

Carbon isotope excursions and the oxidant budget of the Ediacaran atmosphere and ocean

Thomas F. Bristow*, Martin J. Kennedy

Department of Earth Sciences, University of California–Riverside, Riverside, California 92521, USA

ABSTRACT

A possible global drop in marine carbon isotope values to as low as -12‰ Peedee belemnite (PDB), recorded in the Ediacaran Shuram Formation of Oman, has been attributed to the non-steady-state oxidation of oceanic dissolved organic carbon (DOC) resulting from the rise in atmospheric oxygen to near modern values at the end of the Precambrian. Geologic constraints indicate that the excursion lasted between 25 and 50 m.y., requiring a DOC pool thousands of times to 10,000 times the modern inventory to conform with carbon isotope mass balance calculations for a -12‰ excursion. At the consequent rates of DOC oxidation, oceanic sulfate and oxygen in the atmosphere and oceans are exhausted on a time scale of ~ 800 k.y. Oxidant depletion is incompatible with independent geochemical and biological indicators that show oceanic sulfate and oxygen levels were maintained or increased during the Shuram excursion. Furthermore, a DOC-driven excursion does not explain strong covariation between the carbon and oxygen isotope record. These indicators show that negative isotope excursions recorded in the Shuram and other Ediacaran sections are unlikely to represent a global ocean signal.

INTRODUCTION

Unusually depleted carbon isotope values from Ediacaran-aged carbonates in Oman, Australia, southern China, southwestern United States, Norway, and Siberia record a nadir of -12‰ Peedee belemnite (PDB), and are interpreted as an unprecedented shift in global ocean values, termed the Shuram excursion, that lasted for millions of years (Condon et al., 2005; Melezhik et al., 2005; Le Guerroue et al., 2006; Fike et al., 2006; Jiang et al., 2007; Kaufman et al., 2007). If these isotope values record the isotopic composition of inorganic carbon in the ocean, then the Shuram excursion indicates a fundamentally different carbon isotope mass balance combined with a severe long-lived perturbation in the carbon cycle that may have resulted from the oxidation of the atmosphere and oceans (Fike et al., 2006; Jiang et al., 2007; Kaufman et al., 2007). Interpreted in this way, negative carbon isotope excursions are used to support a link between increasing oxygen levels, the development of macroscopic animal life (Fike et al., 2006), and the radiation of multicellular algae and acanthomorphic acritarchs (McFadden et al., 2008).

The magnitude and persistence of this excursion, however, are difficult to accommodate within limits prescribed by the current understanding of the carbon cycle (Melezhik et al., 2005). At the present time and throughout the Phanerozoic there has not been the sustainable source of ^{12}C needed to change inorganic oceanic values to $<-12\text{‰}$ PDB for millions of years. While oceanic negative carbon isotopic anomalies occur in the geological record, they are based on rapid injection of pools of depleted carbon that are quickly exhausted. Sources include methane clathrate release (Dickens et al., 1995), ocean stagnation and overturn (Knoll et al., 1996), and oxidative decay of exposed marine organic sediments and/or terrestrial organic matter (Higgins and Schrag, 2006). However, even when combined, these inputs are only capable of producing a perturbation of $\sim 5\text{‰}$ with a recovery time of 0.5 m.y. (Berner, 2002). Biological crises return oceanic inorganic carbon to mantle values on time scales of hundreds of thousands of years (Kump, 1991).

The resulting “Strangelove” ocean may last as long as primary productivity is suppressed, millions of years in the case of the original snowball Earth hypothesis (Hoffman et al., 1998), but oceanic carbon values drop no lower than $\sim 6\text{‰}$, the canonical mantle value (Kump and Arthur, 1999). The same lower limit applies to isotope perturbations driven by enhanced volcanism (Renne et al., 1995).

These mechanisms fail to explain the magnitude (nadir of -12‰) and the duration of the Shuram excursion; estimated to last for 25, <30 , and 50 m.y., respectively (Jiang et al., 2007; Fike et al., 2006; Le Guerroue et al., 2006). A shorter duration of between 1 and 10 m.y., based on the duration of a potentially correlative negative excursion in southern China (Condon et al., 2005), is not supported by thermal subsidence age models of the Shuram excursion in Oman, and seems unlikely because of the persistence of negative isotope values through >500 m of complex stratigraphy in Oman and Australia that represents numerous changes in sea level (Le Guerroue et al., 2006; Calver, 2000). Accepting this excursion as a primary oceanic signal requires a departure from an understanding of the carbon cycle from the standpoint of modern fluxes and carbon inventories.

Rothman et al. (2003) hypothesized a Precambrian ocean containing between 100 and 1000 times the modern inventory of dissolved organic carbon (DOC). In this scenario periodic oxidation of a small fraction of this pool dominated the carbon isotope mass balance of ocean dissolved inorganic carbon (DIC), producing transient (tens of thousands of years) negative excursions in carbon isotope values, like those observed in cap carbonates. It is posited that the final oxidation and removal of the excess DOC pool, triggered by a rise in ocean and atmospheric oxygen, resulted in the Shuram excursion (Fike et al., 2006). A steady increase in the difference between $\delta^{34}\text{S}$ isotopes of coeval pyrite and carbonate-associated sulfur ($\Delta\delta^{34}\text{S}$) for at least 25 m.y. following the Marinoan glaciation (ca. 635 Ma) indicates an increase in ocean sulfate concentrations during that period. This implies a buildup of oxygen and sulfate before the onset of DOC oxidation (Fike et al., 2006; Halverson and Hurtgen, 2007). A strong chemocline is hypothesized as keeping these pools apart, with the final ventilation of the ocean triggered by increased fluxes of sulfate from oxidative weathering of shelf sediments during sea-level fall (Kaufman et al., 2007; Jiang et al., 2007). Beyond the negative C isotope values, there is no physical or geological evidence of a large DOC pool in the Precambrian ocean.

This mechanism is potentially problematic given independent geochemical and biological evidence that oxygen levels were maintained or increased during the Shuram excursion (Fike et al., 2006; Canfield et al., 2007; Runnegar, 1982), despite the large demand for oxidants resulting from decay of DOC (Halverson and Hurtgen, 2007). There are other explanations for strongly depleted carbon isotope values. Carbonates from the extensive Permian lacustrine systems of southwest Gondwana have values as low as -20‰ PDB (Faure and Cole, 1999). Highly negative isotope values observed in the Ediacaran Wonoka Formation of South Australia, commonly correlated with the Shuram (Le Guerroue et al., 2006), are attributed to analogous processes occurring in salinity-stratified basins with limited oceanic connections (Calver, 2000). In addition, diagenetic alteration, particularly by meteoric fluids, can cause substantial shifts from primary marine values. Altered Pleistocene limestones have values between 0 and

*E-mail: tbris001@student.ucr.edu

<-11‰ (Land 1986). A diagenetic origin for C isotopic values <-4‰ from the Shuram was proposed by Burns and Matter (1993).

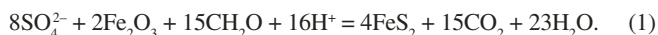
In this paper we use numerical methods to quantify the demand for oxidants needed to drive a carbon isotope excursion of the magnitude and duration of the Shuram by oxidative decay of a DOC pool, allowing us to test if this mechanism is plausible.

MODEL

Our simulation is based on a simple box model shown schematically in Figure 1. Box 1 is a well-known representation of the marine carbon cycle (Kump and Arthur, 1999) that calculates the evolution of carbon isotope values of seawater. Box 2 represents the hypothesized reservoir of DOC in excess of modern concentrations and is linked to box 1. The decay of DOC produces an additional flux of inorganic carbon with an isotopic value (δ_{DOC}) of -30‰, a typical value of marine organic carbon during the Shuram (Fike et al., 2006), and drives the negative isotope excursion.

Oxidative decay of DOC is fueled by consumption of oxygen and sulfate. Oxygen in the atmosphere and ocean is represented by a single reservoir (box 3), initially in equilibrium. The decay of 1 mol of DOC consumes 1 mol of oxygen. Oxygen levels are set to modern values of 36.6×10^{18} mol (Chameides and Perdue, 1997), as a conservative maximum. Although oxygen levels in the Ediacaran Period are poorly constrained, 15% present atmospheric level (PAL) is proposed as a minimum estimate for post-Gaskiers (younger than 580 Ma) time (Canfield et al., 2007). Our model neglects several feedbacks in the carbon cycle that actively regulate oxygen levels. This is justified because enhanced net oxygen production, either by increased burial of organic matter or reduced rates of oxidative weathering of organic carbon in exhumed sediments, results in positive shifts in inorganic marine $\delta^{13}\text{C}$, canceling out the negative excursion (for further discussion, see the GSA Data Repository¹).

Oxygen represents only a portion of oxidants capable of mineralizing organic carbon in the ocean. The modern sulfate pool is 4.1×10^{19} mol (Bottrell and Newton, 2006), slightly larger than the quantity of oxygen in the atmosphere and ocean. DOC is consumed by bacterial sulfate reduction. In this reaction 8 mol of sulfate remineralize 15 mol of DOC:



Sulfate is supplied to the ocean by dissolution of sulfate-bearing minerals and oxidative weathering of pyrite exposed on land. The rise of ocean sulfate concentrations through geological time reflects the coupling of atmospheric oxygen levels and the flux of sulfate to the oceans from pyrite weathering (Kah et al., 2004). Modern fluxes from pyrite weathering are estimated as 0.82×10^{12} mol/yr. Weathering of sulfates gives a flux of 0.5×10^{12} mol/yr (Chameides and Perdue, 1997). At equilibrium these inputs are balanced by pyrite and gypsum burial, but it is hypothesized that the sulfur cycle was out of balance before the Shuram excursion and additional sulfate was supplied to the ocean at that time (Kaufman et al., 2007). Therefore, in the model oceanic sulfate is represented by a single reservoir (box 4) whose size changes as a result rate of DOC consumption and a constant input of sulfate equivalent to the modern flux into the ocean (1.32×10^{12} mol/yr). Based on the sulfur isotope record, marine sulfate concentrations before the Shuram excursion have been estimated as between 0.2 mM and 5 mM, compared to 28.4 mM in the modern ocean (Fike et al., 2006). Higher estimates, of up to 48 mM (Halverson and Hurtgen, 2007), are incompatible with a DOC-rich ocean, as there is no way to keep these pools apart.

¹GSA Data Repository item 2008221, Table DR1 and a more detailed description of the model, including equations and constants, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

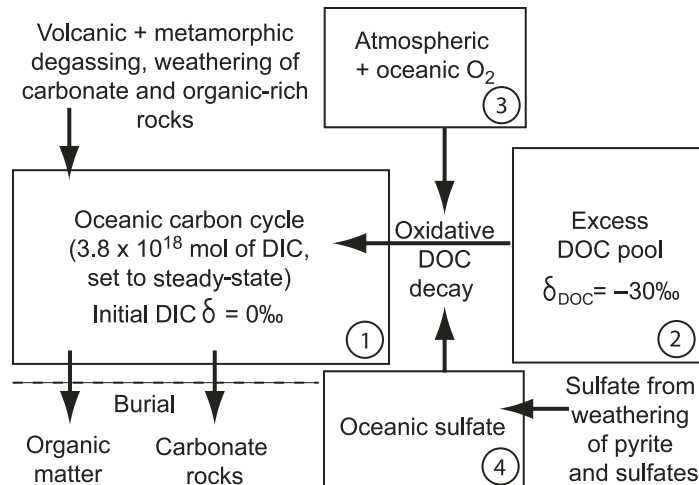


Figure 1. Schematic representation of main elements of the model. DOC—dissolved organic carbon; DIC—dissolved inorganic carbon. See Data Repository (see footnote 1) for more detailed description.

RESULTS

To estimate the size of the oceanic DOC pool and DOC decay rates needed to produce an isotope excursion the size and duration of the Shuram, the rate of decay of the excess DOC pool is initially set as a linear function of DOC concentration. With this model configuration the concentration of oxidants does not affect DOC decay rates. This simple function gives model results a temporal isotopic profile that resemble the pattern of isotopic change recorded in the stratigraphic record (Fig. 2), when the decay constant is set to produce a nadir of -12‰, the most negative value observed in the carbon isotope record from Oman. The model is initially run using a DOC pool of 32×10^{18} mol, the minimum value proposed by Rothman et al. (2003), and is ~250–500 times the modern inventory (60 to $>125 \times 10^{15}$ mol of C; Hansell and Carlson, 1998, and references therein). Under these conditions, isotopic recovery and the complete oxidation of the DOC pool occurs within 1.3 m.y. (Table DR1; see footnote 1). To produce an excursion lasting 30 m.y., a more typical estimate for the duration of the Shuram, a pool of DOC ~6000–12,000 times the modern is needed. At these DOC decay rates, the combined Ediacaran oxidant inventory of oxygen (100% PAL) and sulfate (5 mM) is consumed in ~800 k.y. This result shows that it is impossible to sustain a negative isotope excursion on time scales of multimillions of years if oxidant limitation of rates of DOC decay is considered.

There is no independent measure of the dependence of DOC decay rate on oxygen and sulfate concentration in the Precambrian ocean. Furthermore, the proportion of DOC oxidation that occurred above and below the hypothetical chemocline, which would also affect the relative rate of consumption of oxygen and sulfate, is unknown. However, to illustrate a best guess at the impact of oxidant availability on DOC decay rates, Figure 2 shows the modeled isotope response when the DOC decay rate is set to be proportional to the fraction of initial oxidants remaining and DOC concentration (see the Data Repository). Sulfate and oxygen are consumed at the same relative rate. Isotope values remain below the canonical mantle average of -6‰ for just over 900 k.y. and return to equilibrium in just over 2.5 m.y.

SMALLER DIC POOL?

Rothman et al.'s (2003) model of the Neoproterozoic oceanic carbon cycle involves a DOC reservoir at least 10 times larger than the DIC reservoir. Because DIC levels in the ocean have probably changed through Earth history (Bartley and Kah, 2004), it might be possible

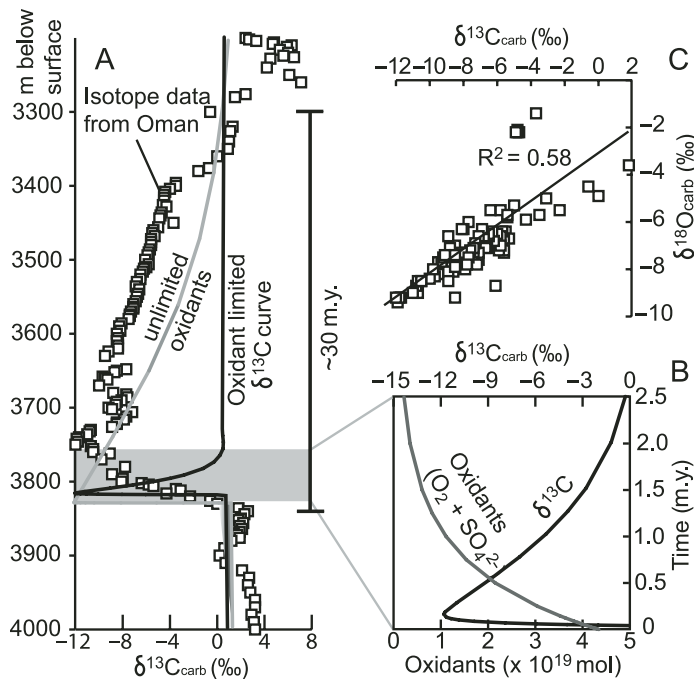
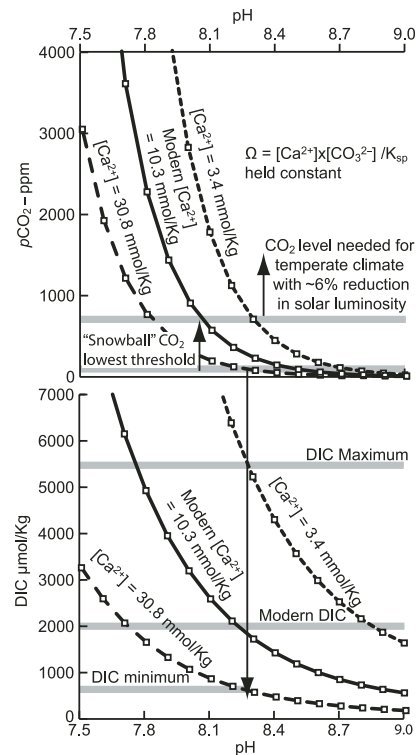


Figure 2. A: Temporal profiles of modeled inorganic carbon isotope curves driven by oxidative decay of dissolved organic carbon (DOC) compared with chemostratigraphic data from Oman (isotope data from Fike et al., 2006). Gray curve shows isotope response with unlimited supply of oxidants and serves as means of estimating size of the DOC pool needed to drive excursion lasting ~30 m.y. Using same initial DOC pool (7×10^{20} mol) and an oxidant inventory equivalent to modern oxygen content of the atmosphere and ocean and oceanic sulfate reservoir of 7×10^{18} mol (equivalent to a concentration ~5 mM), black line shows limiting effect of oxidant availability on duration of isotope excursion. **B:** Depletion of oxidants accompanying the isotope excursion. Model parameters: $\delta_i = -6\%$, $\delta_{\text{DOC}} = -30\%$, $\epsilon = -25\%$, $f_{\text{org}} = 0.3$, dissolved inorganic carbon (DIC) = 3800×10^{15} mol, $F_w = 5 \times 10^{13}$ mol (based on Kump and Arthur, 1999), except δ_{DOC} (Fike et al., 2006). **C:** Crossplot of carbon and oxygen isotope values from the Shuram Formation (from Fike et al., 2006).

to reduce the oxygen demand of a DOC-driven carbon isotope excursion by having much smaller DIC and DOC pools while maintaining a similar size ratio between them. The size of the ocean DIC reservoir is regulated by the saturation state of the ocean with respect to calcium carbonate (Ω), which is a function of carbonate $[\text{CO}_3^{2-}]$ and calcium $[\text{Ca}^{2+}]$ ion concentrations. Reductions in total DIC can be made while keeping Ω constant by increasing ocean pH and/or $[\text{Ca}^{2+}]$ (Fig. 2). However, evaporite records and models of ocean chemistry suggest that calcium concentration in the ocean did not vary beyond limits proposed for the Phanerozoic during the late Precambrian, with a maximum variability estimated at factor of 3 (Hardie, 2003; Holland, 1978). The increase in oceanic pH possible is limited by resulting reductions in atmospheric $p\text{CO}_2$ in equilibrium with the ocean.

Figure 3 shows the maximum ocean pH possible for a reasonable range of oceanic $[\text{Ca}^{2+}]$ while keeping atmospheric $p\text{CO}_2$ levels above 90 ppm, the lowest estimated threshold leading to runaway albedo in snowball Earth events (Fairchild and Kennedy, 2007). With a $p\text{CO}_2$ of 90 ppm and $[\text{Ca}^{2+}] = 30.8$ mmol/kg, the DIC pool is ~3 times smaller than in the modern ocean, showing that the DIC pool cannot be reduced enough to negate the oxidant demand of a DOC-driven C isotope excursion. However, these conditions are unrealistic. Levels of $p\text{CO}_2$ at least 800 ppm were needed to maintain a temperate climate with reduced solar luminosity, and $[\text{Ca}^{2+}]$ was probably lower than modern-day levels

Figure 3. Response of ocean dissolved inorganic carbon (DIC) reservoir size and atmospheric $p\text{CO}_2$ concentrations to pH changes in the ocean within likely range of $[\text{Ca}^{2+}]$, with $[\Omega]$ held at the modern oceanic level. Calculations were performed using the routines described in Zeebe and Wolf-Gladrow (2001) using their Matlab code, available at: http://www.soest.hawaii.edu/oceanography/faculty/zebe_files/CO2_System_in_Seawater/csys.html. Conditions used during calculations are temperature = 25 °C, salinity = 35‰, pH scale = total, equilibrium constants = Mehrbach, pressure = 0 bar. See Fairchild and Kennedy (2007), and references therein) for $p\text{CO}_2$ thresholds.



of 10.3 mmol/kg, based on carbonate mineralogy and chemical models (Hardie, 2003). As a result, the DIC pool and oxidant demand of a DOC-driven carbon isotope excursion was probably larger in the Ediacaran than under modern ocean conditions.

DISCUSSION

Our results demonstrate that oxidant availability limits the duration of DOC-driven negative carbon isotope anomalies to time scales that are incompatible with current estimates of the duration of the Shuram excursion. With the conservatively high levels of oxygen and sulfate used in our calculations, marine carbon isotope values can be kept below the canonical mantle average of -6% for ~900 k.y., before oxidants become limiting. More realistic levels of oxidants in the Ediacaran ocean and atmosphere would be severely depleted within hundreds of thousands of years of the start of a DOC oxidation event. However, sulfur isotope records from Fe-speciation evidence from sediments and the emergence of the Ediacaran fauna show that oxygen and sulfate levels were maintained, and may have risen, during the Shuram excursion, making the DOC hypothesis an unlikely mechanism (Fike et al., 2006; Canfield et al., 2007; Runnegar, 1982).

Our findings do not rule out the elevated DOC concentrations hypothesized for the Neoproterozoic ocean of Rothman et al. (2003). A DOC pool 100–1000 times bigger than the modern, as proposed by Rothman et al. (2003), could have decayed over tens of millions of years as a response to rising oxygen levels without placing excessive demands for oxidants. However, the imprint left in the carbon isotope record would be small and therefore is probably not a useful tool to monitor progressive increases in oxygen levels.

In the absence of independent evidence for a large DOC pool as a buffer, the invariance of $\delta^{13}\text{C}$ of organic matter through the same interval (Fike et al., 2006; McFadden et al., 2008) is conservatively interpreted as indicating that the carbonate record is not a robust reflection of the global ocean $\delta^{13}\text{C}$ in this case (Knoll et al., 1986; Calver, 2000). Cross-plots of carbon and oxygen isotope data from the Shuram Formation

from Fike et al. (2006) (Fig. 2C) show positive covariation and support this conclusion, because there is no physical or chemical reason for primary C and O isotopes from marine carbonates deposited under a nominal range of seawater pH to covary in this way. Covariation also gives insights into the origin of the highly depleted carbon isotope values. This pattern is found in carbonates altered by meteoric fluids (Knauth and Kennedy, 2005) and in closed lake systems that undergo changes in salinity (Talbot 1990), a model that may also be applicable to a silled, salinity stratified basin with limited marine connections proposed by Calver (2000) for the Wonoka Formation, Australia. Further investigations focused on time constraints and the assessment of depositional and postdepositional sources of C¹² are needed to identify the origin of negative excursions and determine if they truly record processes unique to the Precambrian carbon cycle.

ACKNOWLEDGMENTS

We thank A. Ridgwell for detailed feedback and discussion of the manuscript. P. Hoffman, D. Schrag, and an anonymous reviewer provided helpful comments. This work was supported by National Aeronautics and Space Administration grant NNG04GJ42G, and National Science Foundation grant EAR-0345207 to Kennedy.

REFERENCES CITED

- Bartley, J.K., and Kah, L.C., 2004, Marine carbon reservoir, C-org-C-carb coupling, and the evolution of the Proterozoic carbon cycle: *Geology*, v. 32, p. 129–132, doi: 10.1130/G19939.1.
- Berner, R.A., 2002, Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling: *National Academy of Sciences Proceedings*, v. 99, p. 4172–4177, doi: 10.1073/pnas.032095199.
- Bottrell, S.H., and Newton, R.J., 2006, Reconstruction of changes in global sulfur cycling from marine sulfate isotopes: *Earth-Science Reviews*, v. 75, p. 59–83, doi: 10.1016/j.earscirev.2005.10.004.
- Burns, S.J., and Matter, A., 1993, Carbon isotopic record of the latest Proterozoic from Oman: *Eclogae Geologicae Helveticae*, v. 86, p. 595–607.
- Calver, C.R., 2000, Isotope stratigraphy of the Ediacarian (Neoproterozoic III) of the Adelaide Rift Complex, Australia, and the overprint of water column stratification: *Precambrian Research*, v. 100, p. 121–150, doi: 10.1016/S0301-9268(99)00072-8.
- Canfield, D.E., Poulton, S.W., and Narbonne, G.M., 2007, Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life: *Science*, v. 315, p. 92–95, doi: 10.1126/science.1135013.
- Chameides, W.L., and Perdue, E.M., 1997, Biogeochemical cycles: A computer-interactive study of Earth system science and global change: New York, Oxford University Press, 224 p.
- Condon, D., Zhu, M., Bowring, S., Wang, W., Yang, A., and Jin, Y., 2005, U-Pb ages from the Neoproterozoic Doushantuo Formation, China: *Science*, v. 308, p. 95–98, doi: 10.1126/science.1107765.
- Dickens, G.R., O'Neil, J.R., Rea, D.K., and Owen, R.M., 1995, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene: *Paleoceanography*, v. 10, p. 965–971, doi: 10.1029/95PA02087.
- Fairchild, I.J., and Kennedy, M.J., 2007, Neoproterozoic glaciation in the earth system: *Geological Society of London Journal*, v. 164, p. 895–921, doi: 10.1144/0016-76492006-191.
- Faure, K., and Cole, D., 1999, Geochemical evidence for lacustrine microbial blooms in the vast Permian Main Karoo, Parana, Falkland Islands and Huab basins of southwestern Gondwana: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 152, p. 189–213, doi: 10.1016/S0031-0182(99)00062-0.
- Fike, D.A., Grotzinger, J.P., Pratt, L.M., and Summons, R.E., 2006, Oxidation of the Ediacaran Ocean: *Nature*, v. 444, p. 744–747, doi: 10.1038/nature05345.
- Hansell, D.A., and Carlson, C.A., 1998, Deep-ocean gradients in the concentration of dissolved organic carbon: *Nature*, v. 395, p. 263–266, doi: 10.1038/26200.
- Halverson, G.P., and Hurtgen, M.T., 2007, Ediacaran growth of the marine sulfate reservoir: *Earth and Planetary Science Letters*, v. 263, p. 32–44, doi: 10.1016/j.epsl.2007.08.022.
- Hardie, L.A., 2003, Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas: *Geology*, v. 31, p. 785–788, doi: 10.1130/G19657.1.
- Higgins, J.A., and Schrag, D.P., 2006, Beyond methane: Towards a theory for the Paleocene-Eocene Thermal Maximum: *Earth and Planetary Science Letters*, v. 245, p. 523–537, doi: 10.1016/j.epsl.2006.03.009.
- Hoffman, P.F., Kaufman, A.J., Halverson, G.P., and Schrag, D.P., 1998, A Neoproterozoic snowball Earth: *Science*, v. 281, p. 1342–1346, doi: 10.1126/science.281.5381.1342.
- Holland, H.D., 1978, *The chemistry of the atmosphere and oceans*: New York, Wiley, 351 p.
- Jiang, G., Kaufman, A.J., Christie-Blick, N., Zhang, S., and Wu, H., 2007, Carbon isotope variability across the Ediacaran Yangtze platform in South China: Implications for a large surface-to-deep ocean $\delta^{13}\text{C}$ gradient: *Earth and Planetary Science Letters*, v. 261, p. 303–320, doi: 10.1016/j.epsl.2007.07.009.
- Kah, L.C., Lyons, T.W., and Frank, T.D., 2004, Low marine sulphate and protracted oxygenation of the Proterozoic biosphere: *Nature*, v. 431, p. 834–838, doi: 10.1038/nature02974.
- Kaufman, A.J., Corsetti, F.A., and Varni, M.A., 2007, The effect of rising atmospheric oxygen on carbon and sulfur isotope anomalies in the Neoproterozoic Johnnie Formation, Death Valley, USA: *Chemical Geology*, v. 237, p. 47–63, doi: 10.1016/j.chemgeo.2006.06.023.
- Knauth, L.P., and Kennedy, M.J., 2005, An alternative view of C isotope variations in Neoproterozoic carbonates: *Geological Society of America Abstracts with Programs*, v. 37, no. 7, p. 43.
- 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, doi: 10.1038/321832a0.
- 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, doi: 10.1126/science.273.5274.452.
- Kump, L.R., 1991, Interpreting carbon-isotope excursions: Strangelove oceans: *Geology*, v. 19, p. 299–302, doi: 10.1130/0091-7613(1991)019<0299:ICIESO>2.3.CO;2.
- Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon-isotope excursions: Carbonates and organic matter: *Chemical Geology*, v. 161, p. 181–198, doi: 10.1016/S0009-2541(99)00086-8.
- Land, L.S., 1986, Limestone diagenesis—Some geochemical considerations, *in* Mumpton, F.A., ed., *Studies in diagenesis*: U.S. Geological Survey Bulletin 1578, p. 129–137.
- Le Guerroue, E., Allen, P.A., Cozzi, A., Etienne, J.L., and Fanning, M., 2006, 50 Myr recovery from the largest negative delta C-13 excursion in the Ediacaran ocean: *Terra Nova*, v. 18, p. 147–153, doi: 10.1111/j.1365-3121.2006.00674.x.
- McFadden, K.A., Huang, J., Chu, X., Jiang, G., Kaufman, A.J., Zhou, C., Yuan, X., and Xiao, S., 2008, Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation: *National Academy of Sciences Proceedings*, v. 105, p. 3197–3202, doi: 10.1073/pnas.0708336105.
- Melezhik, V.A., Fallick, A.E., and Pokrovsky, B.G., 2005, Enigmatic nature of thick sedimentary carbonates depleted in C-13 beyond the canonical mantle value: The challenges to our understanding of the terrestrial carbon cycle: *Precambrian Research*, v. 137, p. 131–165, doi: 10.1016/j.precamres.2005.03.010.
- Renne, P.R., Zichao, Z., Richards, M.A., Black, M.T., and Basu, A.R., 1995, Synchrony and causal relations between Permian-Triassic boundary crises and Siberian flood volcanism: *Science*, v. 269, p. 1413–1416, doi: 10.1126/science.269.5229.1413.
- Rothman, D.H., Hayes, J.M., and Summons, R.E., 2003, Dynamics of the Neoproterozoic carbon cycle: *National Academy of Sciences Proceedings*, v. 100, p. 8124–8129, doi: 10.1073/pnas.0832439100.
- Runnegar, B., 1982, Oxygen requirements, biology and phylogenetic significance of the late Precambrian worm Dickinsonia, and the evolution of the burrowing habit: *Alcheringa*, v. 6, p. 223–239.
- Talbot, M.R., 1990, A Review of the paleohydrological interpretations of carbon and oxygen isotopic ratios in primary lacustrine carbonates: *Chemical Geology*, v. 80, p. 261–279, doi: 10.1016/0168-9622(90)90009-2.
- Zeebe, R.E., and Wolf-Gladrow, D., 2001, *CO₂ in seawater: Equilibrium, kinetics, isotopes*: Amsterdam, Elsevier, 345 p.

Manuscript received 18 March 2008

Revised manuscript received 10 July 2008

Manuscript accepted 22 July 2008

Printed in USA