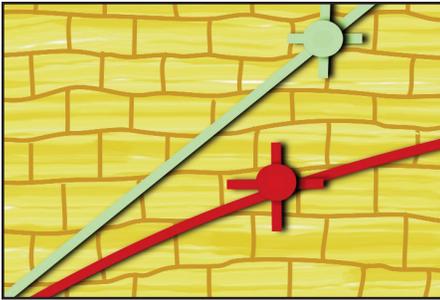


# PAUL F. HOFFMAN SERIES



## A Temperature-Dependent Positive Feedback on the Magnitude of Carbon Isotope Excursions

Seth Finnegan<sup>1,2</sup>, David A. Fike<sup>3</sup>,  
David Jones<sup>4</sup>, Woodward W.  
Fischer<sup>1\*</sup>

<sup>1</sup> *Division of Geological and Planetary Sciences, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA, 91125, USA*

<sup>2</sup> *Department of Integrative Biology, University of California, 1005 Valley Life Sciences Bldg #3140, Berkeley, CA, 94720, USA*

<sup>3</sup> *Department of Earth and Planetary Sciences, Washington University, St. Louis, MO, 63130, USA*

<sup>4</sup> *Department of Geology, 11 Barrett Hill Road, Amherst College, Amherst, MA, 01002-5000, USA*

\* *Corresponding Author:*  
wfisher@caltech.edu

### SUMMARY

The decrease in the average magnitude of carbon isotope excursions in marine carbonates over Phanerozoic time is a longstanding unresolved problem. In addition, carbon isotope excursions

commonly co-occur with oxygen isotope excursions of the same sign, implying the existence of a longstanding link between organic carbon burial fluxes and temperature. It was proposed that this connection was provided by the thermodynamic relationship between temperature and microbial respiration rates – changes in temperature drive changes in organic carbon remineralization rate and organic carbon burial efficiency. Such a mechanism provides the logic for a positive feedback affecting the magnitude of both climate changes and carbon isotope excursions. Here, we employ feedback analysis to quantify the strength of this mechanism with modifications to a simple carbon isotope mass balance framework. We demonstrate that the potential strength of this feedback is large (perhaps several permil) for plausible ranges of historical climate change. Furthermore, our results highlight the importance of the surface temperature boundary condition on the magnitude of the expected carbon isotope excursion. Comparisons of our model predictions with data from the terminal Eocene and Late Ordovician (Hirnantian) greenhouse–icehouse climate transitions suggest that these excursions might be substantially explained by such a thermodynamic microbial respiration feedback. Consequently, we hypothesize that the observed pattern of decreasing excursion magnitude toward the present might be explained at least, in part, by a decrease in the mean temperature of environments of organic carbon burial driven by long-term climate and paleogeographic trends.

### SOMMAIRE

La diminution de l'amplitude moyenne des excursions des isotopes du carbone

dans les carbonates marins au fil du Phanérozoïque est une énigme de longue date. On note en outre que les excursions des isotopes du carbone coexistent couramment avec des excursions isotopiques de même signe de l'oxygène, ce qui implique l'existence d'un lien de longue date entre les flux d'enfouissement du carbone organique et la température. On a suggéré que ce lien découlait de la relation thermodynamique entre la température et les taux de respiration microbienne - les changements de température déterminent le taux de reminéralisation du carbone organique et l'efficacité de l'enfouissement du carbone organique. Un tel mécanisme peut expliquer la rétroaction positive affectant à la fois l'ampleur des changements climatiques et les excursions des isotopes du carbone. Dans le cas présent, nous utilisons l'analyse de la rétroaction pour quantifier la robustesse de ce mécanisme avec des modifications d'un simple bilan de masse des isotopes du carbone. Nous démontrons que la robustesse potentielle de cette rétroaction est forte (peut-être plusieurs pour mille) dans les gammes plausibles du changement climatique historique. De plus, nos résultats mettent en évidence l'importance de la condition aux limites de la température de surface sur l'ampleur de l'excursion isotopique du carbone attendue. Les comparaisons des prédictions de notre modèle avec les données de la fin de l'Éocène et de la fin de l'Ordovicien (Hirnantien) des transitions climatiques à effet de serre/effet/de glaciation permettent de penser que ces excursions pourraient être correctement expliquées par une telle rétroaction de la thermodynamique de la respiration microbienne. Par conséquent, nous émettons l'hypothèse que la tendance observée de

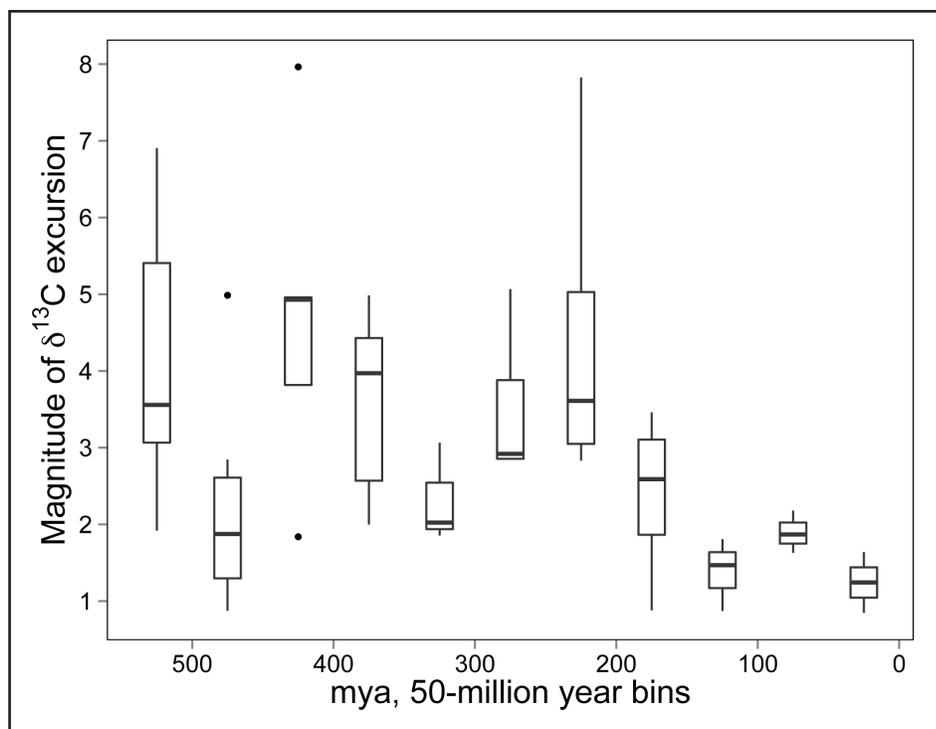
diminution de l'ampleur de l'amplitude des excursions du passé vers le présent peut s'expliquer, au moins en partie, par une diminution de la température moyenne du milieu d'enfouissement du carbone organique engendrée par des tendances climatiques et paléogéographiques à long terme.

## INTRODUCTION

Geologically rapid excursions in the carbon isotopic composition of marine carbonates and organic matter ( $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$ , respectively) are a conspicuous but still incompletely understood feature of the stratigraphic record. The  $\delta^{13}\text{C}$  trends record clear changes in the behaviour of the carbon cycle, but may reflect a variety of processes including volcanic activity, rock weathering, primary production, and organic carbon preservation; and many excursions likely record complex interactions between carbon cycle processes (Kump and Arthur 1999). Nevertheless, some commonalities can be observed that can help identify important, longstanding feedbacks.

Noting that Phanerozoic  $\delta^{13}\text{C}$  excursions commonly exhibit a positive correlation with  $\delta^{18}\text{O}$  excursions, Stanley (2010) suggested that many  $\delta^{13}\text{C}$  excursions were caused by climate change via the thermodynamic linkage between ambient temperature and the metabolic rates of microbial decomposers, using similar logic to biogeochemical models of marine production export efficiency (Laws et al. 2000). The idea is simple and useful: microbial respiration rates are strongly temperature-dependent, and so changes in ocean temperatures affect the efficiency of organic carbon export and burial, and can thereby drive changes in  $\delta^{13}\text{C}$  values. In this framework, climate cooling causes more efficient organic carbon burial and positive  $\delta^{13}\text{C}$  excursions; climate warming has the opposite effect and would cause negative excursions (Stanley 2010). As noted by Stanley (2010), this mechanism additionally provides a potential explanation for the commonly observed coincidence of  $\delta^{13}\text{C}$  excursions with extinction events in the fossil record.

One important aspect of Phanerozoic  $\delta^{13}\text{C}$  excursions that Stanley (2010) was unable to fully explain is the variation in their magnitudes over

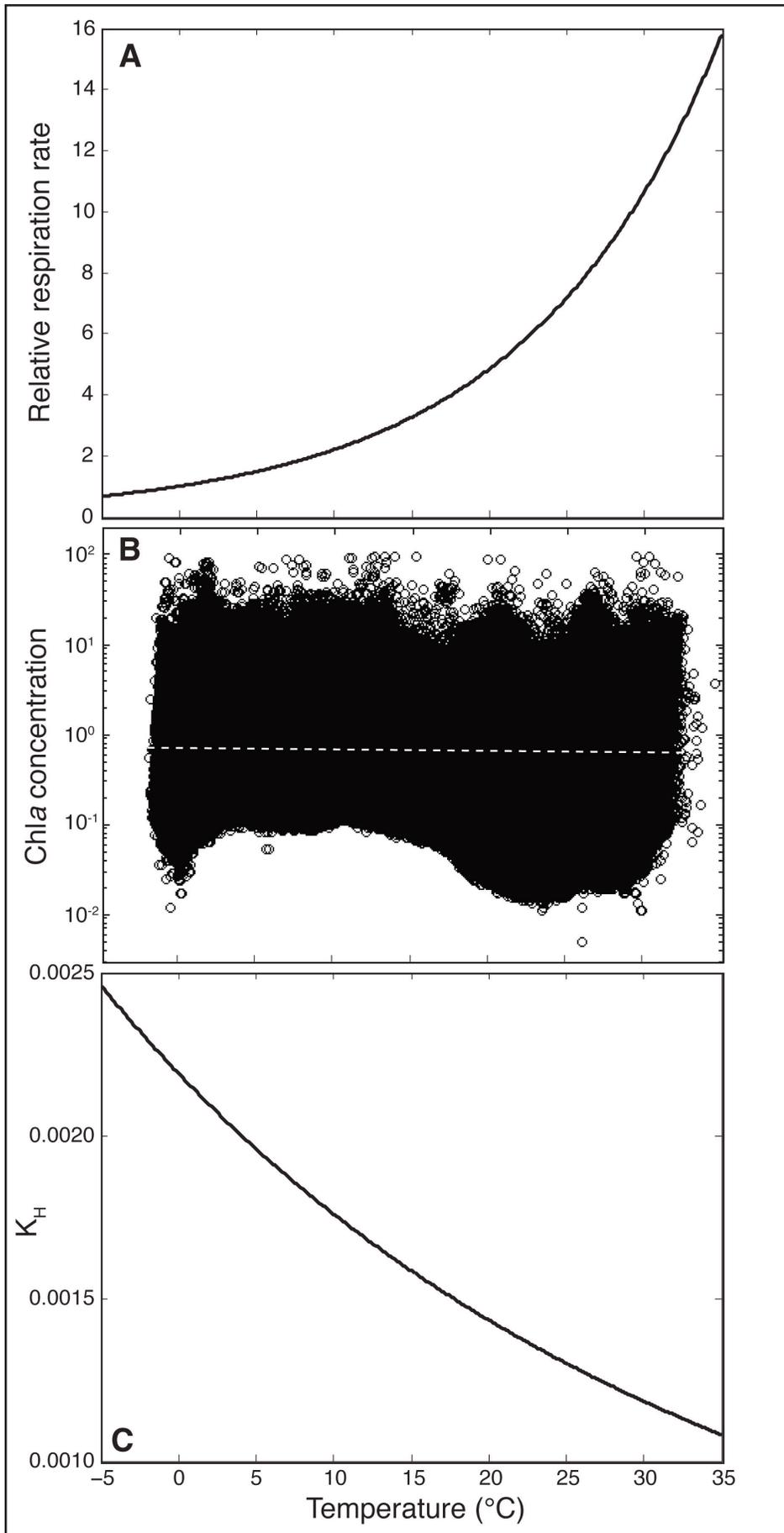


**Figure 1.** Boxplots showing carbon cycle behaviour through the Phanerozoic in terms of the magnitude (absolute value of change, in permil) of  $\delta^{13}\text{C}$  excursions, binned into 50 million year intervals. Horizontal bars are medians, and boxes enclose the interquartile ranges (25<sup>th</sup> through 75<sup>th</sup> percentile), closed circles mark outliers. Data from Saltzman and Thomas (2012), with excursions defined as in Grotzinger et al. (2011).

Earth history. He noted that, “*It is puzzling, for example, that the terminal Eocene excursions were small despite having been associated with substantial global cooling.*” In fact, the terminal Eocene excursion is one of the largest of the Cenozoic interval, but it is comparatively small in the context of Earth history. Indeed, one of the most striking features of the Phanerozoic carbon isotope record is a decline in the average magnitude of isotope ratio excursions through time (Grotzinger et al. 2011; Fig. 1). Here, we elaborate on Stanley’s (2010) hypothesis and draw attention to a possible explanation for the decrease in the magnitude of  $\delta^{13}\text{C}$  excursions observed over Phanerozoic time.

We hypothesize that a key aspect of the temperature–organic carbon burial feedback is its sensitivity to the initial boundary condition: due to the exponential nature of the relationship between environmental temperature and metabolic rates (Fig. 2A), the expected magnitude of change in organic carbon burial (and  $\delta^{13}\text{C}$ ) depends not just on the sign and mag-

nitude of temperature change but also, critically, on the baseline temperature from which temperature change initiates (hereafter referred to as initial temperature). It is possible to modify and employ simple isotope mass-balance calculations to estimate the potential effect strength (i.e. system gain) that this feedback might provide, and then reflect on these estimates by comparison to paleoclimate proxy data generated from the fossil record. The relative magnitudes of the terminal Eocene and Late Ordovician carbon isotope excursions – two events that record greenhouse–icehouse transitions – can be explained, in part, by proxy-based reconstructions of initial temperature and change in temperature during these events. Building on this result, we develop the hypothesis that one possible explanation for the decreasing magnitude of carbon isotope excursions throughout Phanerozoic time is the lower temperatures of organic carbon burial environments due to the overall cooling trend observed in proxies of seawater tem-



**Figure 2.** Temperature dependence of several important feedbacks on marine organic carbon burial. A) Thermodynamic relationship between respiration rate and temperature. The plotted function ( $Q_{10}$  exponent of 2.2, normalized relative to respiration rate at  $0^{\circ}\text{C}$ ) is typical for microbial respiration in marine sediments (Robador et al. 2009; Stanley 2010). B) Relationship between mean annual primary production (SeaWiFS data product for chlorophyll *a* concentration, units of  $\text{mg}/\text{m}^3$ ) and mean annual sea surface temperature (MODISA data product) for equal-area grid cells in the global ocean for year 2010. There are approximately 5.4 million observations plotted. For context, average SST in the MODISA dataset shown here is  $16^{\circ}\text{C}$ . Dotted line is an ordinary least-squares regression – no substantial relationship between temperature and productivity is apparent in the geodetic data. C) Temperature dependence on  $\text{O}_2$  solubility from Henry's law constant. Units are  $\text{mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}$ .  $\text{O}_2$  solubility declines with increasing temperature, but the expected change in seawater  $\text{O}_2$  concentration for a given change in temperature is higher at low starting temperatures than at high starting temperatures.

perature, and to net movement of continents from tropical to temperate latitudes over this interval.

### FEEDBACK ANALYSIS AND EFFECT STRENGTH

It is useful to conceptualize the temperature-dependent organic carbon burial mechanism proposed by Stanley (2010) as a feedback in a dynamic system, rather than an external forcing mechanism, because many other factors can drive and influence  $\delta^{13}\text{C}$  trends in addition to climate (Jones and Jenkyns 2001; Svensen et al. 2004; Tejada et al. 2009). Some  $\delta^{13}\text{C}$  excursions may record changes in total carbon burial flux rather than merely changes in the ratio of organic to inorganic carbon burial (Brenchley et al. 1994; Saltzman and Young 2005), and in these cases climate changes may be a

consequence, rather than a cause, of carbon cycle perturbation. Nonetheless, as long as a given set of changes in the fluid Earth carbon cycle affects temperature, even as a corollary of other drivers, a temperature-dependent thermodynamic feedback on organic carbon burial can be expected.

This thermodynamic feedback is positive, meaning it will tend to amplify the system response in both atmospheric  $p\text{CO}_2$  (and consequently climate) and in  $\delta^{13}\text{C}$  of marine carbonates. For example, it has been hypothesized that increased volcanic  $\text{CO}_2$  outgassing at the Permian–Triassic boundary due to eruption of the Siberian Traps flood basalts produced a negative C isotope excursion (Payne and Kump 2007). In addition, however, warming associated with this  $\text{CO}_2$  injection – supported by proxy observations in Early Triassic paleoenvironments (Retallack 1999; Joachimski et al. 2012) – would have increased microbial respiration rates and decreased organic carbon burial, leading to a larger negative  $\delta^{13}\text{C}$  excursion (and climate perturbation) than expected from the carbon budget of the volcanic outgassing alone. Similarly, the magnitudes of positive  $\delta^{13}\text{C}$  excursions attributed to external factors that would have also caused climate cooling (e.g. nutrient-driven organic carbon burial events (Saltzman 2005)) would have been amplified by the temperature-dependence of respiration.

The increase in respiration rates with temperature is clear in sign, but it is important to consider the effect strength. A useful approach to evaluate the effect of a particular feedback is to consider a simple reference system, and then estimate the system gain as the amount of amplification of the response due to the inclusion of feedback (Roe 2009). The simplest description of the geological carbon cycle is conveyed by classic steady-state isotope mass balance formulations that describe the  $\delta^{13}\text{C}$  values of carbonate and organic carbon as a function of the fraction of total carbon buried as organic carbon over a given interval of time (Summons and Hayes 1992; Kump and Arthur 1999). Formally, this system is not temperature sensitive until the thermodynamic feedback of Stanley (2010) is included. Stanley

(2010) appreciated that the bigger the temperature change, the larger the effect on the carbon cycle (due to exponential differences in remineralization rates), but the nonlinearity between temperature and respiration rate means there is another important additional element that bears on the gain – the initial temperature boundary condition. This feedback is expected to be non-linear. Because global seawater temperatures have almost certainly varied significantly over Phanerozoic time, it is important to estimate the impact this feedback might have had on the global carbon cycle as a function of both amount of temperature change and initial temperature.

We begin with a simple steady-state isotope mass balance framework and assume that the long-term, steady-state remineralization rate of organic carbon ( $F_{\text{remin}}$ ) is tightly controlled by external factors [over long timescales ( $> 10^6\text{yr}$ ) the amount of remineralization is closely tied to production because of negative feedbacks in  $\text{O}_2$  and nutrient cycles (Lasaga and Ohmoto 2002)] and is independent of temperature. This assumption is supported by the observation that baseline values of  $\delta^{13}\text{C}_{\text{carb}}$  are essentially invariant over Phanerozoic time (Saltzman and Thomas 2012) despite well-documented changes to background global climate and surface temperatures over this interval (Frakes et al. 1992). In contrast, short-term ( $\sim 10^3\text{--}10^6\text{ yr}$ ) temperature changes will impact marine respiration rates (and  $\delta^{13}\text{C}$ ) because of the observed thermodynamic (e.g. –  $Q_{10}$ ) dependence on the microbial metabolisms responsible for organic carbon remineralization (Robador et al. 2009; Stanley 2010). The exponent (i.e. strength) of this relationship varies among environments, but a typical open-marine value is  $\sim 2.2$  (Fig. 2A; Robador et al. 2009; Stanley 2010). Thus, the change in organic carbon remineralization flux ( $\Delta F_{\text{remin}}$ ) is expected to approximately double for a  $10^\circ\text{C}$  increase in temperature. It is also important to note that the absolute differences in respiration rates due to a change in temperature depend strongly on initial temperature (Fig. 2A).

In principle, and at organismal scales, the same thermodynamic effects that cause heterotrophs to respire

faster at higher temperature also apply to primary producers. That is, holding all other factors constant, a given change in temperature should influence the metabolic rates and population growth rates of both heterotrophs and autotrophs (Gillooly et al. 2001; Savage et al. 2004). If both productivity and microbial respiration had similar positive exponential relationships to ambient temperature, there would be no net effect on fractional organic carbon burial. However, over even short timescales productivity is limited by light and nutrients (and grazing, phages, etc.). To quantify the relationship between temperature and productivity in the modern ocean we acquired geodetic data products for the year 2010 from the MODIS Aqua (sea surface temperature) and SeaWiFS (sea surface chlorophyll *a* concentration) missions, and coupled them to the same grid matrix using the software SeaDAS (<http://seadas.gsfc.nasa.gov/>) so they could be readily compared. The global observations show no significant relationship between primary production (as measured by *chl a* concentration) and sea surface temperature (Fig. 2B) – if anything, the data support a slight negative relationship as more primary productivity is tied to upwelling of cold, nutrient-rich waters ( $chl a = -0.0218T + 0.7964$ ). Overall, while temperature changes will strongly impact rates of remineralization, primary productivity is expected to operate largely independent of temperature (or may even decline at higher temperatures due to reduced upwelling, e.g. Behrenfeld et al. 2006). Consequently, there is no strong relationship between mean surface temperature and mean annual productivity ( $F_{\text{prod}}$ ) in the modern ocean (Fig. 2B), and no consensus on the expected relationship, if any, between changes in climate and changes in primary productivity (Taucher and Oschlies 2011).

If we assume that  $F_{\text{prod}}$  does not vary as a strong function of temperature, it follows that the proportion of gross primary production that is remineralized ( $f_{\text{rem}}$ ) is expected to increase with temperature. The magnitude of the expected change in  $f_{\text{rem}}$  for a given change in temperature can be estimated by:

$$\Delta f_{rem} = \left( \frac{\Delta F_{rem}}{F_{prod}} \right) = 10^{(T_1 Q_{10})} - 10^{(T_2 Q_{10})} \quad (Eq. 1)$$

Where  $T_1$  represents the initial mean temperature,  $T_2$  the mean temperature following a climate change, and  $Q_{10}$  represents the mean relative change in global microbial respiration rate for a 10°C change in temperature. Here, we assume that remineralization scales as a simple function of global mean temperature, though the global remineralization flux may depend not just on the mean but also on the shape of the probability distribution function of global temperatures. Under a steady-state model with invariant  $F_{prod}$  a change in relative remineralization rate must be offset by an equal but opposite change in organic carbon burial:

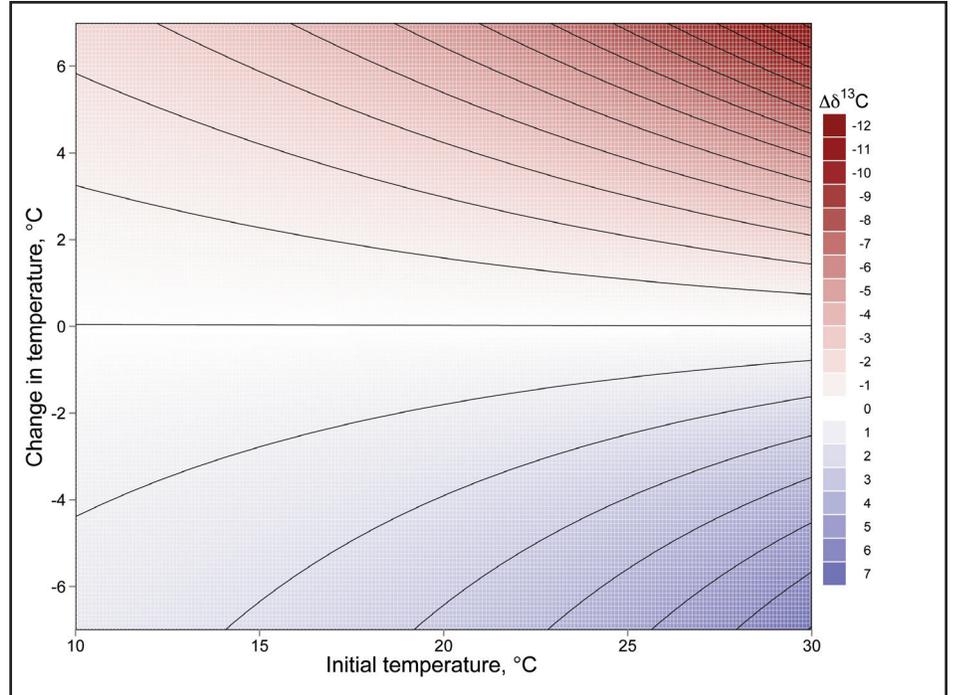
$$\Delta f_{org} = -\Delta f_{rem} \quad (Eq. 2)$$

The corresponding change in the relative organic carbon burial flux ( $f_{org}$ ) will shift the stable isotopic composition of the marine dissolved inorganic carbon reservoir according to the following expression:

$$\Delta \delta^{13}C = \Delta f_{org} \varepsilon \quad (Eq. 3)$$

Where  $\varepsilon$  represents the fractionation factor (due to biological kinetic isotope effects) between coeval dissolved inorganic carbon and organic carbon in the oceans. The isotopic composition of marine DIC, in turn, is recorded in marine limestones as  $\delta^{13}C_{carb}$ . Thus, using the above formulation, it is possible to relate the sign and magnitude of an isotope excursion in  $\delta^{13}C_{carb}$  to a temperature-driven change in the efficiency of organic carbon respiration.

Critically, because the relationship between  $F_{rem}$  and temperature is exponential rather than linear, the magnitude of  $\delta^{13}C_{carb}$  excursion expected for a given change in mean temperature will also change as a function of initial mean temperature ( $T_1$ ). For example, cooling from a mean temperature of 25° to 20°C would be expected to generate a larger positive  $\delta^{13}C_{carb}$  excursion than cooling from 20° to



**Figure 3.** Expected sign and magnitude of marine carbonate  $\delta^{13}C$  excursions as a function of starting temperature and change in temperature for a steady-state isotope mass balance carbon cycle model with a temperature-dependent organic carbon burial feedback. Note the strong effect of the initial boundary condition as well as the asymmetry of isopleths with respect to sign of temperature change: because of the exponential relationship between temperature and respiration rate, the magnitude of the negative  $\delta^{13}C$  excursion expected from a given amount of warming exceeds the magnitude of the positive excursion expected from an equal amount of cooling.

15°C, which in turn would be expected to generate a larger positive  $\delta^{13}C_{carb}$  excursion than cooling from 15° to 10°C.

Figure 3 quantifies the non-linear system gain from including a thermodynamic respiration rate-organic carbon burial feedback, in a classic geological carbon cycle isotope mass balance framework. These relationships illustrate the sign and magnitude of  $\delta^{13}C_{carb}$  excursion expected for different combinations of initial temperature and change in temperature, assuming the same value for  $\varepsilon$ , here set at the Phanerozoic average of  $-29\text{‰}$  (Hayes et al. 1999). Note that the available feedback strength estimates are potentially large (several ‰) for plausible ranges of historical Earth system climate changes. An additional interesting consequence of the exponential relationship between temperature and respiration rate is that the magnitude of negative  $\delta^{13}C$  excursion, expected from a given amount of warming,

exceeds the magnitude of the positive excursion expected from an equal amount of cooling.

## DISCUSSION AND CONCLUSIONS

There are many aspects of physical, chemical, and biological oceanographic systems that exhibit temperature dependence – some of these may drive positive or negative feedbacks on organic carbon remineralization rate that would act to amplify or damp the system response in addition to the feedback discussed above. One such feedback that is immediately apparent is the inverse relationship between  $O_2$  solubility (and concentration in seawater) and water temperature (Emerson and Hedges 2008; Fig. 2C). Because organic carbon preservation is strongly affected by oxygen availability (Hartnett et al. 1998; Hedges et al. 1999), increased  $O_2$  concentrations at lower seawater temperatures could act as a negative feedback to counter the expected decrease in remineralization

rate due to reduced microbial metabolic activity. Although the potential importance of this negative feedback is difficult to evaluate rigorously, we point out that the inverse relationship between  $O_2$  solubility and water temperature also has an exponential form (Fig. 2C) and will be differentially sensitive to an initial temperature boundary condition (i.e.  $dO_2/dT$  is not a constant). Whereas relative changes in microbial carbon remineralization for a given change in temperature are expected to increase at higher baseline temperatures, relative changes in  $O_2$  solubility decrease at higher baseline temperatures. Thus, to the extent that a change in  $\delta^{13}C_{DIC}$  reflects the net effects of changes in microbial metabolic activity and changes in oxygen availability on  $F_{rem}$ , the magnitude of these changes is still expected to depend strongly on initial temperature.

Temperature changes could also influence the delivery of  $O_2$  to bottom waters and sediments via changes in ocean circulation, but for a given change in temperature it is, at present, difficult to predict even the sign, much less the magnitude, of expected changes in the ocean mixing processes (IPCC 2007). Furthermore, changes in the mean temperature of the global oceans would not be felt equally everywhere – the magnitude of  $\delta^{13}C_{DIC}$  change expected would likely depend disproportionately on coastal temperature changes, and changes in seasonality in the high-productivity regions where most organic carbon burial and remineralization takes place. Because most of organic carbon burial takes place on continental shelves (Reimers et al. 1992), especially in deltaic systems (McKee et al. 2004), and organic carbon remineralization is concentrated in the upper 1 km of the ocean (Jørgensen and Kasten 2006),  $\delta^{13}C_{DIC}$  changes will be especially sensitive to temperature changes in shallow ocean basins.

Though the calculations explored above do not represent a comprehensive biogeochemical view of the geological carbon cycle, the approach can be used to predict the sign and magnitude of the  $\delta^{13}C_{carb}$  excursion accompanying a rapid change in mean ocean temperature, if  $T_1$ ,  $T_2$ ,  $Q_{10}$ , and  $\epsilon$  are known. And the

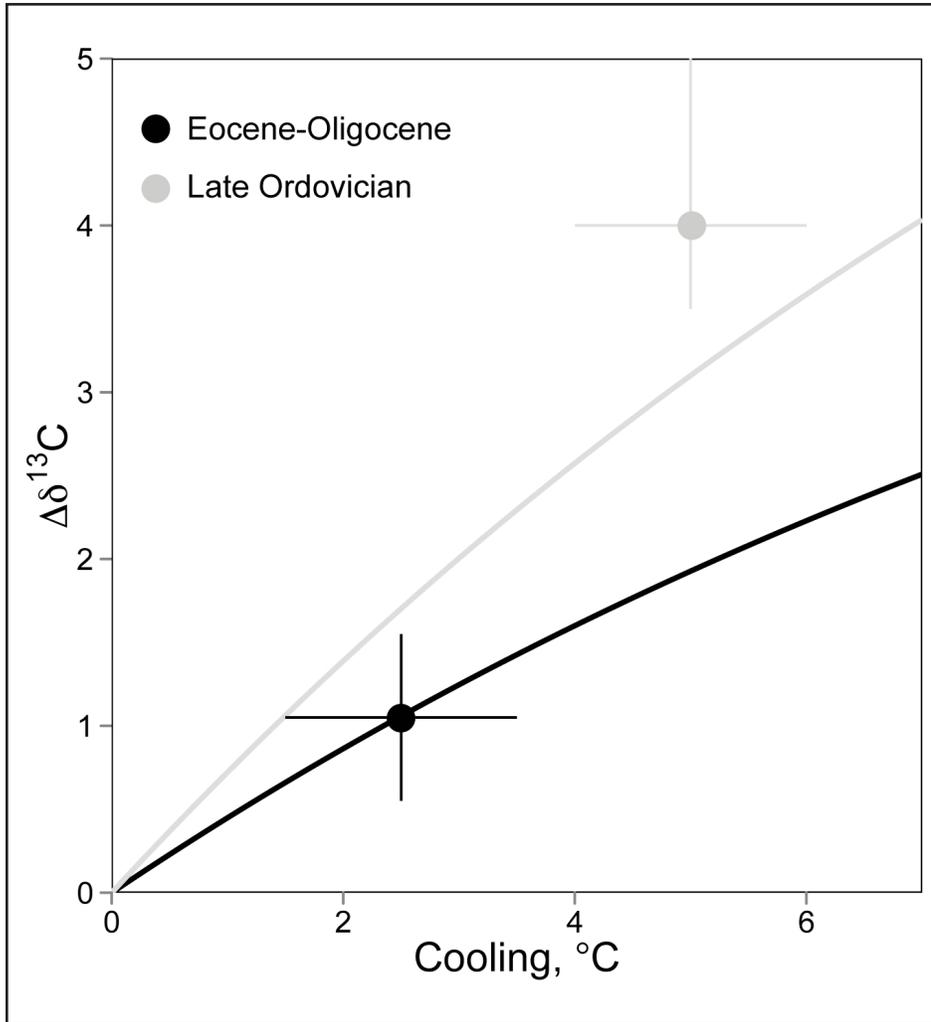
expectations can be compared to geological observations of two well-known carbon isotopic excursions in the Phanerozoic record—both of which are known to be associated with transitions from relatively warm conditions to glacial 'icehouse' states but are separated by more than 400 million years: the Paleogene Eocene–Oligocene boundary excursion and the Late Ordovician Hirnantian excursion.

As noted above, Stanley (2010) singled out the Eocene–Oligocene event as puzzling because the climate cooling produced only a relatively small  $\sim 1\%$  positive  $\delta^{13}C_{carb}$  excursion. The Mg/Ca data from planktic foraminifera suggest that tropical surface waters cooled by about  $2.5^\circ C$  across this boundary, from  $\sim 30.5^\circ$  to  $28^\circ C$ . Although we have some constraints on tropic SSTs from proxy data, we do not know the distribution of temperatures in the upper kilometre of the oceans with any certainty. Consequently, we make the simplifying assumption (based on the distribution of temperatures in the 2010 MODISA dataset) that the difference between the mean temperature of tropical surface waters and the mean temperature of the upper 1 km of the ocean was the same in the Eocene–Oligocene as it is today – about  $15^\circ C$  (Robador et al. 2009; Locarnini et al. 2010). Using a typical early Cenozoic  $\epsilon$  value of  $29\%$  (Hayes et al. 1999), a mean  $Q_{10}$  exponent of 2.2, and assuming a change in mean temperature from  $15.5^\circ$  to  $13^\circ C$ , our model predicts a positive  $\delta^{13}C_{carb}$  excursion of nearly  $1\%$  (Fig. 4). For the Hirnantian glacial maximum, we make the same calculation with a somewhat higher initial mean temperature for the upper oceans of  $20^\circ C$ . This assumes the same  $15^\circ C$  difference between tropical surface temperatures and the mean temperature of the upper 1 km of the oceans as above, and a mean tropical sea surface temperature of  $35^\circ C$  based on clumped isotope measurements of well-preserved, shallow-marine carbonates (Finnegan et al. 2011). Using  $\epsilon$  of  $29\%$  (a value typical for this interval (Hayes et al. 1999; Jones et al. 2011)), the observed  $5^\circ C$  cooling predicts an excursion of roughly  $3\%$  (Fig. 4). This estimate is slightly less than the observed excu-

sion, which varies from 4–6% globally (Brenchley et al. 2003; Jones et al. 2011), but implies that reduced organic carbon remineralization driven by cooling can plausibly account for a substantial portion of this large positive excursion. This predicted value also substantially exceeds the  $\sim 1.7\%$  excursion that would be predicted for a similar drop in temperature using the Late Eocene mean temperature estimate (Fig. 4).

Although we only have sufficient data to rigorously consider two examples from opposite ends of the Phanerozoic Eon, a temperature-dependent organic carbon burial mechanism may help to explain the relative magnitudes of other conspicuous  $\delta^{13}C$  excursions observed in the Phanerozoic record. It is notable, for example, that some of the largest post-Cambrian carbon isotope excursions – both positive and negative – occur during the Early Triassic (Payne et al. 2004), an interval that appears to have been exceptionally warm (Retallack 1999). This feedback could also help to explain the overall decline in the average magnitude of  $\delta^{13}C$  excursions over Phanerozoic time, if the average temperature of organic carbon burial environments also declined over the same interval. Several lines of reasoning suggest this was the case.

The mean  $\delta^{18}O$  of benthic calcifiers has increased by more than several permil since Cambrian time (Prokoph et al. 2008), with similar trends observed in marine cherts (Karhu and Epstein 1986), and phosphates (Luz et al. 1984; Karhu and Epstein 1986; Trotter et al. 2008). This pattern implies either a substantial cooling of the seawater temperatures or a systematic increase in the  $\delta^{18}O$  of seawater through exchange with oceanic crust or some other mechanism (Jaffrés et al. 2007). Robust interpretation of this trend remains controversial (e.g. Giles 2012), but recent new analytical approaches using the clumped isotope proxy applied to Ordovician–Silurian carbonates (Came et al. 2007; Finnegan et al. 2011) reconstruct warm tropical ocean temperatures (e.g.  $30^\circ$  –  $39^\circ C$ ) and do not support the hypothesis of exceptionally light early Paleozoic seawater  $\delta^{18}O$  values. Although these clumped isotope studies provide broad



**Figure 4.** Two functions depict the expected relationship between amount of cooling and change in  $\delta^{13}\text{C}$  for the terminal Eocene (black line) and Late Ordovician (grey line) glaciations, respectively. These calculations were made using boundary conditions based on tropical sea surface temperature estimates from (Lear et al. 2008) and (Finnegan et al. 2011), respectively, and assuming a constant  $15^\circ\text{C}$  difference between tropical SST and mean temperature and using a  $Q_{10}$  of 2.2. Points and error bars represent actual estimated cooling and from the same sources and the magnitude of the accompanying  $\delta^{13}\text{C}$  excursion. Excursion magnitudes from Saltzman and Thomas (2012) and Jones et al. (2011), respectively.

support for the hypothesis of long-term Phanerozoic climate cooling (interposed by episodes of glaciation), coverage of the sedimentary record is currently limited and work is ongoing to better understand how this new proxy records climate information over geological time in a regime of ever-present carbonate diagenesis.

Another line of logic also suggests that a general decline in the average temperature of organic carbon burial environments occurred – even in the hypothetical case that average surface temperatures have been constant throughout the Phanerozoic. This is

due to the changing distribution of continents through time and to secular changes in the nature and environments of organic carbon burial (e.g. Scotese 2001; Peters 2006). Most organic carbon burial takes place on continental margins, and consequently the meridional distribution of continental shelf and slope area captures a first-order control on global mean carbon remineralization rates. Given the general movement of continents from tropical to temperate latitudes following the Triassic breakup of Pangea (Scotese 2001), it is reasonable to conclude that most carbon burial today

takes place under cooler environmental temperatures than it did during much of Paleozoic time.

We emphasize the utility of thinking about this temperature-dependent organic carbon burial mechanism as an internal feedback operating in the carbon cycle that may amplify the system response (as observed by the magnitude of  $\delta^{13}\text{C}$  excursions) to a given perturbation. What we find particularly surprising is that the strength of this feedback could be quite large. Our estimates of effect strength reveal that this feedback may play a first order role in carbon isotope excursions, and explain a substantial portion (up to several permil) of the magnitude of a given excursion. While these estimates may not remain as large when considered more comprehensively in more complex biogeochemical models that include other (positive and negative) feedbacks (e.g. Ridgwell and Zeebe 2005), we would expect the effect to remain important and ever-present. More specifically, the dependence of this thermodynamic organic carbon burial feedback on the initial temperature boundary condition raises the possibility that the decreasing magnitude of carbon isotope excursions over time may be due, at least in part, to long-term Phanerozoic climate and geodynamic trends.

Finally, reflecting on carbon isotope trends through all of Earth history, the volatile Neoproterozoic record (Knoll et al. 1986; Halverson et al. 2005) highlights a yawning divide between the ways in which Phanerozoic climate and the carbon cycle interacted and that of earlier Earth history. Although Proterozoic paleotemperature proxy estimates do not yet exist that allow direct comparisons to be drawn, it appears clear that the observed sign is opposite of expected – Neoproterozoic glaciations coincide with large negative (Hoffman et al. 1998; Rose et al. 2012), rather than positive carbon isotope excursions. To the degree that the temperature-dependent feedback discussed here is correct, it must have been overridden by stronger drivers during much of Neoproterozoic time (Schrag et al. 2002; Tziperman et al. 2011). Uncovering the nature of these differences will be critical to understanding the

behaviour and evolution of climate and the carbon cycle over long intervals of Earth history.

## ACKNOWLEDGEMENTS

We wish to express our gratitude to Paul Hoffman who introduced us to, and greatly stimulated our interests in, paleoclimate and the history of the carbon cycle during many late nights in Cambridge, MA. We thank Andy Thompson and Ian Eisenman for insight into the complexities of predicting ocean circulation changes as a function of temperature. The observations in Fig. 2B, collected and made available by the MODIS and SeaWiFS missions, were made possible, in part, by NASA. This work was supported by Agouron Institute awards to WWF and DAF, Packard Fellowships to WWF and DAF, and a National Science Foundation (EAR-1053523) award to WWF.

## REFERENCES

- Behrenfeld, M.J., O'Malley, R.T., Siegel, D.A., McClain, C.R., Sarmiento, J.L., Feldman, G.C., Milligan, A.J., Falkowski, P.G., Letelier, R.M., and Boss, E.S., 2006, Climate-driven trends in contemporary ocean productivity: *Nature*, v. 444, p. 752-755, <http://dx.doi.org/10.1038/nature05317>.
- Brenchley, P.J., Marshall, J.D., Carden, G.A.F., Robertson, D.B.R., Long, D.G.F., Meidla, T., Hints, L., and Anderson, T.F., 1994, Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period: *Geology*, v. 22, p. 295-298, [http://dx.doi.org/10.1130/0091-7613\(1994\)022<0295:BAIEFA>2.3.CO;2](http://dx.doi.org/10.1130/0091-7613(1994)022<0295:BAIEFA>2.3.CO;2).
- Brenchley, P.J., Carden, G.A., Hints, L., Kaljo, D., Marshall, J.D., Martma, T., Meidla, T., and Nölvak, J., 2003, High-resolution stable isotope stratigraphy of Upper Ordovician sequences: Constraints on the timing of bioevents and environmental changes associated with mass extinction and glaciation: *Geological Society of America Bulletin*, v. 115, p. 89-104, [http://dx.doi.org/10.1130/0016-7606\(2003\)115<0089:HRSISO>2.0.CO;2](http://dx.doi.org/10.1130/0016-7606(2003)115<0089:HRSISO>2.0.CO;2).
- Came, R.E., Eiler, J.M., Veizer, J., Azmy, K., Brand, U., and Weidman, C.R., 2007, Coupling of surface temperatures and atmospheric CO<sub>2</sub> concentrations during the Palaeozoic era: *Nature*, v. 449, p. 198-201, <http://dx.doi.org/10.1038/nature06085>.
- Emerson, S., and Hedges, J., 2008, *Chemical Oceanography and the Marine Carbon Cycle*: Cambridge University Press, Cambridge, UK, 453 p., <http://dx.doi.org/10.1017/CBO9780511793202.001>.
- Finnegan, S., Bergmann, K., Eiler, J.M., Jones, D.S., Fike, D.A., Eisenman, I., Hughes, N.C., Tripathi, A.K., and Fischer, W.W., 2011, The Magnitude and Duration of Late Ordovician-Early Silurian Glaciation: *Science*, v. 331, p. 903-906, <http://dx.doi.org/10.1126/science.1200803>.
- Frakes, L.A., Francis, J.E., and Syktus, J.I., 1992, *Climate Modes of the Phanerozoic*: Cambridge University Press, Cambridge, UK, 286 p.
- Giles, P.S., 2012, Low-latitude Ordovician to Triassic brachiopod habitat temperatures (BHTs) determined from  $\delta^{18}\text{O}_{\text{[brachiopod calcite]}}$ : A cold hard look at ice-house tropical oceans: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 317-318, p. 134-152, <http://dx.doi.org/10.1016/j.palaeo.2012.01.002>.
- Gillooly, J.F., Brown, J.H., West, G.B., Savage, V.M., Charnov, E.L., 2001, Effects of size and temperature on metabolic rate: *Science*, v. 293, p. 2248-2251, <http://dx.doi.org/10.1126/science.1061967>.
- Grotzinger, J.P., Fike, D.A., and Fischer, W.W., 2011, Enigmatic origin of the largest-known carbon isotope excursion in Earth's history: *Nature Geoscience*, v. 4, p. 285-292, <http://dx.doi.org/10.1038/ngeo1138>.
- Halverson, G.P., Hoffman, P.F., Schrag, D.P., Maloof, A.C., and Rice, A.H.N., 2005, Toward a Neoproterozoic composite carbon-isotope record: *Geological Society of America Bulletin*, v. 117, p. 1181-1207, <http://dx.doi.org/10.1130/B25630.1>.
- Hartnett, H.E., Keil, R.G., Hedges, J.I., and Devol, A.H., 1998, Influence of oxygen exposure time on organic carbon preservation in continental margin sediments: *Nature*, v. 391, p. 572-575, <http://dx.doi.org/10.1038/35351>.
- Hayes, J.M., Strauss, H., and Kaufman, A.J., 1999, The abundance of <sup>13</sup>C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma: *Chemical Geology*, v. 161, p. 103-125, [http://dx.doi.org/10.1016/S0009-2541\(99\)00083-2](http://dx.doi.org/10.1016/S0009-2541(99)00083-2).
- Hedges, J.I., Hu, F.S., Devol, A.H., Hartnett, H.E., Tsamakis, E., and Keil, R.G., 1999, Sedimentary organic matter preservation; a test for selective degradation under oxic conditions: *American Journal of Science*, v. 299, p. 529-555, <http://dx.doi.org/10.2475/ajs.299.7-9.529>.
- Hoffman, P.F., Kaufman, A.J., Halverson, G.P., and Schrag, D.P., 1998, A Neoproterozoic Snowball Earth: *Science*, v. 281, p. 1342-1346, <http://dx.doi.org/10.1126/science.281.5381.1342>.
- IPCC, Ed., *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*: Cambridge University Press, Cambridge, UK, and New York, N.Y., 582 p.
- Jaffrés, J.B.D., Shields, G.A., and Wallman, K., 2007, The oxygen isotope evolution of seawater: A critical review of a long-standing controversy and an improved geological water cycle model for the past 3.4 billion years: *Earth-Science Reviews*, v. 83, p. 83-122, <http://dx.doi.org/10.1016/j.earscirev.2007.04.002>.
- Joachimski, M.M., Lai, X., Shen, S., Jiang, H., Luo, G., Chen, B., Chen, J., and Sun, Y., 2012, Climate warming in the latest Permian and the Permian-Triassic mass extinction: *Geology*, v. 40, p. 195-198, <http://dx.doi.org/10.1130/G32707.1>.
- Jones, C.E., and Jenkyns, H.C., 2001, Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous: *American Journal of Science*, v. 301, p. 112-149, <http://dx.doi.org/10.2475/ajs.301.2.112>.
- Jones, D.S., Fike, D.A., Finnegan, S., Fischer, W.W., Schrag, D.P., and McCay, D., 2011, Terminal Ordovician carbon isotope stratigraphy and glacioeustatic sea-level change across Anticosti Island (Quebec, Canada): *Geological Society of America Bulletin*, v. 123, p. 1645-1664, <http://dx.doi.org/10.1130/B30323.1>.
- Jørgensen, B., and Kasten, S., 2006, Sulfur cycling and methane oxidation, *in* Schulz, H.D., and Zabel, M., eds., *Marine Geochemistry*: Berlin, SpringerLink, p. 271-309, [http://dx.doi.org/10.1007/3-540-32144-6\\_8](http://dx.doi.org/10.1007/3-540-32144-6_8).
- Karhu, J., and Epstein, S., 1986, The implication of the oxygen isotope records

- in coexisting cherts and phosphates: *Geochimica et Cosmochimica Acta*, v. 50, p. 1745-1756, [http://dx.doi.org/10.1016/0016-7037\(86\)90136-5](http://dx.doi.org/10.1016/0016-7037(86)90136-5).
- Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K., and Lambert, I.B., 1986, Secular variation in carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland: *Nature*, v. 321, p. 832-838, <http://dx.doi.org/10.1038/321832a0>.
- Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon-isotope excursions: carbonates and organic matter: *Chemical Geology*, v. 161, p. 181-198, [http://dx.doi.org/10.1016/S0009-2541\(99\)00086-8](http://dx.doi.org/10.1016/S0009-2541(99)00086-8).
- Lasaga, A.C., and Ohmoto, H., 2002, The oxygen geochemical cycle: dynamics and stability: *Geochimica et Cosmochimica Acta*, v. 66, p. 361-381, [http://dx.doi.org/10.1016/S0016-7037\(01\)00685-8](http://dx.doi.org/10.1016/S0016-7037(01)00685-8).
- Laws, E.A., Falkowski, P.G., Smith, W.O., Jr., Ducklow, H., and McCarthy, J.J., 2000, Temperature effects on export production in the open ocean: *Global Biogeochemical Cycles*, v. 14, p. 1231-1246, <http://dx.doi.org/10.1029/1999GB001229>.
- Lear, C.H., Bailey, T.R., Pearson, P.N., Coxall, H.K., and Rosenthal, Y., 2008, Cooling and ice growth across the Eocene-Oligocene transition: *Geology*, v. 36, p. 251-254, <http://dx.doi.org/10.1130/G24584A.1>.
- Locarnini, R.A., Mishonov, A.V., Antonov, J.I., Boyer, T.P., Garcia, H.E., Baranova, O.K., Zweng, M.M., and Johnson, D.R., 2010, *World Ocean Atlas 2009, Volume 1: Temperature*, in Levitus, S., ed., NOAA Atlas NESDIS 68, U.S. Government Printing Office, Washington, D.C., p. 184.
- Luz, B., Kolodny, Y., and Kovach, J., 1984, Oxygen isotope variations in phosphate of biogenic apatites, III. Conodonts: *Earth and Planetary Science Letters*, v. 69, p. 255-262, [http://dx.doi.org/10.1016/0012-821X\(84\)90185-7](http://dx.doi.org/10.1016/0012-821X(84)90185-7).
- McKee, B.A., Aller, R.C., Allison, M.A., Bianchi, T.S., and Kineke, G.C., 2004, Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: benthic boundary layer and seabed processes: *Continental Shelf Research*, v. 24, p. 899-926, <http://dx.doi.org/10.1016/j.csr.2004.02.009>.
- Payne, J.L., and Kump, L.R., 2007, Evidence for recurrent Early Triassic massive volcanism from quantitative interpretation of carbon isotope fluctuations: *Earth and Planetary Science Letters*, v. 256, p. 264-277, <http://dx.doi.org/10.1016/j.epsl.2007.01.034>.
- Payne, J.L., Lehrmann, D.J., Wei, J., Orchard, M.J., Schrag, D.P., and Knoll, A.H., 2004, Large perturbations of the carbon cycle during recovery from the end-Permian extinction: *Science*, v. 305, p. 506-509, <http://dx.doi.org/10.1126/science.1097023>.
- Peters, S.E., 2006, Macrostratigraphy of North America: *The Journal of Geology*, v. 114, p. 391-412, <http://dx.doi.org/10.1086/504176>.
- Prokoph, A., Shields, G.A., and Veizer, J., 2008, Compilation and time-series analysis of a marine carbonate delta  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{34}\text{S}$  database through Earth history: *Earth-Science Reviews*, v. 87, p. 113-133, <http://dx.doi.org/10.1016/j.earscirev.2007.12.003>.
- Reimers, C.E., Jahnke, R.A., and McCorkle, D.C., 1992, Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle: *Global Biogeochemical Cycles*, v. 6, p. 199-224, <http://dx.doi.org/10.1029/92GB00105>.
- Retallack, G.J., 1999, Postapocalyptic greenhouse paleoclimate revealed by earliest Triassic paleosols in the Sydney Basin, Australia: *Geological Society of America Bulletin*, v. 111, p. 52-70, [http://dx.doi.org/10.1130/0016-7606\(1999\)111<0052:PGPRBE>2.3.CO;2](http://dx.doi.org/10.1130/0016-7606(1999)111<0052:PGPRBE>2.3.CO;2).
- Ridgwell, A., and Zeebe, R.E., 2005, The role of the global carbonate cycle in the regulation and evolution of the Earth system: *Earth and Planetary Science Letters*, v. 234, p. 299-315, <http://dx.doi.org/10.1016/j.epsl.2005.03.006>.
- Robador, A., Brüchert, V., and Jørgensen, B.B., 2009, The impact of temperature change on the activity and community composition of sulfate-reducing bacteria in arctic versus temperate marine sediments: *Environmental Microbiology*, v. 11, p. 1692-1703, <http://dx.doi.org/10.1111/j.1462-2920.2009.01896.x>.
- Roe, G., 2009, Feedbacks, Timescales, and Seeing Red: Annual Review of Earth and Planetary Sciences, v. 37, p. 93-115, <http://dx.doi.org/10.1146/annurev.ea>
- rth.061008.134734.
- Rose, C.V., Swanson-Hysell, N.L., Husson, J.M., Poppick, L.N., Cottle, J.M., Schoene, B., and Maloof, A.C., 2012, Constraints on the origin and relative timing of the Trezona  $\delta^{13}\text{C}$  anomaly below the end-Cryogenian glaciation: *Earth and Planetary Science Letters*, v. 319-320, p. 241-250, <http://dx.doi.org/10.1016/j.epsl.2011.12.027>.
- Saltzman, M.R., 2005, Phosphorus, nitrogen, and the redox evolution of the Paleozoic oceans: *Geology*, v. 33, p. 573-576, <http://dx.doi.org/10.1130/G21535.1>.
- Saltzman, M.R., and Thomas, E., 2012, in press, Carbon Isotope Stratigraphy, in eds. Gradstein, F.M., Ogg, J.G., Schmitz, M., Ogg, G., *The Geologic Timescale 2012*: Elsevier, Oxford, UK, p. 207-232, <http://dx.doi.org/10.1016/B978-0-444-59425-9.00011-1>.
- Saltzman, M.R., and Young, S.A., 2005, Long-lived glaciation in the Late Ordovician? Isotopic and sequence-stratigraphic evidence from western Laurentia: *Geology*, v. 33, p. 109-112, <http://dx.doi.org/10.1130/G21219.1>.
- Savage, V.M., Gillooly, J.F., Brown, J.H., West, G.B., and Charnov, E.L., 2004, Effects of body size and temperature on population growth: *The American Naturalist*, v. 163, p. 429-441, <http://dx.doi.org/10.1086/381872>.
- Schrag, D.P., Berner, R.A., Hoffman, P.F., and Halverson, G.P., 2002, On the initiation of a snowball Earth: *Geochemistry, Geophysics, Geosystems*, v. 3, p. 1036-1057, <http://dx.doi.org/10.1029/2001GC00219>.
- Scotese, C.R., 2001, *Atlas of Earth History*: v. 1, Paleogeography, PALEOMAP project, Arlington, TX, 52 p.
- Stanley, S.M., 2010, Relation of Phanerozoic stable isotope excursions to climate, bacterial metabolism, and major extinctions: *Proceedings of the National Academy of Sciences*, v. 107, p. 19185-19189, <http://dx.doi.org/10.1073/pnas.1012833107>.
- Summons, R.E., and Hayes, J.M., 1992, Principles of molecular and isotopic biogeochemistry, in Schopf, J.W. and Klein, C., eds., *The Proterozoic Biosphere: A multidisciplinary study*: Cambridge University Press, Cambridge, UK, p. 83-93.
- Svensen, H., Planke, S., Malthes-Sørensen, A., Jamtveit, B., Myklebust, R., Eidem, T.R., and Rey, S.S., 2004, Release of methane from a volcanic basin as a

mechanism for initial Eocene global warming: *Nature*, v. 429, p. 542-545  
<http://dx.doi.org/10.1038/nature02566>.

Taucher, J., and Oeschies, A., 2011, Can we predict the direction of marine primary production change under global warming?: *Geophysical Research Letters*, v. 38, p. L02603,  
<http://dx.doi.org/10.1029/2010GL045934>.

Tejada, M.L.G., Suzuki, K., Kuroda, J., Coccioni, R., Mahoney, J.J., Ohkouchi, N., Sakamoto, T., and Tatsumi, Y., 2009, Ontong Java Plateau eruption as a trigger for the early Aptian oceanic anoxic event: *Geology*, v. 37, p. 855-858,  
<http://dx.doi.org/10.1130/G25763A.1>.

Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C., and Nicoll, R.S., 2008, Did Cooling Oceans Trigger Ordovician Biodiversification? Evidence from Conodont Thermometry: *Science*, v. 321, p. 550-554,  
<http://dx.doi.org/10.1126/science.1155814>.

Tziperman, E., Halevy, I., Johnston, D.T., Knoll, A.H., and Schrag, D.P., 2011, Biologically induced initiation of Neoproterozoic snowball-Earth events: *Proceedings of the National Academy of Sciences*, v. 108, p. 15091-15096,  
<http://dx.doi.org/10.1073/pnas.1016361108>.

**Received June 2012**

**Accepted as revised September 2012**