

Relation of Phanerozoic stable isotope excursions to climate, bacterial metabolism, and major extinctions

Steven M. Stanley¹

Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822

Contributed by Steven M. Stanley, September 10, 2010 (sent for review June 2, 2010)

Conspicuous global stable carbon isotope excursions that are recorded in marine sedimentary rocks of Phanerozoic age and were associated with major extinctions have generally paralleled global stable oxygen isotope excursions. All of these phenomena are therefore likely to share a common origin through global climate change. Exceptional patterns for carbon isotope excursions resulted from massive carbon burial during warm intervals of widespread marine anoxic conditions. The many carbon isotope excursions that parallel those for oxygen isotopes can to a large degree be accounted for by the Q10 pattern of respiration for bacteria: As temperature changed along continental margins, where ~90% of marine carbon burial occurs today, rates of remineralization of isotopically light carbon must have changed exponentially. This would have reduced organic carbon burial during global warming and increased it during global cooling. Also contributing to the $\delta^{13}\text{C}$ excursions have been release and uptake of methane by clathrates, the positive correlation between temperature and degree of fractionation of carbon isotopes by phytoplankton at temperatures below ~15°, and increased phytoplankton productivity during “ice-house” conditions. The Q10 pattern for bacteria and climate-related changes in clathrate volume represent positive feedbacks for climate change.

paleoclimatology | paleoceanography

Many possible explanations have been advanced for one or more of the abrupt excursions in the $\delta^{13}\text{C}$ of marine carbonates and organic matter that have been documented in the geologic record (see Fig. 1). Most of these hypotheses have focused on factors that change the global rate of burial of organic carbon, which is isotopically light: changes in upwelling and primary productivity; fluctuations of sea level; changes in ocean dynamics, including ones affecting the extent of anoxic conditions; changes in carbonate weathering rates; release of methane from sediments; changes in nutrient input from the land to the oceans; volcanic degassing; and release of isotopically light CO_2 from the deep sea (for literature, see *SI Text, Section I*). Given the strong positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions in shallow marine sediments (Fig. 1), however, parsimony suggests that one or more unifying explanations should be sought to explain all of these phenomena.

Missing from previous explanations for geologically brief $\delta^{13}\text{C}$ excursions has been a consideration of the role of microbial processes, even though microbes have an enormous global biomass and play a prominent role in the exogenic carbon cycle. Particulate organic matter in ecosystems has three possible fates: It can be consumed by primary consumers, decomposed by bacteria (or fungi, in the case of lignocellulose), or buried. The relative importance of these fates varies from place to place and time to time. For example, carbon burial on land increased markedly during the late Paleozoic, when coal swamps became widespread (1). In the oceanic realm beyond continental rises, organic carbon burial plays a minor role in the global carbon cycle. Owing to consumption by primary consumers and microbes, less than 1% of particulate organic matter in the upper oceanic realm ends up being buried on the deep seafloor (2). In contrast, continental shelves, slopes, and rises account for ~90%

of global carbon burial in the ocean (3). In these regions, elevated nutrient levels produce high rates of primary productivity; rivers and marshes supply large amounts of organic detritus; and high rates of sedimentation result in the burial and preservation of ~75% of the organic carbon reaching the seafloor, about half of this amount being buried in deltaic depositional systems (4).

Temperature has a profound effect on the role of decomposers, as indicated by the effective fungal destruction of plant debris in tropical rainforests, which results in very thin, humus-poor soils. The Arrhenius pattern for chemical reactions, an exponential increase in rate with temperature, yields a Q10 value: the fractional increase in the rate of a reaction per 10 °C of temperature elevation (Fig. 2). Bacteria and fungi adhere approximately to the Q10 pattern because of the effect of temperature on enzymes utilized in their metabolic processes. For marine and freshwater sediments above very low temperatures, the average Q10 for respiration is ~2.2 (Fig. 2) (5). This relationship has been incorporated into models of the carbon cycle on long time scales (6) but has not previously been invoked to explain the $\delta^{13}\text{C}$ excursions of Fig. 1, which occurred on short time scales (generally <10⁶ y) and are distinct from long-term secular isotopic trends (2).

It is true that growth rates of phytoplankton also increase with temperature, but the net primary productivity of marine phytoplankton nonetheless decreases with global warming, which results in decreased turbulent mixing and upwelling of ocean waters. With warming, the reduced supply of nutrients exerts a much stronger negative influence on the productivity of phytoplankton than the positive effect of the Q10 relationship (7).

In this paper, I investigate the causes of abrupt $\delta^{13}\text{C}$ excursions that occurred in association with major extinctions. I attribute these excursions to four factors: first, and perhaps most importantly, changes in global respiration rates of remineralizing marine bacteria; second, release or uptake of methane by clathrates; third, the positive correlation between carbon isotope fractionation by marine phytoplankton and temperature at relatively low temperatures; and fourth, changes in the productivity of phytoplankton and hence in the burial rate of organic carbon, with changes in global temperature that alter wind stress and rates of nutrient supply.

Results

A compilation of conspicuous isotopic excursions associated with major extinctions reveals a close correspondence between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions throughout Phanerozoic time. Fig. 1 displays 18 plots of $\delta^{13}\text{C}$ for carbonates and organic matter in shallow marine stratigraphic sections. These exhibit a total of 26 $\delta^{13}\text{C}$ excursions, each associated with a major extinction. Of these 26, 19 are known to have been accompanied by a $\delta^{18}\text{O}$ excursion, and in every case the paired excursions have both been either positive or negative. It is common knowledge that $\delta^{18}\text{O}$ excursions reflect

Author contributions: S.M.S. designed research, performed research, analyzed data, and wrote the paper.

The author declares no conflict of interest.

¹E-mail: stevenst@hawaii.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1012833107/-DCSupplemental.

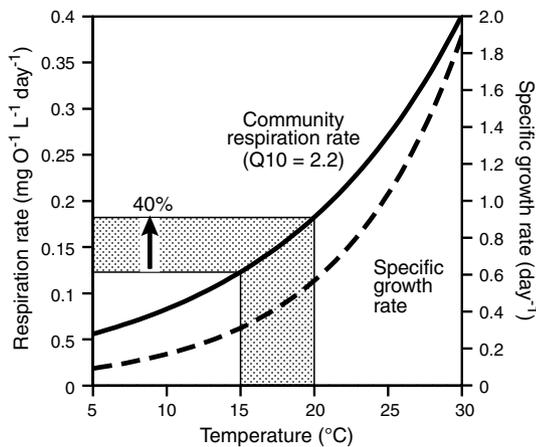


Fig. 2. Relationship to temperature of respiration rate and specific growth rate (fractional increase in cell mass per unit time) for freshwater and marine benthic bacteria (data from ref. 5). An increase in mean temperature from 15–20 °C results in an increase in respiration rate of ~40% (stippled area).

margins to shift $\delta^{13}\text{C}$ for dissolved inorganic carbon in the ocean from its present value of $\sim -2\text{‰}$ to -6‰ (a 4‰ excursion, which is a typical magnitude for the excursions illustrated in Fig. 1). The complicating factor is that, although less isotopically light carbon would be buried, a negative feedback would be triggered: Dissolved inorganic carbon would become progressively isotopically lighter, and so would the carbon of phytoplankton and, therefore, of buried carbon. Also, to the degree that warming or cooling of the climate has been protracted, $\delta^{13}\text{C}$ excursions will also have been protracted. In fact, this pattern is evident in Fig. 1, where gradual shifts of $\delta^{18}\text{O}$ are paralleled by gradual shifts of $\delta^{13}\text{C}$.

The bacterial mechanism I am proposing is also consistent with the observation that many carbon isotope excursions, such as those of the Late Ludlow (Fig. 1*L*) (11) and Late Permian (Fig. 1*E*) (12), began at about the time of the associated major extinction, when a global climate shift occurred, and peaked slightly later. The high-resolution record for the Eocene/Oligocene transition shows the associated $\delta^{13}\text{C}$ excursion to have begun slightly ($<10,000$ y) after the associated $\delta^{18}\text{O}$ excursion (13). These patterns are understandable, given the exponential response of respiration rate to temperature change (Fig. 2).

Changes in global rates of bacterial respiration at times of CO_2 -induced climate change have represented positive feedbacks because changes in bacterial respiration rates as a function of temperature are accompanied by little change in the fraction of acquired carbon that is respired (14). Every rapid global shift of $\delta^{13}\text{C}$ for shallow marine sediments has been reversed at some point, however, either by one or more negative feedbacks, such as a change in terrestrial weathering rates, or by a reversal of whatever factor or factors produced the initial climate change. In fact, many intervals of glacial expansion and contraction have been quite brief. For example, the Late Ordovician Hirnantian interval and its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions were confined to 0.5–1 Myr (15).

Three additional factors have presumably also contributed to the $\delta^{13}\text{C}$ excursions associated with climate change. The co-occurrence of positive global $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions is compatible with the possibility that sequestration or release of methane hydrates in marine and terrestrial settings has been partly responsible for the $\delta^{13}\text{C}$ excursions (16). However, quantitative evaluations have concluded that release of methane hydrates from the seafloor cannot fully account for the Paleocene/Eocene (17) or terminal Permian (18) negative $\delta^{13}\text{C}$ excursions; one or more positive feedbacks are required. The response of bacterial respiration to climatic warming would have been one such feedback.

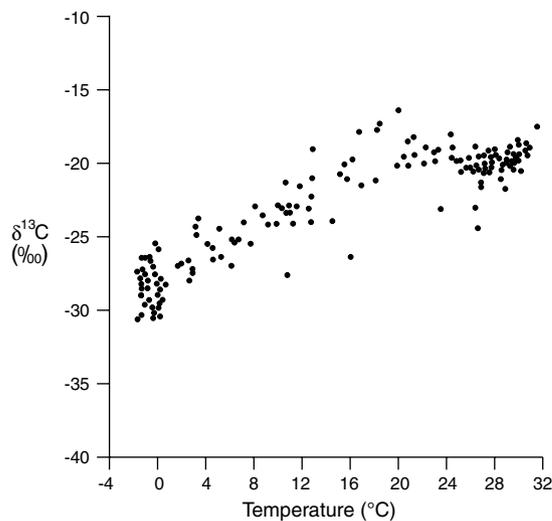


Fig. 3. Positive correlation between temperature and $\delta^{13}\text{C}$ of marine particulate organic matter, including phytoplankton cells, for temperatures below $\sim 15^\circ\text{C}$ (after ref. 19).

Another, secondary factor contributing to the $\delta^{13}\text{C}$ excursions of Fig. 1 would have been the positive correlation between temperature and the $\delta^{13}\text{C}$ of phytoplankton and particulate organic carbon for temperatures below $\sim 15^\circ\text{C}$ (Fig. 3) (19). During “greenhouse” intervals of the past, seawater temperatures were above 15°C throughout the photic zone, except at relatively high latitudes. The degree to which this condition would have elevated the global average $\delta^{13}\text{C}$ of buried organic carbon above its level during icehouse times is difficult to quantify, but temperature changes equatorward of high-latitude regions would have had no effect.

A third, secondary factor contributing to the $\delta^{13}\text{C}$ excursions would have been the strong turbulent mixing and upwelling that characterize icehouse oceans, which elevate the supply of nutrients and therefore enhance phytoplankton productivity (7) and burial of isotopically light carbon.

Discussion

Not all carbon isotope excursions of Fig. 1 have configurations closely resembling those of the associated oxygen isotope excursions, presumably because of second-order regional and global influences. Relative magnitudes of excursions are difficult to interpret. It is puzzling, for example, that the terminal Eocene excursions were small despite having been associated with substantial global cooling.

During three Mesozoic intervals of global warming when vertical mixing of the ocean weakened and anoxia became widespread, black muds were deposited over broad areas. At each of these times, massive burial of isotopically light carbon overrode the reduction of carbon burial via increased bacterial remineralization in areas that were better oxygenated. The result was a positive excursion for $\delta^{13}\text{C}$. At the end of the Cenomanian, for example, a positive global $\delta^{13}\text{C}$ excursion coincided with a negative global $\delta^{18}\text{O}$ excursion (20). Thus, a pulse of global warming quickly reduced vertical mixing of the ocean to provide widespread anoxia. A different pattern, however, is observed throughout the world for oceanic changes in the mid-Toarcian and late early Aptian (21). At the latter time, a sudden negative $\delta^{13}\text{C}$ excursion of $\sim 2\text{‰}$ coincided with a negative $\delta^{18}\text{O}$ excursion of $\sim 3\text{‰}$, in keeping with the standard pattern for global warming (Fig. 1). Only after the widespread burial of organic-rich sediment began was there a strong positive shift of $\delta^{13}\text{C}$ (Fig. 4). Similarly, a $4\text{--}7\text{‰}$ negative shift in mid-Toarcian time was followed by a positive shift after deposition of dark mud began; Hesselbo et al. (21) interpreted the negative excursion as a result

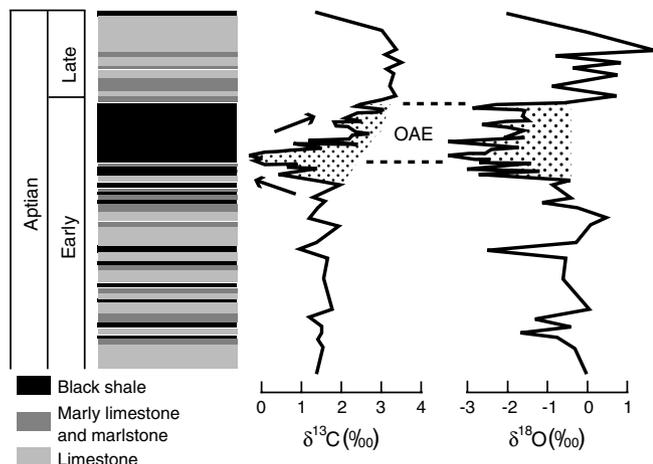


Fig. 4. Excursions of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ near the end of the early Aptian recorded in strata of northwestern Sicily and displaying a global pattern: Both isotopic ratios shifted in a negative direction when global warming began (lower arrow), but the $\delta^{13}\text{C}$ trend was reversed when anoxic conditions produced widespread burial of organic carbon (upper arrow) (after ref. 31). OAE, oceanic anoxic event.

of massive dissociation of gas hydrate, but elevated bacterial remineralization via climate warming may largely account for it.

A sudden negative $\delta^{13}\text{C}$ excursion following the terminal Cretaceous mass extinction, which, perhaps uniquely, was caused by an extraterrestrial impact, was unrelated to factors discussed in the present paper, having resulted from a brief annihilation of marine phytoplankton populations that resulted in a drastic reduction of organic carbon burial (22).

During the Pleistocene, global $\delta^{13}\text{C}$ did not follow the temperature-related pattern of earlier intervals discussed herein: It declined slightly during glacial maxima and rose slightly during glacial minima; the mean value for the ocean was 0.32‰ more negative than today during the most recent glacial maximum (23). One contributing factor must have been the transfer to the ocean of a large amount of isotopically light terrestrial organic carbon during the shrinkage of forests (24), which contracted to about 35% of their present global area during the last glacial maximum

(25). It is also possible that increased burial of organic material along continental margins during eustatic sea level rises reduced $[\text{PO}_4]$ in the ocean, and hence phytoplankton productivity and burial of isotopically light carbon (26). Another likely factor relates to the dramatic change of global carbon dynamics during the Miocene caused by the ecological expansion of marine diatoms. Diatoms assimilate carbon for which $\delta^{13}\text{C}$ is typically ~6‰ heavier than that of other phytoplankton (27), and they are responsible for ~40% of the net primary productivity in the modern ocean (28). Their expanded presence has caused a conspicuous increase in the average $\delta^{13}\text{C}$ of carbon buried in the ocean since the early Miocene and, reciprocally, a decrease in the $\delta^{13}\text{C}$ of seawater and hence in marine calcium carbonate (29). Because of steep latitudinal temperature gradients during glacial maxima, winds were strengthened and, as a result, so were turbulent mixing of the ocean and upwelling along continental margins. Consequently, primary productivity of diatoms increased dramatically (30), largely because a special vacuole in which they store nutrients permits them to respond more effectively than other kinds of phytoplankton to increased nutrient supply (28). An increase in the rate at which diatoms sent relatively heavy carbon to the seafloor during glacial maxima must have significantly reduced the $\delta^{13}\text{C}$ of seawater.

Of the four consequences of global climate change identified here, which in some combination can account for the $\delta^{13}\text{C}$ excursions depicted in Fig. 1, three must be of concern with regard to future global warming: increased respiration by bacteria along continental margins, release of methane by clathrates, and reduced assimilation of CO_2 by phytoplankton. All of these processes represent significant feedbacks that will enhance global warming that results from human-induced increases in the partial pressure of atmospheric CO_2 .

Methods

The $\delta^{13}\text{C}$ excursions depicted in Fig. 1 are the set of excursions associated with major extinctions that were encountered in a literature survey. Where multiple plots were encountered depicting a particular excursion, one was selected for Fig. 1. The remainder are cited in *SI Text, Section II*.

ACKNOWLEDGMENTS. I thank Robert A. Berner, A. Hope Jahren, Fred T. Mackenzie, Isabel Montañez, and Neil Tabor for their critical reading of my manuscript and Jennifer Engels for her clerical assistance.

- Berner RA (1990) *The Phanerozoic Carbon Cycle* (Oxford, New York) p 48.
- Duarte CM, Cebrían J (1996) The fate of marine autotrophic production. *Limnol Oceanogr* 41:1758–1766.
- Reimers CE, Jahnke RA, McCorkle DC (1992) Carbon fluxes and burial rates over the continental slope and rise off Central California with implications for the global carbon cycle. *Global Biogeochem Cy* 6:199–224.
- McKee BA, Aller RC, Allison MA, Bianchi TS, Kineke GC (2004) Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: Benthic boundary layer and seabed processes. *Cont Shelf Res* 24:899–926.
- Hargrave BT (1969) Similarity of oxygen uptake by benthic communities. *Limnol Oceanogr* 14:801–805.
- Ver LMB, MacKenzie FT, Lerman A (1999) Biogeochemical responses of the carbon cycle to natural and human perturbations: Past, present, and future. *Am J Sci* 299:762–801.
- Behrenfeld MJ, et al. (2006) Climate-driven trends in contemporary ocean productivity. *Nature* 444:752–755.
- Stanley SM (1984) Temperature and biotic crises in the marine realm. *Geology* 12:205–208.
- Li Y-H (2000) *A Compendium of Geochemistry—from the Solar Nebula to the Human Brain* (Princeton Univ Press, Princeton) p 365.
- Zhu Z, Aller RC, Mak J (2002) Stable carbon isotope cycling in mobile coastal muds of Amapa, Brazil. *Cont Shelf Res* 22:2065–2079.
- Lehnert O, et al. (2007) $\delta^{13}\text{C}$ records across the late Silurian Lau event: New data from middle paleo-latitudes of northern peri-Gondwana (Prague Basin, Czech Republic). *Palaeogeogr Palaeoclimatol* 245:227–244.
- Holser WT, et al. (1989) A unique geochemical record at the Permian/Triassic boundary. *Nature* 337:39–44.
- Coxall HK, Wilson PA, Palike H, Lear CH, Backman J (2005) Rapid stepwise onset of Antarctic glaciation and deeper calcite compensation in the Pacific Ocean. *Nature* 433:53–57.
- Vasquez-Dominguez E, Vaque D, Gasol JM (2007) Ocean warming enhances respiration and carbon demand of coastal microbial plankton. *Glob Change Biol* 13:1327–1334.
- Brenchley PJ, et al. (1994) Bathymetric and isotopic evidence for a short-lived Late Ordovician glaciation in a greenhouse period. *Geology* 22:295–298.
- Sloan LC, Walker JCG, Moore TC, Jr, Rea DK, Zachos JC (1992) Possible methane-induced polar warming in the early Eocene. *Nature* 357:320–322.
- Zachos JC, et al. (2003) A transient rise in tropical sea surface temperature during the Paleocene-Eocene Thermal Maximum. *Science* 302:1551–1554.
- Berner RA (2002) Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling. *Proc Natl Acad Sci USA* 99:4172–4177.
- Freeman KH, Hayes JM (1992) Fractionation of carbon isotopes by phytoplankton and estimates of ancient CO_2 levels. *Global Biogeochem Cy* 6:185–198.
- Huber BT, Hodell DA, Hamilton CP (1995) Middle-Late Cretaceous climate of the southern high latitude: Stable isotope evidence for minimal equator-to-pole gradients. *Geol Soc Am Bull* 107:1164–1191.
- Hesselbo SP, et al. (2000) Massive dissociation of gas hydrates during a Jurassic Oceanic Anoxic Event. *Nature* 406:392–395.
- Hsu KJ, et al. (1982) Mass mortality and its environmental and evolutionary consequences. *Science* 216:249–256.
- Duplessy JC, et al. (1988) Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation. *Paleoceanography* 3:343–360.
- Shackleton NJ (1977) Carbon-13 in *Uvigerina*: Tropical rainforest history and the equatorial Pacific carbonate dissolution cycle. *The Fate of Fossil Fuel CO₂ in the Oceans*, eds NR Anderson and A Malahoff (Plenum, New York), pp 401–428.
- Adams JM, Faure H, Faure-Denard L, McGlade JM, Woodward FI (1990) Increases in terrestrial carbon storage from the Last Glacial Maximum to the present. *Nature* 348:711–714.
- Broecker WS (1982) Glacial to interglacial changes in ocean chemistry. *Prog Oceanogr* 11:151–197.
- Fry B, Wainright SC (1991) Diatom sources of ^{13}C -rich carbon in marine food webs. *Mar Ecol—Prog Ser* 76:149–157.

28. Falkowski PG, et al. (2004) The evolution of modern eukaryotic phytoplankton. *Science* 305:354–360.
29. Katz ME, et al. (2005) Biological overprint of the geological carbon cycle. *Mar Geol* 217:323–338.
30. Schrader H (1992) Coastal upwelling and atmospheric CO₂ changes over the last 400,000 years: Peru. *Mar Geol* 107:239–248.
31. Bellanca A, et al. (2002) Palaeoceanographic significance of the Tethyan 'Livello Selli' (Early Aptian) from the Hybla Formation, northwestern Sicily: Biostratigraphy and high-resolution chemostratigraphic records. *Palaeogeogr Palaeoclimatol* 185:175–196.