Eutrophication by decoupling of the marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian mass extinction

Adam E. Murphy
Bradley B. Sageman
David J. Hollander
Department of Geological Sciences, Northwestern University, Evanston, Illinois 60208, USA

ABSTRACT

The Late Devonian mass extinction was unusually protracted and ecologically selective, with preferential diversity losses among reef-building organisms and tropical, shallow-water faunas in general. We have investigated the link between the extinction’s unique characteristics and changes in biogeochemical cycling through analyses of the δ¹³C and C:N:P atomic ratios of organic matter buried across the Kellwasser Horizons in western New York State. Each horizon is characterized by (1) a long-term, +4‰–5‰ excursion in δ¹³C, ~3‰ of which occurs within the horizon, and (2) a dramatic increase in the burial ratios of C:N:P, from values of ~100:15:1 to an average of ~5000:170:1. On the basis of these results, we propose that (1) increased efficiency of biolimiting nutrient recycling, resulting from cyclic water column stratification and mixing, promoted eutrophication during Kellwasser deposition in New York, and (2) the isotope excursions represent the composite effect of long-term, global organic C burial, and local changes in photosynthetic C isotope fractionation related to nutrient availability. This eutrophication model forges a mechanistic link between proposed Late Devonian climatic cooling and the selective demise of taxa likely to have been narrowly adapted to oligotrophic conditions.

Keywords: nutrients, C isotopes, organic matter, extinction, Devonian.

INTRODUCTION

The link between changes in biogeochemical cycles and evolutionary biology on geologic time scales may be controlled by changes in the extent to which biogeochemically important elements remain in the short-term, biotically influential part of their global cycles or are “leaked” into their long-term, geologic subcycles. Changes in elemental fluxes between the biosphere and geosphere could fundamentally drive major ecological and evolutionary events by inducing changes in the trophic structures of ecosystems. Valentine (1971) stated that trophic resource supply is the single most important ecological factor in determining marine biotic diversity, and Hallock (1987) further suggested that marine biotic diversity crises may stem from the expansion of eutrophic conditions. The strongest connections between the biotic and abiotic constituents of marine ecosystems are the intertwined biogeochemical cycles of C, N, and P. These elements together form the basis for life-sustaining mass and energy transfer down marine trophic chains. The stratigraphic record of perturbations in these cycles has great potential to provide an important mechanistic link between environmental changes and faunal response, but has not previously been investigated for the Late Devonian mass extinction.

The Late Devonian mass extinction is recognized as one of the five greatest biotic crises of the Phanerozoic (Sepkoski, 1986), with species-level extinction in the marine biosphere estimated to have been as high as 82% (Jablonski, 1991). Although nominally culminating at the Frasnian-Famennian stage boundary, the extinction was unusual in that it spanned as much as 3 m.y. (McGhee, 1996), and carried a distinct ecological signature, including preferential losses of low-latitude, shallow-water organisms, particularly the reef-building corals and stromatoporoids (Copper, 1986; Stearn, 1987) (Fig. 1). Even among brachiopods, however, there was pronounced differential extinction across latitudinal and bathymetric gradients; the extinction of tropical forms was about 300% greater than that among higher latitude taxa, and shallow-water extinctions exceeded those in deeper water by more than 50% (McGhee, 1996).

The causes of the extinction have been extensively, but inconclusively debated; mechanisms advanced include global cooling (McGhee, 1989),
global warming (Thompson and Newton, 1988), sea-level change (Johnson, 1974), oceanic anoxia (e.g., Joachimski and Buggisch, 1993), and bolide impact (McLaren, 1970). Multiple-causality scenarios that integrate several mechanisms through biogeochemical-climatic feedbacks have also been proposed (Buggisch, 1991). Much of the evidence, however, remains equivocal, although the protracted nature and systematic selectivity of the extinction would seem to suggest a dominantly Earth-bound cause.

In this work we test the hypothetical link between changes in trophic resource availability and marine biodiversity by analyzing the stratigraphic records of changes in the C:N:P atomic ratios and $\delta^{13}C$ content of organic matter buried through the intervals containing the lower and upper Kellwasser Horizons in western New York State. These horizons are globally correlated and span the period of maximum Late Devonian biodiversity loss in the Appalachian basin and worldwide (McGhee, 1996). They have been identified in the Upper Devonian strata of western New York by conodont biostratigraphy (Over, 1997) as the Pipe Creek black shale (the lower Kellwasser Horizon) and a thinner black shale (the upper Kellwasser Horizon) containing the Frasnian-Famennian boundary within the Hanover Formation.

METHODS

Samples were cut from a drill core (West Valley NX#1) from western New York (Fig. 1) and crushed in a Spex shatterbox to <200 mesh. Organic C content was measured with standard coulometric techniques (Huffman, 1977) as the difference between total C and inorganic C; the average error was <±1%. Organic C:N ratios were determined chromatographically on a Fisons ISOCHROM-EA elemental analyzer in duplicate; their reproducibilities were ±2%. Extractions of total P and inorganic P (organic P was determined by difference) were performed with the ignition procedure of Aspila et al. (1976). The P concentrations were then measured using spectrophotometry (Murphy and Riley, 1967). Reproducibility between duplicates was ±4%. Sample aliquots for stable C isotope work were treated overnight with excess $\text{HCl}$ and analyzed in duplicate with a VG Optima mass spectrometer following combustion at 1020 °C in a Fisons ISOCHROM-EA elemental analyzer. Average reproducibility was ±0.1‰ relative to the PDB (Peedee belemnite) standard.

RESULTS

Organic petrography of samples from each of the detailed intervals (Fig. 2) revealed no significant (<5%) contribution from terrigenous herbaceous or woody material. Similar petrographic results were obtained in another study, in which a dominantly aquatic source of organic matter was confirmed with molecular source indicators (Murphy et al., 2000). Average vitrinite reflectance values of ~0.7 for these samples indicate a relatively low and consistent degree of thermal maturation, which would not have differentially biased the geochemical record over narrow stratigraphic intervals. Elemental and isotopic changes are therefore interpreted to reflect changes in production and preservation of marine organic matter. To establish an overall context, C isotope analyses were first performed at a stratigraphic resolution of ~5 m. These results (Fig. 1) show long-term +4‰ – 5‰ excursions in the ($\delta^{13}C$)OM across each of the Kellwasser Horizons. Analyses of narrower intervals were carried out at finer stratigraphic resolutions to document the detailed structure of biogeochemical changes (Fig. 2).

The lower Kellwasser interval spans, in stratigraphic ascent, the fine-grained sandstone of the uppermost Nunda Formation, the laminated black shale of the Pipe Creek Formation, and the silty, greenish-gray mudstone of the lowermost Hanover Formation (Figs. 1 and 2A). The upper Kellwasser Horizon, containing the Frasnian-Famennian boundary, is entirely within the Hanover Formation and spans lithologic transitions between silty greenish-gray mudstone and laminated black shale (Figs. 1 and 2B). The Kellwasser Horizons, relative to overlying and underlying strata, are characterized by (1) high organic C content, with average values of 3% – 4% by weight; (2) an approximately five-fold increase in ($\delta^{13}C$)OM values; (3) an increase in (C:P)OM of as much as two orders of magnitude; and (4) an ~3‰ increase in ($\delta^{13}C$)OM.

DISCUSSION

Because the availability of N and P constrain primary productivity in marine environments (e.g., Broecker and Peng, 1982), these nutrients control the health and stability of marine ecosystems. In offshore settings at continental-shelf depth, it is largely the regeneration of N and P from organic matter during decomposition that determines the extent and continuity of their availability for autotrophs (Tyson and Pearson, 1991). The mudy strata in this study were deposited at least 150 km from shore at water depths unlikely to have exceeded ~150 m (Ettensohn, 1985) and are, therefore, likely to contain the record of an ecosystem strongly controlled by the supply of regenerated nutrients. Photosynthesis in marine surface waters proceeds via the following generalization reaction:

$$H_3PO_4 + 16 HNO_3 + 106 CO_2 + 122 H_2O \Rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138 O_2.$$  

This reaction gives the classic Redfield C:N:P atomic ratio of 106:16:1 (Redfield et al., 1963). Aerobic respiration is essentially the reverse reaction, liberating nutrients in the same ratio with which they were assimilated. If organic matter is buried with the same elemental ratios that were
conferred at synthesis, and compositional release is the major source of N and P renewal, then the balance of photosynthesis and respiration in an aquatic ecosystem is maintained and organic C burial is minimized. If, however, changes in the pathway of organic matter decomposition stoichiometrically decouple these elements such that their burial ratios increase relative to the Redfield model, the photosynthesis-respiration loop may become imbalanced, resulting in anomalous biolimiting nutrient availability and elevated organic C burial.

Preferential P regeneration from organic matter under anoxic conditions has been recognized in shelf sediments (Ingall and Jahnke, 1997) and proposed as a mechanism for enhancing marine primary productivity on geologic time scales (Van Capellen and Ingall, 1994), but Falkowski (1997) showed that N may limit productivity even on geologic time scales. Profiles of (C:N)OM of Baltic Sea sediments, however, show a steady increase with depth, suggesting that N is also preferentially regenerated from sedimentary organic matter (Jorgensen, 1983). Because N or P may limit production, the preferential regeneration of both N and P that has been shown to occur during bacterial decomposition under oscillating redox conditions (releasing N during the oxic phase and P during the anoxic phase) (Aller, 1994) is particularly significant, and a sustained decrease in N and P burial should produce a corresponding increase in their water column availability.

The two Kellwasser Horizons show C:N:P increases from Redfield-order values in overlying and underlying strata to an average of ~5000:150:1 within the black shales. We suggest that it is the preferential regeneration of N and P from organic matter by bacteria under variable redox conditions that produced this increase in atomic burial ratios. Variable redox conditions would be expected if the water column underwent cycles of stratification and mixing, perhaps on a seasonal basis. Mixing would also return nutrients to surface waters, enhancing phytoplankton production and establishing internally driven eutrophication through the maintenance of higher steady-state nutrient concentrations (e.g., Kump and Arthur, 1999). This scenario is consistent with suggested Late Devonian climatic cooling (McGhee, 1989), which would have increased seasonality and produced the thermal changes in density contrast between surface and bottom waters necessary for the short-term development of both stratification and mixing of the water column.

Primary increases in (δ¹³C)OM may occur as a result of increased ¹³C content or decreased size of the CO₂(aq) reservoir used during photosynthesis (Hayes, 1993), increased phytoplankton growth rates, which decrease photosynthetic isotope fractionation in the presence of abundant nutrients (Laws et al., 1995), or changes in phytoplanktonic cell geometries, which affect CO₂(aq) assimilation (Popp et al., 1998). The long-term (δ¹³C)OM excursion (Fig. 1) through each of the New York Kellwasser Horizons is consistent with positive ¹³C shifts in the carbonates of the central European horizons (Joachimski and Buggisch, 1993) as well as shifts in Kellwasser organic matter from German sites (Joachimski, 1997) (Fig. 1). Arthur et al. (1988) suggested that increased worldwide burial of ¹²C-rich organic matter during the Cretaceous caused ¹³C-enrichment in the oceanic CO₂(aq) reservoir and a consequent increase in the ¹³C content of marine organic matter and carbonates. The Late Devonian has also been recognized as a time of widespread organic matter burial (Berner and Raiswell, 1983), and although the absence of carbonates in the Appalachian basin precludes their isotopic characterization, this consistency suggests that at least part of our (δ¹³C)OM excursions represents reservoir shifts as in the Cretaceous.

The high-resolution data (Fig. 2) show that ~3‰ of the 4‰–5‰ excursions (Fig. 1) across each of the Kellwasser Horizons occurs within the black shales, suggesting that much of the shift in New York State was relatively rapid, and perhaps more locally controlled. Given the evidence for higher biolimiting nutrient availability during Kellwasser deposition in New York, we propose that decreased isotopic fractionation associated with rapid phytoplankton growth (Laws et al., 1995) may also have contributed to the observed positive shifts. The positive (δ¹³C)OM excursions in New York may, therefore, represent the composite signal of two phenomena: (1) local high productivity, and (2) global organic C burial, with the first being a potentially significant cause of the second.

Two of the most ecologically significant consequences of eutrophication are (1) high surface-water productivity leading to loss of water clarity, and (2) the development of bottom-water anoxia as respiratory demands exceed O₂ supply in the presence of overabundant food (Brasier, 1995). With modern marine reef ecosystems narrowly adapted to clear-water, oligotrophic conditions, the inception of eutrophy would produce substantial ecological diversity loss among reef builders, and other marine taxa (Hallock, 1987; Brasier, 1995). If widespread and prolonged, eutrophication in shallow-marine environments could contribute significantly to mass extinction. This scenario would be especially likely if, as Martin (1995) suggested, shallow-marine ecosystems in the Paleozoic were characterized by superoligotrophic conditions. If this were so, the effects of eutrophication would likely have been more profound in the Devonian than in the modern ocean, because oligotrophically adapted ecosystems would have been highly sensitive to even small increases in nutrient availability and primary productivity. In his summary of the effects of the Late Devonian mass extinction on reef ecosystems, Buggisch (1991) stated that there are two distinct pulses of global reef demise, which may correspond to the Kellwasser Horizons (Fig. 1).

The specific ecological characteristics of the Late Devonian mass extinction, including the preferential extinction of reef builders and of shallow-water tropical faunas in general, seem consistent with episodic and progressively widespread eutrophication. The immediate causes of ecological decimation associated with this process would likely have been the deterioration of surface-water clarity and the development of benthic anoxia, in environments that are normally continuously well oxygenated. The onset of eutrophication is consistent with climatic cooling, as proposed by McGhee (1989). Shallow epeiric seas, such as existed in the Appalachian basin, would have become cooler and more frequently mixed as thermal contrasts between surface and bottom waters became less pronounced, or perhaps only seasonal in duration. This development would account for the differential survival of cooler and deeper water taxa, which would have been better adapted to cooler conditions. They would also have been more tolerant of the oxygen deficiency associated with eutrophication, as the intermittent development of bottom-water anoxia is more common in deeper waters, which are mixed less frequently and which may show elevated benthic O₂ demand due to organic matter concentration by limited clastic influx (e.g., Tyson and Pearson, 1991). The marine transgressions associated with the Kellwasser pulses (Joachimski and Buggisch, 1993) would have facilitated the more pervasive development of eutrophication and seasonal benthic anoxia as more shelf area fell below the depth of the summer thermocline. The shallow-shelf ecosystems, normally accommodating high biotic diversity, would have been decimated by the imposition of environmental stresses previously confined to deeper waters.

CONCLUSIONS

Changes in the elemental and C isotope composition of organic matter buried through the New York Kellwasser Horizons suggest that episodes of eutrophication resulted from decreases in the burial of N and P relative to C. This process increased the size of the biologically active reservoirs of these productivity-limiting nutrients and provided an effective mechanism for sequestering excess C in sedimentary organic matter. The immediate local effect of high nutrient availability was a decrease in photosynthetic C isotope fractionation, while the cumulative effect of worldwide organic C burial was a positive shift in the ¹³C content of marine CO₂(aq), manifested in New York as two positive (δ¹³C)OM excursions. The eutrophication process we suggest provides an immediate, Earth-bound mechanism for biodiversity loss (e.g., Hallock, 1987) that is consistent with the unusual duration, the specific ecological signatures, and one of the leading proposed
ultimate causes of the Late Devonian mass extinction, i.e., climatic cooling (McGhee, 1989). The enhanced rate of organic C burial in the Late Devonian may be a direct result of this process and would have served as a positive feedback to climatic cooling through C transfer from the atmospheric to the sedimentary reservoir.

ACKNOWLEDGMENTS
We acknowledge the financial support of the National Science Foundation (grant EAR-97-25441), the generosity of the New York State Geological Survey for providing core material, and improvements made to this manuscript by the reviews of James Marshall and an anonymous reader. We also sincerely thank Chuck Ver Straeten for help and guidance in core-related labors and in all things Devonian.

REFERENCES CITED

Manuscript received October 12, 1999
Revised manuscript received February 11, 2000
Manuscript accepted February 23, 2000