak oxygen demand and shifting the zone of maximum oxygen demand from shallower to deeper realms (Lenton *et al.* 2014), and also deeper into the sedimentary column beneath oxygenated waters (McIlroy & Logan 1999, Brasier & Callow 2007). A decrease in global oxygen demand would reduce the volume, in which sulphate reduction could be supported, thus causing a shift towards more ferruginous or even oxic conditions in the sediment and water columns. The existence of a vast pool of DOC complicates this scenario because DOC acts as a redox buffer in the ocean, counteracting ocean oxygenation (Fig. 5). Sponges (and cnidaria and ctenophores) are undoubtedly capable of clearing the water column of organic material, especially picoplankton and DOC, thus transferring oxygen demand to the sediment interface. However, DOC oxidation caused solely by the onset of filter feeding or planktonic grazing would upset the world's oxidant balance, rapidly draining the atmosphere of oxygen, long before it could be expressed in the carbon isotope record (Bristow & Kennedy 2008, Lenton *et al.* 2014). Biologically-triggered oxidation of DOC, e.g. by sponges (Sperling *et al.* 2007), would therefore be implausibly self-limiting.

Instead of viewing times of net DOC oxidation as times of additional oxidant sink, we can alternatively view it as a dynamic response to excess oxidant. A more parsimonious account of the Ediacaran-Cambrian isotope record views net DOC oxidation as the predictable response to a net oxidant imbalance during times of higher organic production and/or lowered oxidant demand, due to external factors. Oxygenation, thus caused, would have permitted waves of expansion of the benthic animal kingdom throughout the oceans, in a form of co-evolutionary piggyback between life and its environment, through which the Earth system moved in oscillatory fashion towards its new steady state.

Causes and consequences of the Proterozoic marine organic carbon capacitor

One of the only studies to investigate the source of the organic matter deposited during the Shuram excursion concluded that there were two distinct pools (Lee et al., 2015). One pool derived from autotrophs fixing ^{13}C-depleted DIC, thus confirming again the primary character of the excursion. The other pool was shown to derive from a less ^{13}C-depleted heterotrophic microbial biomass feeding on a marine organic pool. Their interpretation was that this second pool was generated from petroleum expelled from sedimentary rocks beneath the seafloor, although it was found to be compositionally identical to the UCM (unresolved complex mixture) found commonly in other Proterozoic sedimentary rocks (Pawlowska *et al.* 2013). According to the petroleum seepage model, negative excursions are predicted to coincide with expulsion events. This explanation for negative δ^{13}C excursions suffers from the same problem as other disequilibrium hypotheses outlined above, in that petroleum oxidation would ultimately be self-limiting, and therefore unsustainable in the absence of a coincidental oxidant imbalance. It could be that petroleum was indeed a major contributor to the dissolved organic carbon reservoir and became oxidized during times of oxidant imbalance, but it is as yet unclear whether all Proterozoic kerogen bearing the characteristic UCM signature must derive from petroleum. Alternatively, it could yet prove to be a diagnostic signature for any long-lived, microbially recycled organic carbon component in the ocean, for which we may not have appropriate modern analogues.

Another likely source of the organic carbon pool would be the remains of phytoplankton, and/or the remains of bacteria that processed this phytoplankton. From theoretical considerations, organic carbon seems to have had a much longer residence time in the Proterozoic ocean than today (Butterfield 2009) with the inevitable consequence that recalcitrant DOC was more abundant (Jiao *et al.* 2010, Hansell 2013). One intriguing recent suggestion, based on comparative molecular phylogeny, is that ocean-going nitrogen fixers evolved only in the Tonian Period (Sanchez-Baracaldo *et al.* 2014). If confirmed, this shift in organic production from the shallow marine environment to the global surface ocean, potentially facilitated by an increased availability of nitrogenase co-factors, such as Mo, might explain why negative excursions only feature after about 0.9 Ga. The spread of N-fixers would also have facilitated the spread of eukaryotic phytoplankton that are dependent on bacterial sources for fixed nitrogen. Although speculative, the onset of negative excursions could mark an increase in pelagic organic production. Despite my attraction to this idea, I think it more likely, that some pelagic organic production and small negative excursions (net increases in DOC oxidation) occurred periodically throughout the Proterozoic, but that these were damped by a far more substantial DIC reservoir in the ocean. A vastly greater DIC pool prior to the Cryogenian glaciations is consistent with the geological record (Arp *et al.* 2001) and could explain why extreme cooling events did not take place during the preceding ~1.5 billion years or more. In this case, the appearance of larger $\delta^{13}C$ excursions, both positive and negative, could signify a diminished ratio between DIC and DOC in the Neoproterozoic Era.

The persistence of a large DOC pool in the lower oceans would have acted as a carbon capacitor, buffering against the effects of any imbalances in the net carbon cycle via a negative feedback (Peltier *et al.* 2007), whereby increases in organic production release oxidizing power that remineralizes DOC, releasing CO_2, thus rebalancing both carbon and oxygen budgets (Fig. 5). As long as DOC oxidation matched the oxidant imbalance, oxygenation and climate change, via the carbon cycle, would have been strongly regulated (Liu & Peltier 2011). However, once depleted, any continuing imbalance would result in a rise in atmospheric oxygen and ocean sulphate, and concomitant decrease in CO_2. In the absence of any strong negative feedback, the Earth’s climate would have been rendered vulnerable to any subsequent perturbation to the net carbon cycle. A key prediction of this scenario is that negative excursions ought to precede evidence for cooling, but importantly should recover to more positive values before the onset of glaciation, consistent with the complete removal of the DOC climate buffer, but continuation of significant organic production.

Towards a synthetic model for Tonian to Cambrian Earth system changes

A test of the above model is provided by the onset of the Cryogenian glaciations, which began after about 717 Ma (Macdonald *et al.* 2010, Lan *et al.* 2014). Recent radiometric age constraints suggest that the pre-glacial 'Islay' negative anomaly (Brasier & Shields 2000) preceded the onset of this glaciation by as much as 15 million years (Rooney *et al.* 2014), and was accompanied by falling seawater $^{87}Sr/^{86}Sr$ (Sawaki *et al.* 2010, Rooney *et al.* 2014). The fall in $^{87}Sr/^{86}Sr$ coincides approximately with the eruption and exposure to weathering of less radiogenic volcanic rocks associated with the rifting of Rodinia (Macdonald *et al.* 2010, Gernon *et al.* 2016) The enhanced weatherability of these volcanic rocks (Cox *et al.* 2016), made more potent by the postulated removal of the marine organic capacitor, could have led to runaway glaciation (Donnadieu *et al.* 2004). High nutrient levels around this time (Horton 2015, Cox *et al.* 2016) are also supported by Fe-speciation data from the Chuar Group (USA) that demonstrate euxinic conditions prior to the onset of glaciation (Nagy *et al.* 2009, Johnston *et al.* 2010). Euxinia was unusual during the otherwise 'ferruginous' Neoproterozoic times (Guilbaud *et al.* 2015), and suggests enhanced chemical weathering rates and a short-lived build-up of oxidant sulphate in the pre-glacial ocean. The switch to euxinic conditions coincides with a biotic turnover, whereby diverse acritarch assemblages (e.g. *Cerebrosphaera buickii*) were replaced by low diversity assemblages, comprising the simple smooth-walled acritarchs (leiosphaerids) that were destined to become the typical phytoplankton of the Cryogenian Period (Grey *et al.* 2011, Riedman *et al.* 2014), and vase-shaped microfossils (VSMs), widely interpreted to be the fossilized remains of testate amoebae (Strauss *et al.* 2014). Future studies will undoubtedly strengthen the global stratigraphic framework that underpins our understanding of the relative timing of these pre-glacial events, but at present they appear to be consistent with nutrient-driven DOC oxidation, leading to glaciation.

A similar exhaustion of the DOC pool is envisaged for the onset of the ~650 Ma, end-Cryogenian *'Marinoan'* glaciation (Swanson-Hysell *et al.* 2010), which is preceded by the extraordinary *'Trezona'* $\delta^{13}C$ anomaly (McKirdy *et al.* 2001). Importantly, the non-glacial Sturtian (*sensu stricto*) successions of South Australia, representing the Late Cryogenian Warm interval (Shields-Zhou *et al.* 2016, Fairchild *et al.* 2016), are very thick compared with carbonate successions elsewhere in the world, and so have the greatest likelihood of recording immediately pre-glacial $\delta^{13}C$ trends. A recent study confirms that the 'recovery' to ~0‰ coincides precisely with the onset of glaciation at tropical latitudes (Rose *et al.* 2012). Onset of glaciation following recovery from a major and prolonged negative excursion is a key prediction of the synthetic model proposed here, and implies that the extremely high $\delta^{13}C$ values of the non-glacial interval of the Cryogenian Period, from ~665 Ma - ~650 Ma, were due in part to the build-up of a DOC pool in the lower oceans.

Several authors consider that the ~580 Ma Gaskiers glaciation coincided with a relatively small, negative C-isotope excursion in the Yangtze Gorges area of South China (Macdonald *et al.* 2013b). Because cold waters contain more oxygen, this negative anomaly could reflect the negative feedback between cooling and DOC oxidation (Fig. 5) that has been suggested would prevent a runaway ice age (Peltier *et al.* 2007), but only as long as the DOC reservoir was not exhausted. The end-Ediacaran Shuram anomaly, however, is much larger. Considering the duration of the anomaly, and the magnitude of any associated DOC oxidation, it seems unlikely that glaciation coincided with the anomaly. However, its existence perhaps lends weight to published arguments for an Ediacaran-Cambrian boundary glaciation (Chumakov 2009). In any case, the Shuram anomaly is consistent with pervasive oxygenation of the world's oceans by 550 Ma, something that is supported by numerous lines of other geochemical evidence (Shields-Zhou & Och 2011).

After the Shuram anomaly, which ended by 550 Ma (Condon *et al.* 2005), negative excursions became lesser in magnitude, suggesting that the DOC pool attained much smaller proportions during ever shorter pulses of growth during the early Cambrian (Fig. 3). The exhaustion of the DOC reservoir would have had the effect not only of securing the oxygenation of the deeper seafloor on a global scale, but also of allowing oxygen in the atmosphere to build up for a time during continued oxidant imbalance. This may help to explain the evolutionary expansion of energy-sapping metabolic processes and biological traits during the ensuing Ediacaran-Cambrian transition, including mobility (Liu *et al.* 2010, Chen *et al.* 2013), carnivory (Sperling *et al.* 2013) and biomineralization (Penny *et al.* 2014). With the buffering effects of the global DOC capacitor dwindling, oxygen may have eventually stabilized at higher baseline levels via less efficient terrestrial oxygen sinks (Kump 2014), and/or the more efficient nutrient (P) removal mechanisms under oxic conditions (Shields-Zhou & Zhu 2013, Boyle *et al.* 2014, Dale *et al.* 2016), especially following the introduction of pervasive bioturbation (Buatois *et al.* 2014), which vastly increased the volume of reduced sedimentary materials exposed to ocean oxidants (Aller 1994, Teal *et al.* 2008). It is conceivable, therefore, that the actions of animals, such as bioturbation, also helped the climate system to achieve greater resilience against any subsequent net carbon cycle perturbations, in the absence of the stabilizing effects of the vast DOC pool (Shields-Zhou & Zhu 2013, Boyle *et al.* 2014).

Concluding remarks

The Proterozoic Earth system was a highly non-uniformitarian world, whereby the Tonian to Cambrian interval of exceptional upheaval can be viewed as a series of oscillations towards greater oxygenation of the marine environment. The existence of a vast DOC reservoir, which waxed and waned in response to climatic and tectonic events, helped to buffer both climate and oxygen levels on Earth for over a billion years. Times of excessive nutrient availability led to net oxidation and at least three times between 720 and 520 Ma to near complete exhaustion of this DOC capacitor. This rendered the Earth's climate balance vulnerable to continued carbon cycle perturbations, caused, for example, by enhanced weathering of freshly exposed volcanic provinces. Removal of the DOC pool led to a series of glaciations, beginning after about 717 Ma, and potentially ending close to the Ediacaran-Cambrian boundary. Oxygen levels also experienced volatility following depletion of the DOC reservoir, facilitating opportunistic radiations of animal life during the Ediacaran-Cambrian transition. Higher oxygen levels were likely stabilized by the further evolution of animals and their behavioural traits, including the introduction of bioturbation, which strengthened redox-related nutrient feedbacks. This synthesis makes a number of predictions that can be tested against our improving understanding of the geological record. It does not seek to explain biodiversification as such because that is a fundamentally biological process. However, it does aim to provide a backdrop against which the evolutionary expansion of animals and other biological innovations during the Tonian to Cambrian interval can be viewed.

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Figure captions

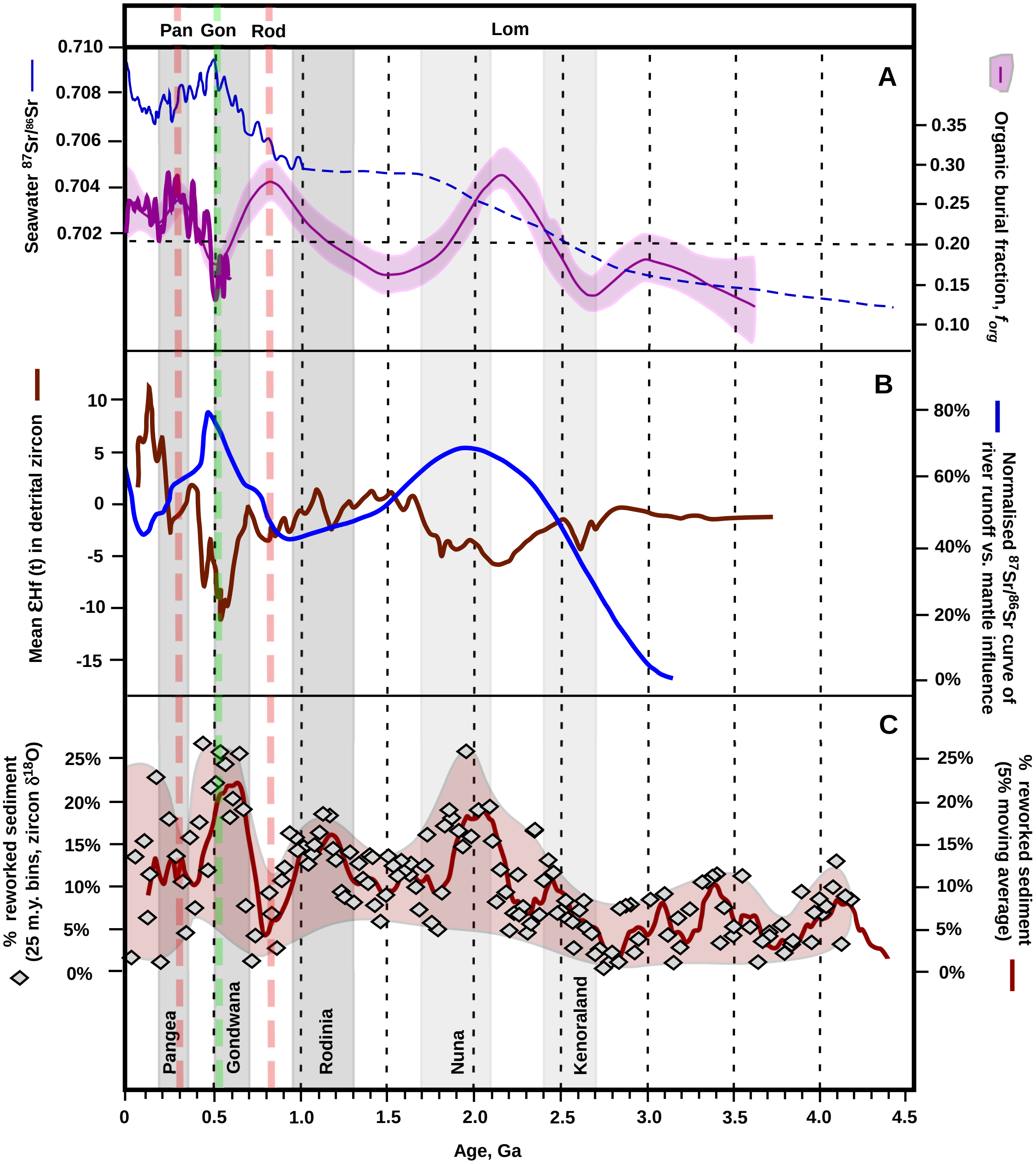
Fig. 1. Secular trends in key isotopic parameters in zircons and marine carbonates. Part C: Magmatic zircon abundances and δ^{18}O values reveal when five supercontinents formed through orogenic collision (vertical grey bars), leading to greatly increased reworking of sediment during magmatism (Spencer et al. 2014). Part B: The zircon Hf (Cawood et al., 2013) and seawater Sr isotope (Shields, 2007) records anti-correlate, confirming that the Ediacaran-Cambrian interval was a time of exceptional erosional unroofing of crustal roots. Part A: The δ^{13}C (f_{org}) minimum at ~500 Ma (Krissansen-Totton et al. 2015), shown as a dashed green line, occurred during the peak in Gondwanan orogenesis. δ^{13}C (f_{org}) maxima, shown as dashed red lines, coincide with the existence of Pangea and Rodinia, respectively, before onset of break-up. The time-averaged δ^{13}C record for the Ediacaran-Present (Fig. 2) is shown superimposed on the smoothed curve of Krissansen-Totton et al. (2015: Fig. 3c).

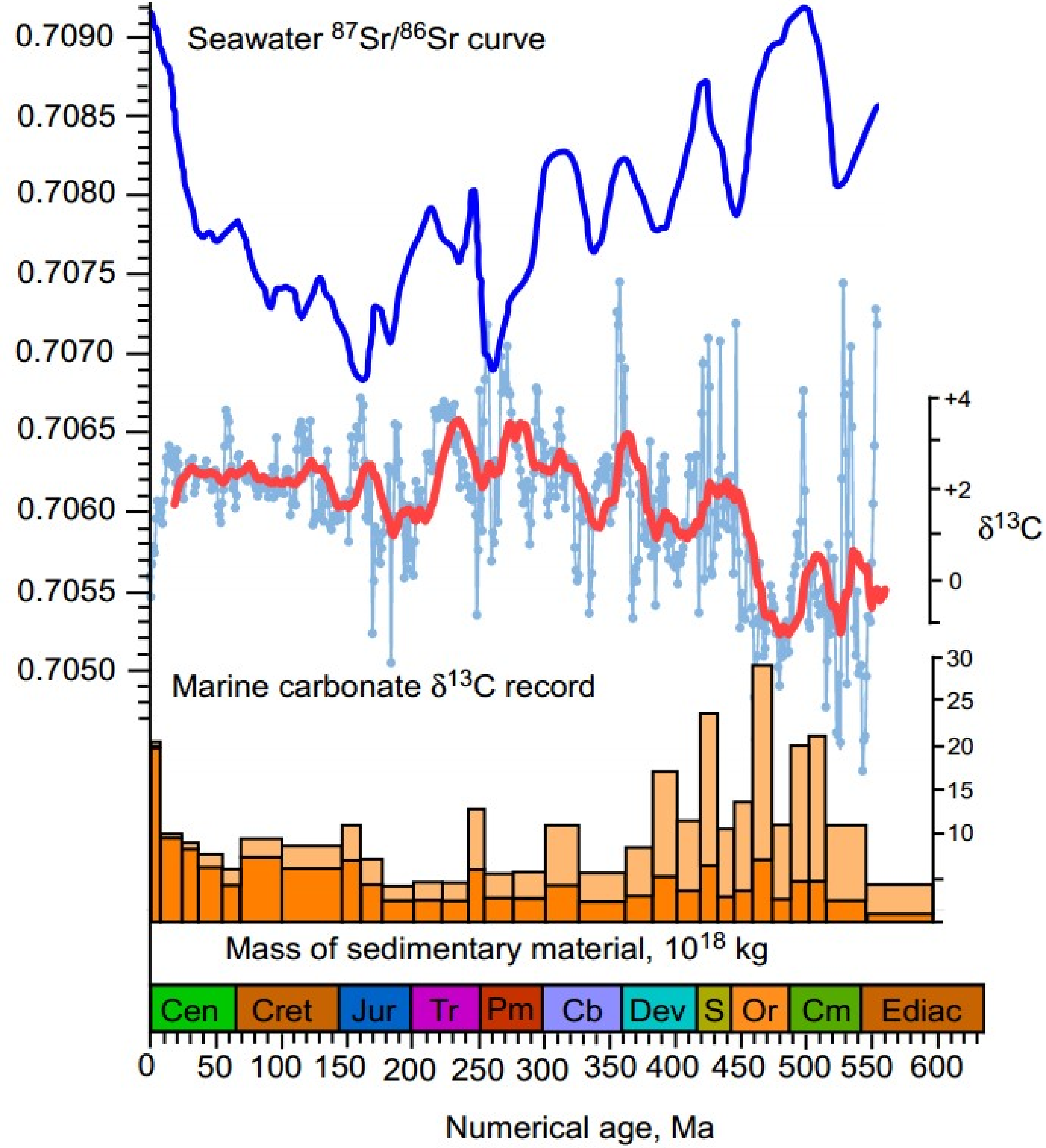
Fig. 2. Phanerozoic records of marine carbonate δ^{13}C (Saltzman & Thomas 2012), seawater ^{87}Sr/^{86}Sr (McArthur et al. 2012) and mass of sedimentary material (Hay et al. 2006) (Hay et al. 2006). The δ^{13}C record is shown as averages of 1 Myr bins, as well as a 20 point moving average. The Ediacaran-Cambrian interval of high erosion (Fig. 1) is marked by a peak in sedimentary deposition, generally low δ^{13}C, and a succession of high amplitude δ^{13}C excursions that become less extreme after the early Cambrian.

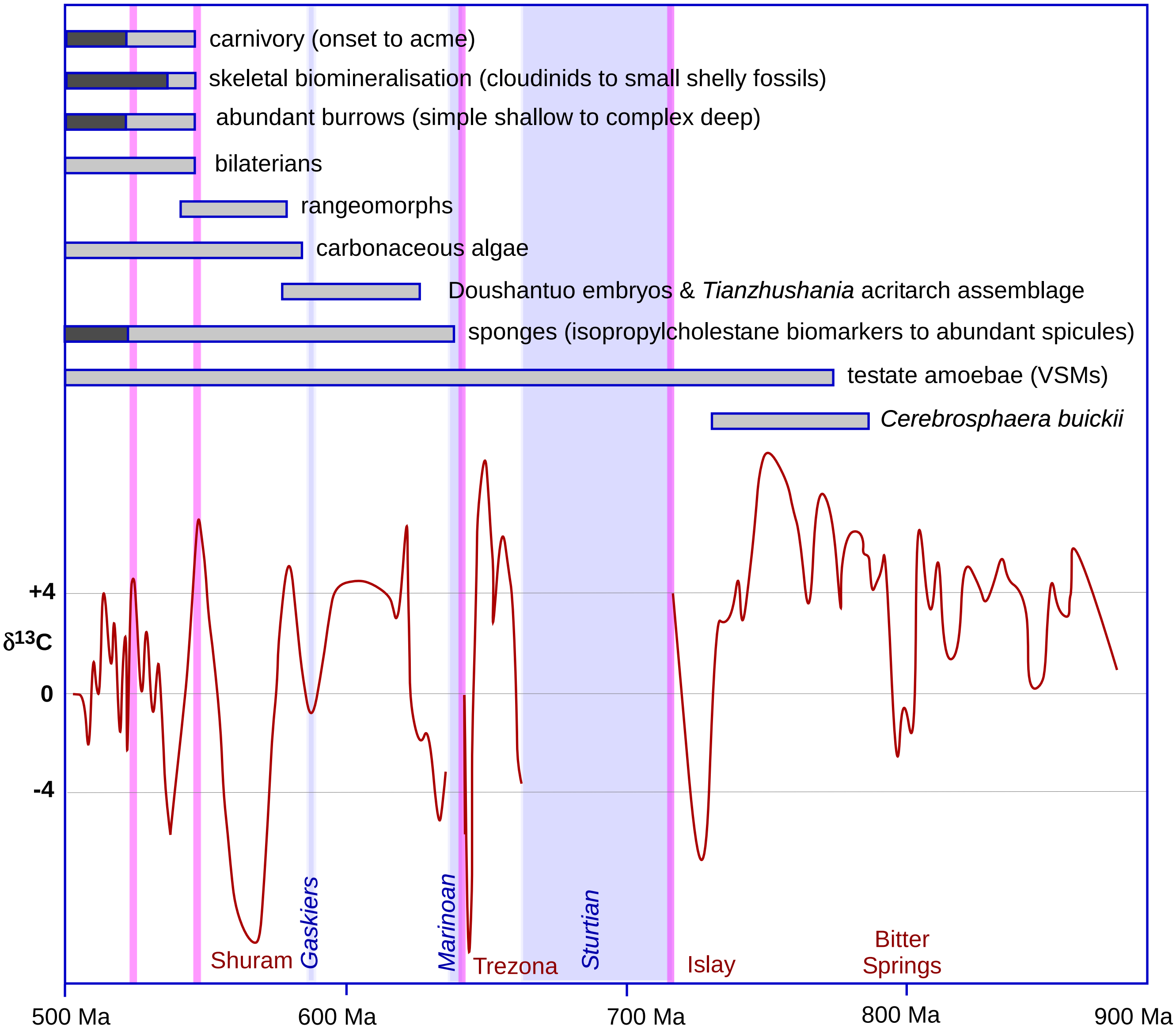
Fig. 3. Cross calibration of the carbonate carbon isotope, fossil and climate records for the Tonian to Cambrian interval (Narbonne et al. 2012, Shields-Zhou et al. 2016). Dark pink bars mark four times of δ^{13}C recovery that directly follow postulated exhaustion of the ocean DOC pool. Three paler blue bars mark glaciations, whereby the relative timing of the Gaskiers glaciation is less certain.

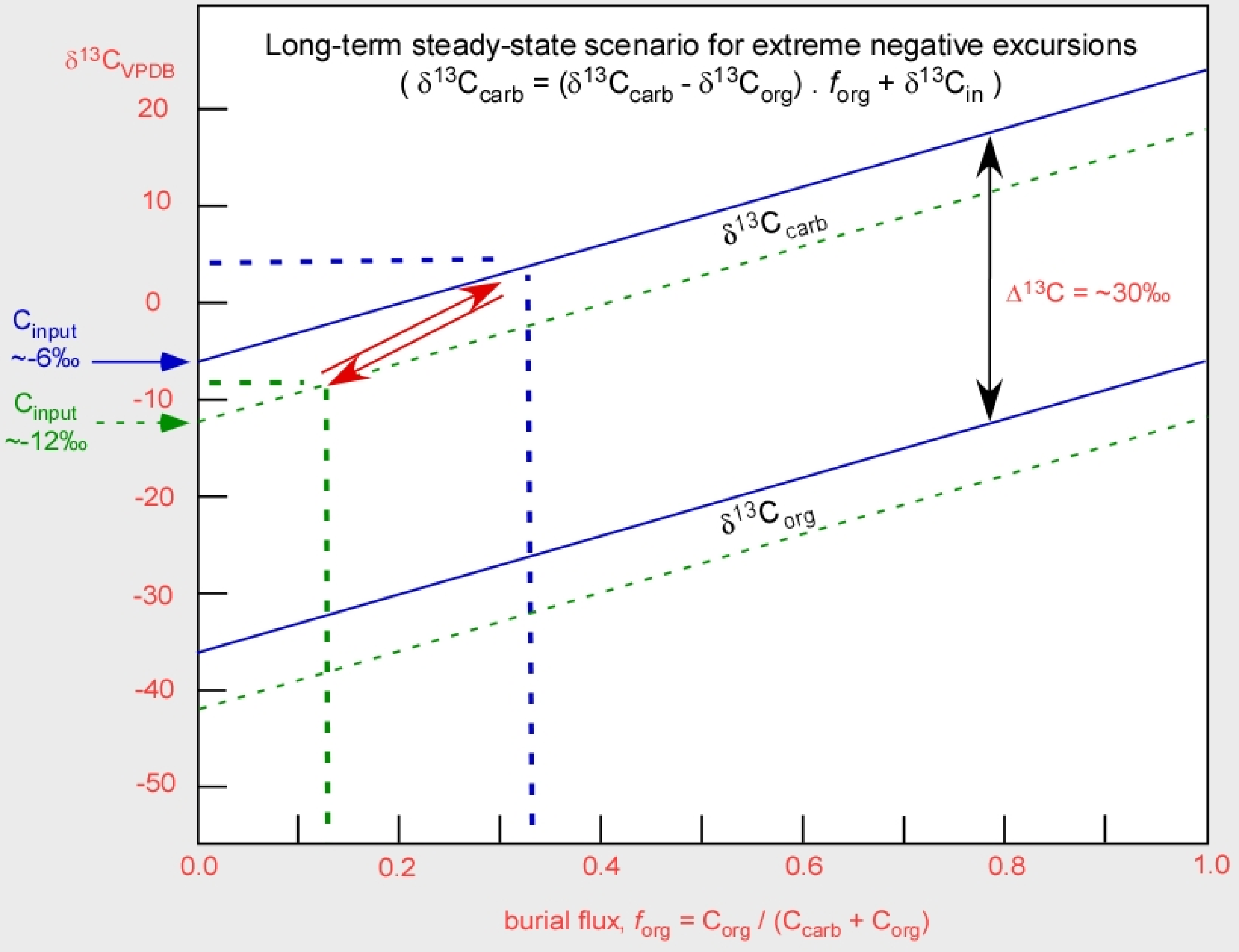
Fig. 4. Long-term carbon isotope mass balance shown as linear relationship between $\delta^{13}C_{carb}$ (carbon isotopic composition of ocean-atmosphere system) and f_{org} (proportion that organic carbon burial makes of total carbon throughput). A change in the steady state from $\delta^{13}C = +4‰$ to $-8‰$ could be related to a change in $\delta^{13}C_{input}$ from $-6‰$ to $-12‰$ and a change in f_{org} from 0.33 to 0.13 (red arrows show evolution between the two steady states). This equates to sustained injection of remineralised organic carbon ($\delta^{13}C = -30‰$), amounting to ~20% of the total throughput (see main text).

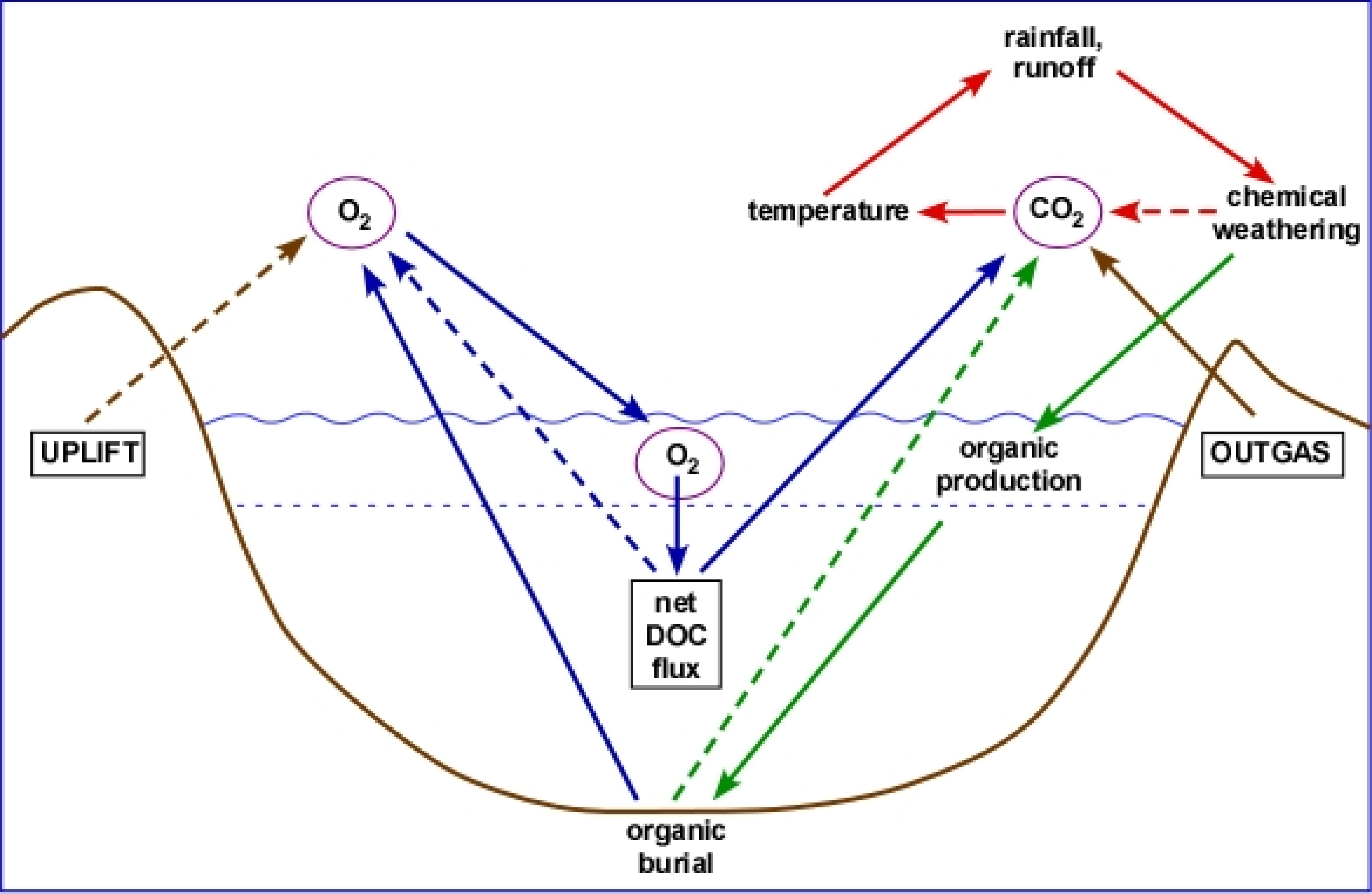
Fig. 5. System analysis diagram (Lenton & Watson 2000) showing reservoirs in circles, and flux in square boxes. The arrows indicate a functional dependence of one component on another and its directionality, whereby dashed lines indicate an inverse relationship. Loops with odd numbers of dashed lines represent negative feedbacks. For example, the cooling effect caused by increased chemical weathering (red and green loops) is mitigated here by the positive feedback loop (blue loop) via DOC oxidation (net DOC flux) that restores atmospheric CO_2 levels. Likewise, oxygen levels are kept low but stable via the related negative feedback (blue loop), which allows the DOC reservoir to wax and wane in response to flux imbalances.


Pan
Gon
Rod
Lom
A
Seawater $^{87}Sr/^{86}Sr$
0.710
0.708
0.706
0.704
0.702
Organic burial fraction, f_{org}
0.35
0.30
0.25
0.20
0.15
0.10
B
Mean ƐHf (t) in detrital zircon
10
5
0
-5
-10
-15
Normalised $^{87}Sr/^{86}Sr$ curve of river runoff vs. mantle influence
80%
60%
40%
20%
0%
C
% reworked sediment (25 m.y. bins, zircon $\delta^{18}O$)
% reworked sediment (5% moving average)
25%
20%
15%
10%
5%
0%
Pangea
Gondwana
Rodinia
Nuna
Kenoraland
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Age, Ga


0.7090
0.7085
0.7080
0.7075
0.7070
0.7065
0.7060
0.7055
0.7050
Seawater $^{87}Sr/^{86}Sr$ curve
+4
+2
0
δ^{13}C
Marine carbonate δ^{13}C record
30
25
20
15
10
Mass of sedimentary material, 10^{18} kg
Cen
Cret
Jur
Tr
Pm
Cb
Dev
S
Or
Cm
Ediac
0
50
100
150
200
250
300
350
400
450
500
550
600
Numerical age, Ma


carnivory (onset to acme)
skeletal biomineralisation (cloudinids to small shelly fossils)
abundant burrows (simple shallow to complex deep)
bilaterians
rangeomorphs
carbonaceous algae
Doushantuo embryos & *Tianzhushania* acritarch assemblage
sponges (isopropylcholestane biomarkers to abundant spicules)
testate amoebae (VSMs)
Cerebrosphaera buickii
+4
δ13C
0
-4
Shuram
Gaskiers
Marinoan
Trezona
Sturtian
Islay
Bitter Springs
500 Ma
600 Ma
700 Ma
800 Ma
900 Ma


Long-term steady-state scenario for extreme negative excursions
($\delta^{13}C_{carb} = (\delta^{13}C_{carb} - \delta^{13}C_{org}) \cdot f_{org} + \delta^{13}C_{in}$)
$\delta^{13}C_{VPDB}$
20
10
0
-10
-20
-30
-40
-50
C_{input} ~-6‰
C_{input} ~-12‰
$\delta^{13}C_{carb}$
$\delta^{13}C_{org}$
$\Delta^{13}C$ = ~30‰
0.0
0.2
0.4
0.6
0.8
1.0
burial flux, $f_{org} = C_{org} / (C_{carb} + C_{org})$


rainfall,
runoff
O2
temperature
CO2
chemical
weathering
O2
UPLIFT
organic
production
OUTGAS
net
DOC
flux
organic
burial