

Phosphorus, nitrogen, and the redox evolution of the Paleozoic oceans

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ABSTRACT

A new high-resolution Paleozoic $\delta^{13}\text{C}_{\text{carb}}$ curve from the Great Basin shows an amount of variation that appears transitional between the highly unsettled Neoproterozoic and the increasingly stable Mesozoic to Cenozoic periods. Large positive excursions were common during cool periods (e.g., Late Ordovician–Silurian and Late Devonian–Early Mississippian), but rare during greenhouse climates. Some periods of stability in $\delta^{13}\text{C}_{\text{carb}}$ lasted for $>10^7$ yr and are interpreted to reflect negative feedbacks on productivity in a nitrogen-limited (low oceanic N/P) ocean in which anoxia led to increased denitrification. Suppression of N fixation, likely due to low levels of essential trace elements, is a requirement of N limitation. In contrast, cool periods that ventilated the oceans switched the ultimate limiting nutrient to P and allowed for $\delta^{13}\text{C}$ excursions, which signal episodic organic carbon burial that could be sustained by positive feedbacks between productivity and anoxia.

Keywords: Paleozoic, carbon isotope, phosphorus, nitrogen, glaciation.

INTRODUCTION

The progressive ventilation of the oceans is believed to have taken place between two major Earth-surface oxidation events ca. 2.2 and 0.6 Ga (Holland, 1984; Canfield, 1998). The first episode resulted in a moderately well oxygenated surface ocean, and the second likely produced an aerobic deep ocean. However, anoxic conditions returned for long periods of the Paleozoic, characterized by greenhouse climates that limited supply of downwelling O_2 relative to demand from sinking organic matter (Berry and Wilde, 1978). Oceanic anoxia can profoundly influence organic carbon production and burial by enhancing recycling of phosphorus from sedimentary organic matter (e.g., Van Cappellen and Ingall, 1994; Filippelli et al., 2003). The nitrogen cycle is also affected because anoxia promotes denitrification, which is the primary loss mechanism for biologically available (or “fixed”) nitrogen (Gruber and Sarmiento, 1997). The resulting N deficits may theoretically persist on geologic time scales (e.g., Piper and Codispoti, 1975; Lenton and Watson, 2000), particularly if accompanied by decreased availability of trace metals (Fe, Mo) essential for N-fixing bacteria (Falkowski, 1997; Anbar and Knoll, 2002). As a consequence of long-term transitions in oceanic redox state, fixed N could thus alternate with P as the ocean’s ultimate limiting nutrient.

Secular trends in the carbon isotope composition of marine carbonate ($\delta^{13}\text{C}_{\text{carb}}$) are a proxy for global organic carbon production and burial (Kump and Arthur, 1999; Godd eris and Joachimski, 2004) and can provide important constraints on models of oceanic redox

and nutrient cycling during the past 2 b.y. The period from ca. 1.8 to 1.3 Ga is notable for its lack of variation in $\delta^{13}\text{C}$, consistent with an anoxic-sulfidic (euxinic) deep ocean that sustained an N-limited, low-productivity marine ecosystem (Anbar and Knoll, 2002). In contrast, major fluctuations in $\delta^{13}\text{C}$ characterize the late Mesoproterozoic and Neoproterozoic ($\pm 10\text{‰}$), culminating in a snowball Earth period of maximum volatility (e.g., Hoffman et al., 1998). The extreme Neoproterozoic positive $\delta^{13}\text{C}$ excursions may indicate episodes of deep-ocean ventilation that switched the ultimate limiting nutrient back to P, which permitted episodes of enhanced productivity sustained by P remobilization from O_2 -poor tropical deltas (Schrag et al., 2002).

Oceanic $\delta^{13}\text{C}_{\text{carb}}$ fluctuations during the Paleozoic appear transitional between the highly unsettled Neoproterozoic and the increasingly stable Mesozoic to Cenozoic periods. The $\delta^{13}\text{C}$ record shows several positive excursions

to values as high as $+7\text{‰}$ (e.g., Kump et al., 1999; Saltzman, 2003), which are on par with Neoproterozoic peaks but apparently shorter in duration (and lacking in associated negative excursions, which are well known only at the beginning and end of the Paleozoic; Knoll et al., 1996; Monta ez et al., 2000). Some of the largest mass extinctions of the Phanerozoic are associated with these Paleozoic positive $\delta^{13}\text{C}$ excursions and suggest a link with redox state transitions that altered deep-ocean circulation patterns and nutrient cycling (Finney et al., 1999; Saltzman et al., 2000; Joachimski et al., 2002).

I present a new high-resolution $\delta^{13}\text{C}_{\text{carb}}$ curve for the Paleozoic from the Great Basin region of the western United States. The results show several intervals in the Late Cambrian, Late Ordovician–Silurian, and Late Devonian–Early Mississippian that are marked by large transient excursions ($\sim 10^6$ yr) interpreted to have occurred during cooler climates in which the ocean’s ultimate limiting nutrient was P. Long periods ($>10^7$ yr) of stasis in $\delta^{13}\text{C}$ during greenhouse climates indicate the existence of a strong negative feedback on productivity, which would be present in an N-limited ocean in which anoxia enhanced denitrification.

METHODS AND DATA

The new composite $\delta^{13}\text{C}_{\text{carb}}$ curve presented here minimizes the potential for gaps that can result from miscorrelation by relying entirely on the exceptionally thick and well-dated sections in the Great Basin (Fig. 1). The Great Basin contains an ~ 10 -km-thick early Paleozoic passive margin and later foreland basin succession that can be pieced together in dominantly carbonate facies. The Middle Cambrian through Pennsylvanian segments utilized have been correlated globally using trilobites, conodonts, graptolites, or foraminifera (see Data Repository Table DR1).¹ The composite (Fig. 2) is based on my unpublished and published data (complete reference list in Appendix DR1; see footnote 1), and also incorporates two short Great Basin seg-

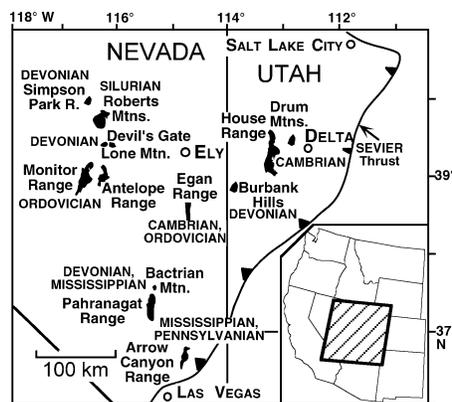


Figure 1. Locality map showing segments included in Great Basin Paleozoic $\delta^{13}\text{C}_{\text{carb}}$ composite.

¹GSA Data Repository item 2005114, Appendix DR1, complete reference list for published $\delta^{13}\text{C}_{\text{carb}}$ data and methods, Table DR1, biostratigraphic zonation, and Figures DR1 and DR2, $\delta^{13}\text{C}_{\text{carb}}$ vs. $\delta^{18}\text{O}$ and numerical ages, is available online at www.geosociety.org/pubs/ft2005.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

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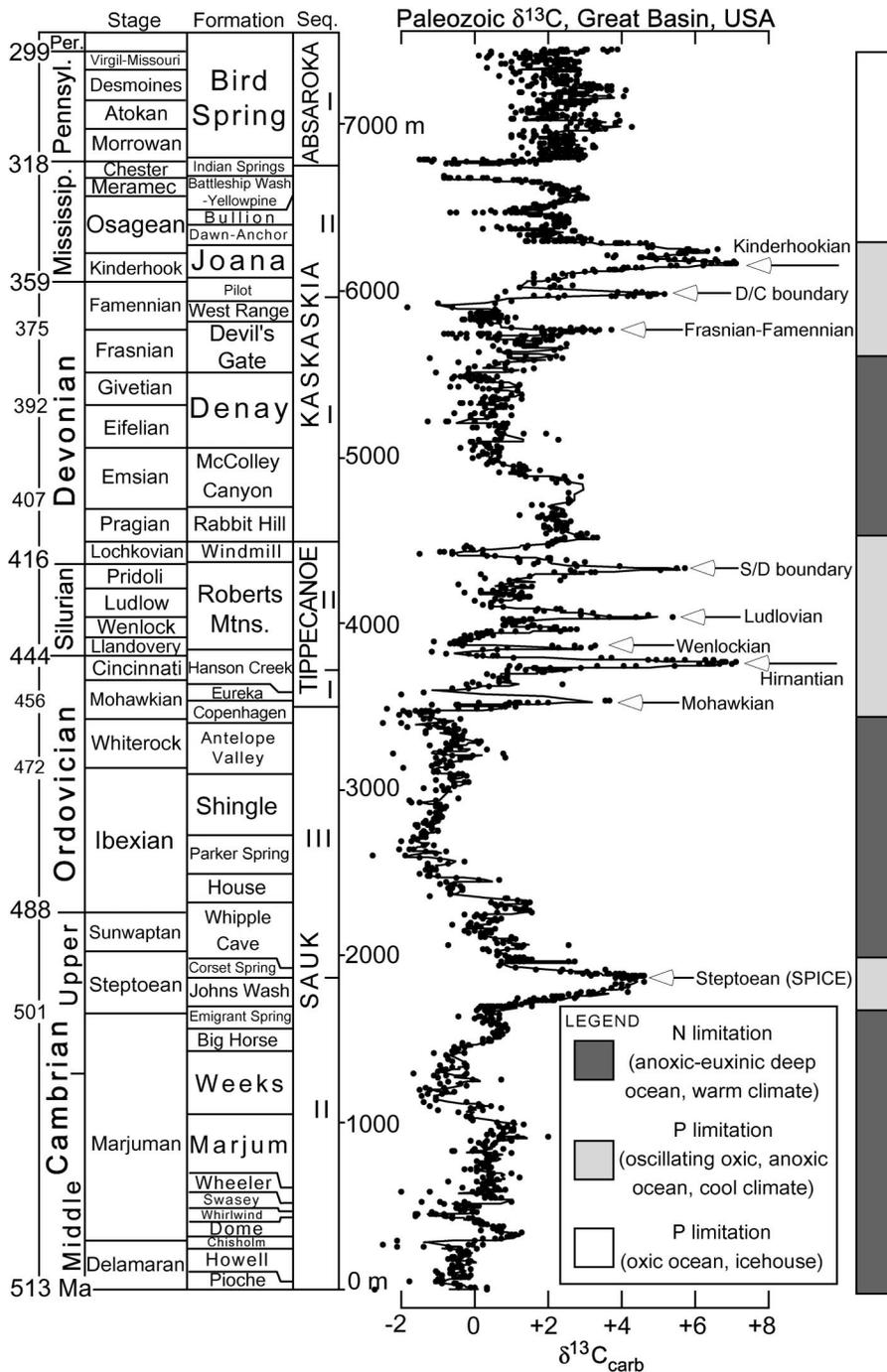


Figure 2. Great Basin Paleozoic $\delta^{13}\text{C}_{\text{carb}}$ composite against formation and age (see footnote 1). Composite is based on my unpublished and published data (complete reference list in Appendix DR1; see footnote 1), and two short Great Basin segments published for Late Ordovician (Kump et al., 1999) and Late Devonian (Joachimski et al., 2002). Seq. = Sloss second-order sea-level cycles. Arrows mark excursions known to occur on other continents. Legend (shading) delineates periods of volatility and relative stasis in $\delta^{13}\text{C}$ driven by changes in climate and oceanic redox state that determined whether nitrogen or phosphorus limited C_{org} production and burial. N-limited oceans in greenhouse periods are characterized by negative feedback between anoxia and productivity that curbs $\delta^{13}\text{C}$ excursions. P-limited oceans in cooler climates are characterized by positive feedback between anoxia and productivity that can sustain $\delta^{13}\text{C}$ excursions.

ments published for the Late Ordovician (Kump et al., 1999) and Late Devonian (Joachimski et al., 2002).

Researchers have constructed detailed

$\delta^{13}\text{C}_{\text{carb}}$ curves using brachiopod shells (Mii et al., 1999; Veizer et al., 1999), fine-grained carbonate (Kump et al., 1999), and, less commonly, marine cements (Montañez et al.,

2000). This study uses petrographically well preserved, fine-grained carbonate microsampled from polished slabs. One argument for the reliability of this method is the robustness of the Late Cambrian SPICE $\delta^{13}\text{C}$ excursion, which is preserved in a remarkably wide range of depositional and diagenetic settings in a number of sections from North America, Australia, China, and Kazakhstan (Saltzman et al., 2000). Although diagenetic resetting can affect micrite-based curves (e.g., Railsback et al., 2003), the field, petrographic, and geochemical (see footnote 1) indicators of diagenesis in the sections studied indicate a degree of alteration that is unlikely to have compromised the general nature of the stratigraphic trends discussed here.

DISCUSSION

The nine documented Paleozoic excursions, which shifted $\delta^{13}\text{C}$ by $\geq +3\text{‰}$ and lasted for a few million years or less (Fig. 2), have all been recognized outside of North America (e.g., Veizer et al., 1999; Joachimski et al., 2002) and represent significant paleoceanographic events. Intervals characterized by $\delta^{13}\text{C}$ volatility in the Late Cambrian (Steptoean), Late Ordovician–Silurian, and Late Devonian–Early Mississippian are separated by relatively stable periods with values between -2‰ and $+2\text{‰}$ (Fig. 2). The $\delta^{13}\text{C}$ excursions are commonly modeled as episodes of enhanced organic carbon burial (relative to carbonate) resulting from increases in oceanic nutrient availability (Kump and Arthur, 1999; Goddérís and Joachimski, 2004). These models assume that phosphate limits marine productivity and drives excursions by increasing P fluxes to the surface oceans, either from the continents or deep ocean. The control of primary production in the world's oceans by either nitrogen or P is, however, a long-standing debate in paleoceanography (e.g., Falkowski, 1997; Tyrrell, 1999).

Although N/P ratios in most of today's oceans are less than the classic Redfield ratio of $\sim 16:1$ for fresh organic matter (e.g., Wu et al., 2000), the argument for phosphate as the ultimate limiting nutrient is based on the essentially limitless supply of N_2 in the atmosphere. Therefore, waters in which the N/P falls below the Redfield ratio can be restored on ecological time scales by the competitive advantage conferred upon cyanobacteria that can convert N_2 into biologically available fixed N (Gruber and Sarmiento, 1997). Then, as N/P ratios rise, N fixation becomes less advantageous as a result of the high energy demands, and the N inventory starts to level off. In this view, the ocean regulates its own N/P ratio like a thermostat ("nitrostat"). Phosphorus, however, must enter the oceans through continental weathering, has a relatively long residence time, and therefore is predicted to

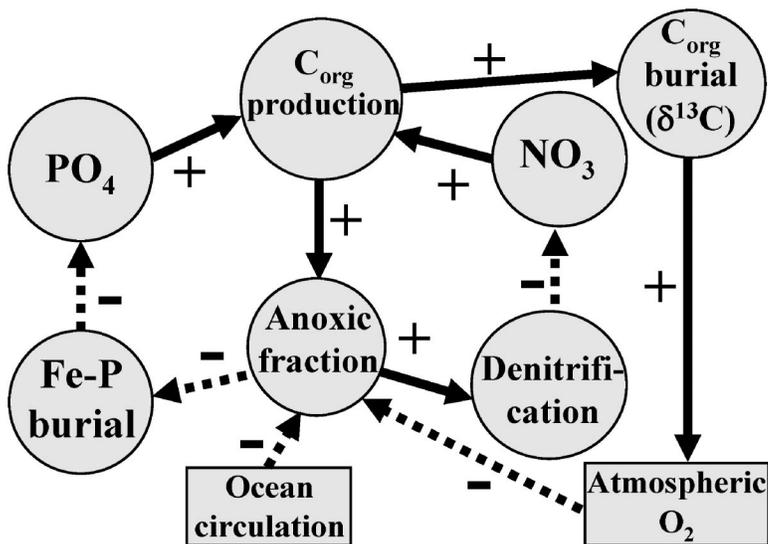


Figure 3. Systems-analysis diagram (cf. Lenton and Watson, 2000; Berner, 2003) showing contrasting effects of enhanced C_{org} production and anoxia in P- vs. N-limited oceans. Loop with even number of plus signs represents positive feedback loop; odd number of plus signs is negative loop. Anoxic fraction is fraction of ocean where O₂ demand from sinking organic matter exceeds supply, which is determined by C_{org} production at surface and increases in deep ocean circulation (ventilation) that occurs during cool climates. P-limited oceans are characterized by positive feedback with anoxia because of decreases in Fe-P burial, which are counteracted by negative feedback with rising O₂ levels. N-limited oceans have negative feedback between anoxia and productivity because of enhanced denitrification (assuming that N fixation is suppressed and cannot balance loss).

control total ocean productivity (Tyrrell, 1999).

However, in greenhouse climates much warmer than today, N could in theory control total ocean productivity if widespread oceanic anoxia drove denitrification to such high levels (e.g., Jenkyns et al., 2001) that N fixation could not keep pace with loss. Today, water-column denitrification occurs only in a small fraction of the ocean's thermocline (~0.1% by volume), where O₂ demand from sinking organic matter exceeds supply, but accounts for as much as ~25%–60% of fixed N loss (the balance is mostly sedimentary denitrification). A much greater anoxic fraction of the water column could lower N/P below the Redfield ratio on geologic time scales (Lenton and Watson, 2000). In such an N-limited ocean, any increase in marine productivity (and δ¹³C) would be opposed by a negative feedback with anoxia due to denitrification (Fig. 3). In contrast, a positive feedback with anoxia in a P-limited ocean could sustain positive excursions in δ¹³C (e.g., Schrag et al., 2002).

The major uncertainty in sustaining an N-limited ocean in greenhouse conditions is the rate at which N fixation would act to raise N/P ratios that were lowered by denitrification. The existence of an imbalance in the modern ocean is a subject of debate (Tyrrell, 1999; Wu et al., 2000), and it has been proposed that the oceanic fixed N inventory may have been as much as 30% greater during the last glacial maximum (~20 k.y. ago) (Deutsch et al., 2004). A glacial-stage increase in fixed N could be generated by ventilation of the thermocline that lessened the spatial extent of denitrification (e.g., Altabet et al., 1995), driven ultimately by lowered sea surface temperatures, increased oxygen solubility, and stronger winds in high-latitude regions. During deglaciation, sluggish circulation of warmer, O₂-poor thermocline waters caused expansion

of water-column denitrification. Sedimentary denitrification would also increase during postglacial transgression in proportion to continental shelf area, further reducing fixed N (Christensen, 1994).

If the oceanic fixed N inventory was significantly depleted by denitrification during greenhouse compared to icehouse conditions in the Paleozoic, N fixation would be expected to increase in response to excess P available in upwelling waters (Sanudo-Wilhelmy et al., 2001; Galbraith et al., 2004). However, if iron and P colimit N fixation, as occurs today in the eastern tropical North Atlantic (Mills et al., 2004), this could pose a problem in a greenhouse world characterized by a low equator to pole thermal gradient and high sea level that limited supply of eolian Fe mineral dust to the surface oceans (Falkowski, 1997; Wu et al., 2000). Rates of N₂ fixation may also be limited by redox-sensitive trace metals such as molybdenum, which may be less available if euxinic water masses promoted scavenging (e.g., Anbar and Knoll, 2002; Algeo, 2004).

Keeping in mind the caveats discussed here, if fluctuations in oceanic redox state during the Paleozoic have driven changes in the limiting nutrient (P, N), then this may in part account for the periods of relative stasis and volatility in the δ¹³C curve in Figure 2. High rates of denitrification compared to N fixation would be expected during warm periods of high sea level, including the ice-free Middle Cambrian, Early-Middle Ordovician, and Early-Middle Devonian intervals. These intervals are marked by stability in δ¹³C, consistent with an N limited ocean that curbed excursions by a negative feedback on productivity in which an increase in sinking organic matter lowers O₂ and enhances denitrification (Fig. 3). Euxinic deep oceans, for example in the Middle Cambrian and Early-

Middle Ordovician (e.g., Berner and Raiswell, 1983; Strauss, 1999), may have drawn down redox sensitive trace elements and suppressed N fixation.

The transition to a P-limited ocean would occur during climatic cooling, likely related to tectonically induced thresholds in long-term pCO₂, which switched deep-water formation to high latitudes and ventilated the oceans. Higher dissolved O₂ in the oceans would lower denitrification rates, while at the same time strengthened winds increase eolian Fe input and stimulate N fixation. Rising N would restore N/P to the Redfield ratio over a time period dependent on the residence times of the two elements and initial P levels at onset of ventilation. Primary productivity (and δ¹³C) is then determined by the balance between P sinks (e.g., Fe-P burial) and P sources to the surface oceans from upwelling (including potentially high residual P levels from a previously stratified ocean) or continental weathering (Kump and Arthur, 1999; Goddérís and Joachimski, 2004).

In a P-limited ocean, thresholds in productivity can lead to the spread of anoxia and more efficient P remobilization in a positive feedback loop (Fig. 3), which may initiate positive excursions in δ¹³C in the Late Cambrian, Late Ordovician–Silurian, and Late Devonian–Early Mississippian (Fig. 2). In order to sustain this rising phosphate fueled production, trace element inventories and N fixation must remain high enough in certain parts of the ocean (assuming strict enforcement of the Redfield ratio; Ganeshram et al., 2000) to counterbalance accompanying loss of N to denitrification in anoxic waters (e.g., Murphy et al., 2000; Kuypers et al., 2004). Positive δ¹³C excursions may also be sustained by enhanced organic carbon preservation during rises in sea level (interglacials in icehouse periods) that temporarily switched the site of deep-water

formation back to low latitudes and increased stratification. In this high “preservation” scenario, for example as indicated by oligotrophic shelf conditions during Silurian $\delta^{13}\text{C}$ excursions (e.g., Cramer and Saltzman, 2005), overall rates of productivity would still be higher than at any time during greenhouse conditions of N limitation. Regardless of the ultimate cause of enhanced organic carbon burial that sustains positive $\delta^{13}\text{C}$ excursions, cooler climates (falling $p\text{CO}_2$) together with rising O_2 levels and scavenging of P by ferric oxyhydroxides (Fe-P burial) provide a negative feedback (Fig. 3).

The apparent lack of large, transient $\delta^{13}\text{C}$ excursions in the mid-Mississippian through Pennsylvanian icehouse may signal the transition to an aerobic deep ocean that was less susceptible to anoxic events. The overall heavier $\delta^{13}\text{C}$ baselines but less volatile record may also reflect other factors, such as changes in coupling of $C_{\text{org}}:C_{\text{carb}}$ production and burial (e.g., Bartley and Kah, 2004) or the rise of land plants that provided a new source of organic carbon and fixed N to the oceans.

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REFERENCES CITED

Algeo, T.J., 2004, Can marine anoxic events draw down the trace element inventory of seawater?: *Geology*, v. 32, p. 1057–1060.

Altabet, M.A., Francois, R., Murray, D.W., and Prell, W.L., 1995, Climate-related variations in denitrification in the Arabian Sea from sediment $^{15}\text{N}/^{14}\text{N}$ ratio: *Nature*, v. 373, p. 506–509.

Anbar, A.D., and Knoll, A.H., 2002, Proterozoic ocean chemistry and evolution: A bioinorganic bridge?: *Science*, v. 297, p. 1137–1142.

Bartley, J.K., and Kah, L.C., 2004, Marine carbon reservoir, $C_{\text{org}}-C_{\text{carb}}$ coupling, and the evolution of the Proterozoic carbon cycle: *Geology*, v. 32, p. 129–132.

Berner, R.A., 2003, The long-term carbon cycle, fossil fuels and atmospheric composition: *Nature*, v. 426, p. 323–326.

Berner, R.A., and Raiswell, R.A., 1983, Burial of organic-carbon and pyrite sulfur over Phanerozoic time—A new theory: *Geochimica et Cosmochimica Acta*, v. 47, p. 855–862.

Berry, W.B.N., and Wilde, P., 1978, Progressive ventilation of the oceans—An explanation for the distribution of the lower Paleozoic black shales: *American Journal of Science*, v. 278, p. 257–275.

Canfield, D.E., 1998, A new model for Proterozoic ocean chemistry: *Nature*, v. 396, p. 450–453.

Christensen, J.P., 1994, Carbon export from continental shelves, denitrification and atmospheric carbon

dioxide: *Continental Shelf Research*, v. 14, p. 547–576.

Cramer, B.S., and Saltzman, M.R., 2005, Sequestration of ^{12}C in the deep ocean during the early Wenlock (Silurian) positive carbon isotope excursion: *Palaeogeography, Palaeoclimatology, Palaeoecology*, doi: 10.1016/j.palaeo.2005.01.009.

Deutsch, C., Sigman, D.M., Thunell, R.C., Meckler, A.N., and Haug, G.H., 2004, Isotopic constraints on glacial/interglacial changes in oceanic nitrogen budget: *Global Biogeochemical Cycles*, v. 18, doi: 10.1029/2003GB002189.

Falkowski, P.G., 1997, Evolution of the nitrogen cycle and its influence on the biological sequestration of CO_2 in the ocean: *Nature*, v. 387, p. 272–275.

Filippelli, G.M., Sierro, F.J., Flores, J.A., Vasquez, A., Utrilla, R., Perez-Folgado, M., and Latimer, J.C., 2003, A sediment-nutrient-oxygen feedback responsible for productivity variations in late Miocene sapropel sequences of the western Mediterranean: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 190, p. 335–348.

Finney, S.C., Berry, W.B.N., Cooper, J.D., Ripperdan, R.L., Sweet, W.C., Jacobson, S.R., Soufiane, A., Achab, A., and Noble, P.J., 1999, Late Ordovician mass extinction: A new perspective from stratigraphic sections in central Nevada: *Geology*, v. 27, p. 215–218.

Galbraith, E.D., Kienast, M., Pedersen, T.F., and Calvert, S.E., 2004, Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O_2 supply to the global thermocline: *Paleoceanography*, v. 19, doi: 10.1029/2003PA001000.

Ganeshram, R.S., Pedersen, T.F., Calvert, S.E., and Francois, R., 2002, Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories: *Nature*, v. 415, p. 156–159.

Goddéris, Y., and Joachimski, M.M., 2004, Global change in the Late Devonian: Modelling the Frasnian-Famennian short-term carbon isotope excursions: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 202, p. 309–329.

Gruber, N., and Sarmiento, J.L., 1997, Global patterns of marine nitrogen fixation and denitrification: *Global Biogeochemical Cycles*, v. 11, p. 235–266.

Hoffman, P.F., Kaufman, A.J., Halverson, G.P., and Schrag, D.P., 1998, A Neoproterozoic snowball Earth: *Science*, v. 281, p. 1342–1346.

Holland, H.D., 1984, *The chemical evolution of the atmosphere and oceans*: Princeton, New Jersey, Princeton University Press, 582 p.

Jenkyns, H.C., Gröcke, D.R., and Hesselbo, S.P., 2001, Nitrogen isotope evidence for water mass denitrification during the early Toarcian (Jurassic) oceanic anoxic event: *Paleoceanography*, v. 16, p. 593–603.

Joachimski, M.M., Pancost, R.D., Freeman, K.H., Ostertag-Henning, C., and Buggisch, W., 2002, Carbon isotope geochemistry of the Frasnian-Famennian transition: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 181, p. 91–109.

Knoll, A.H., Bambach, R.K., Canfield, D.E., and Grotzinger, J.P., 1996, Comparative Earth history and Late Permian mass extinction: *Science*, v. 273, p. 452–457.

Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon-isotope excursions: Carbonates and organic matter: *Chemical Geology*, v. 161, p. 181–198.

Kump, L.R., Arthur, M.A., Patzkowsky, M.E., Gibbs, M.T., Pinkus, D.S., and Sheehan, P.M., 1999, A weathering hypothesis for glaciation at high atmospheric $p\text{CO}_2$ during the Late Ordovician: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 152, p. 173–187.

Kuypers, M.M.M., van Breugel, Y., Schouten, S., Erba, E., and Damste, J.S.S., 2004, N_2 -fixing cyano-

bacteria supplied nutrient N for Cretaceous anoxic events: *Geology*, v. 32, p. 853–856.

Lenton, T.M., and Watson, A.J., 2000, Redfield revisited 1. Regulation of nitrate, phosphate, and oxygen in the ocean: *Global Biogeochemical Cycles*, v. 14, p. 225–248.

Mii, H., Grossman, E.L., and Yancey, T.E., 1999, Carboniferous isotope stratigraphies of North America: Implications for Carboniferous paleoceanography and Mississippian glaciation: *Geological Society of America Bulletin*, v. 111, p. 960–973.

Mills, M.M., Ridame, C., Davey, M., La Roche, J., and Geider, R., 2004, Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic: *Nature*, v. 429, p. 292–294.

Montañez, I.P., Banner, J.L., Mack, L.E., Musgrove, M., and Osleger, D.A., 2000, Evolution of the Sr and C isotope composition of Cambrian oceans: *GSA Today*, v. 10, no. 5, p. 1–7.

Murphy, A.E., Sageman, B.B., Hollander, D.J., Lyons, T.W., and Brett, C.E., 2000, Black shale deposition and faunal overturn in the Devonian Appalachian basin: Clastic starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling: *Paleoceanography*, v. 15, p. 280–291.

Piper, D.Z., and Codispoti, L.A., 1975, Marine phosphorite deposits and the nitrogen cycle: *Science*, v. 188, p. 15–18.

Railsback, L.B., Holland, S.M., Hunter, D.M., Jordan, M.E., Diaz, J.R., and Crowe, D.E., 2003, Controls on geochemical expression of subaerial exposure in Ordovician limestones from the Nashville Dome, Tennessee, U.S.A.: *Journal of Sedimentary Research*, v. 73, p. 790–805.

Saltzman, M.R., 2003, The late Paleozoic Ice Age: Oceanic gateway or $p\text{CO}_2$?: *Geology*, v. 31, p. 151–154.

Saltzman, M.R., Brasier, M.D., Ripperdan, R.L., Ergaliev, G.K., Lohmann, K.C., Robison, R.A., Chang, W.T., Peng, S., and Runnegar, B., 2000, A global carbon isotope excursion during the Late Cambrian: Relation to trilobite extinctions, organic-matter burial and sea level: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 162, p. 211–223.

Sanudo-Wilhelmy, S., Gobler, C., Hutchins, D., Yang, M., Lwiza, K., Burns, J., Capone, D., Raven, J., and Carpenter, E., 2001, Phosphorus limitation of nitrogen fixation by trichodesmium in the central Atlantic Ocean: *Nature*, v. 411, p. 66–69.

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, U1-U21 JUN 27.

Strauss, H., 1999, Geological evolution from isotope proxy signals—Sulfur: *Chemical Geology*, v. 161, p. 89–101.

Tyrrell, T., 1999, The relative influences of nitrogen and phosphorus on oceanic primary production: *Nature*, v. 400, p. 525–531.

Van Cappellen, P., and Ingall, E.D., 1994, Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus: *Paleoceanography*, v. 9, p. 677–692.

Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., Diener, A., Ebner, S., Godderis, Y., Jasper, T., Korte, C., Pawellek, F., Podlaha, O. G., and Strauss, H., 1999, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater: *Chemical Geology*, v. 161, p. 59–88.

Wu, J., Sunda, W., Boyle, E.A., and Karl, D.M., 2000, Phosphate depletion in the western North Atlantic Ocean: *Science*, v. 289, p. 759–762.

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