

## Late-Middle Ordovician environmental change: molecular and isotopic evidence from North America

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We recently reported inorganic and organic carbon-isotope records for Caradocian units that crop out in central Pennsylvania (Patzkowsky *et al.*, 1997). These data reveal a positive 3 ‰ excursion in the  $^{13}\text{C}$  content of micrites ( $\delta^{13}\text{C}_{\text{CARB}}$ ) sampled across the *P. undatus*-*P. tenuis* boundary in Pennsylvania, and show the same magnitude of change observed in micrites by Ludvigson *et al.* (1996) in coeval core samples from Iowa. These findings confirm that the isotopic excursion extended across the North America, in both the Appalachian Basin and the midcontinental region. Both regions also record a positive excursion in the carbon-isotope composition of total organic matter ( $^{13}\text{C}_{\text{TOC}}$ ). Data from the Iowa section show a +6 ‰ excursion during this time (Hatch *et al.*, 1987; Pancost, 1998), whereas  $\delta^{13}\text{C}_{\text{TOC}}$  data from our Pennsylvania samples show only +3.5 ‰ change (Patzkowsky *et al.*, 1997).

We suggested these results indicate major changes in the carbon cycle accompanied by the lithologic changes noted above. In particular, the similarity in the timing and magnitude of the inorganic isotope excursions observed at both locations indicate an increase in organic carbon burial, possibly due to the widespread deposition of black shales in the foreland basin of the Taconic orogeny and elsewhere. The increased burial of organic matter during this time could have been accompanied by a marked decrease in the concentration of carbon dioxide in the ancient atmosphere. If so, it would have led to a decrease in the isotopic fractionation by marine algae, recorded by a decrease in the isotopic difference between inorganic and total organic carbon ( $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{CARB}} - \delta^{13}\text{C}_{\text{TOC}}$ ). In both sections, values for  $\Delta^{13}\text{C}$  decrease beginning at the base of the *P. tenuis* zone (Patzkowsky *et al.*, 1997), but the extent of change differs between the two locations. Specifically, the Iowa section records a slightly larger change (*c.* 4‰ than in Pennsylvania (3‰). Thus  $\Delta^{13}\text{C}$  data suggest isotopic fractionation decreased at both sections, consistent with a drop in global atmospheric  $\text{CO}_2$  levels. However, the regional variation in the magnitude of change, and the coincident lithologic changes suggest the shift in

$\Delta^{13}\text{C}$  records that fractionation was driven, at least in part, by increased availability of nutrients (Laws *et al.*, 1995) and/or possible changes in the dominant phytoplankton taxa due to the pronounced change in oceanographic conditions. In this work, we examined biomarker distributions in the Iowa section, as well as an addition set of core samples from Ontario. Our specific goals were to determine if the inorganic and organic excursions are also recorded in the Canadian site to evaluate better the geographic extent of these signals. We hoped to use molecular evidence to evaluate if changes in either productivity or in the dominant phytoplankters can account for the regional differences in  $\Delta^{13}\text{C}$ . Further, we expected that biomarker distributions could reveal changes in mechanisms underlying the preservation and/or production of organic matter and possibly enhance our understanding of North American Caradocian palaeoceanography.

### Methods

Values for  $\delta^{13}\text{C}$  of total organic carbon were determined using the seal-tube combustion method described by Patzkowsky *et al.* (1997). Likewise, values for the  $\delta^{13}\text{C}$  of whole-rock carbonate were determined using a common acid-bath inlet device and methods described in the same paper. Powered rock samples were Soxhlet extracted using dichloromethane and methanol in a 2:1 azeotrope. The organic extract was separated into saturated hydrocarbons, aromatic hydrocarbons and polar compounds using column chromatography (8 g activated silica gel; elution with 20 mL of hexane, toluene and methanol, respectively). The saturated hydrocarbon fraction was further subdivided into *n*-alkanes and branched and cyclic compounds by adduction with urea. Molecular distributions were determined using a Hewlett-Packard GC/MS (5972MSD; column: DB-1 phase, 60 m  $\times$  0.25 mm i.d.; 0.25  $\mu\text{m}$  phase thickness) and compound-specific carbon-isotope analyses were determined using a Finnigan 252 stable-isotope mass spectro-

meter, a Varian 3500 GC and a micro-volume combustion interface. Specific details of the methods for molecular structure and isotope analyses are described by Pancost (1998).

## Results and discussion

Molecular and petrographic evidence indicates contributions from the organic-walled microfossil, *Gloeocapsamorpha prisca* were abundant in the units from Iowa during the time of high TOC deposition and the inorganic and organic carbon-isotope excursions. Isotopic analyses of compounds which derived in large part from this organism (low molecular-weight n-alkanes, alkylated benzene homologues) indicate the biomass of *G. prisca* was isotopically enriched by as much as 8 ‰ relative to other sources of organic matter in the same interval. The increased abundance of these compounds and other contributions from *G. prisca* during this interval amplified the isotopic excursion recorded by the total organic matter (Pancost, 1998). Further, the isotopic composition of the residual organic materials (proxied using the isotopic composition of octacosane (*n*-C<sub>28</sub>; Pancost, 1998) indicate that the isotopic excursion in  $\delta^{13}\text{C}_{\text{TOC}}$  was +3.5‰ in Iowa; a similar signal was observed using *n*-C<sub>28</sub> from the Ontario samples. When these values are used to estimate  $\Delta^{13}\text{C}$ , a 2‰ decrease is revealed in both sites, a value similar to that observed using bulk organic matter from the Pennsylvania samples.

Other molecular markers indicate strong changes were associated with the lithologic and isotopic events observed in the Iowa samples. In particular, the onset of clastic-rich cool water-type carbonates are coincident with the occurrence of isotopically enriched aryl isoprenoids, which indicate anoxia reached into the photic zone in the ancient environment. However, the overlying unit which contains the greatest concentration of organic carbon (approaching 40%) contains biomarkers that indicate relatively more oxidizing conditions. Specifically, the aryl isoprenoid compounds are either not present or only in trace amounts. Further, the ratio of C<sub>35</sub>/(C<sub>31</sub> + C<sub>32</sub> + C<sub>34</sub> + C<sub>35</sub>) 17 $\alpha$ ,21 $\beta$ (H),22S+R homohopanes is lower in this interval than in the underlying rocks. This ratio is commonly high in rocks deposited under reducing conditions where the conversion of bacteriohopanetetrol to lower molecular-weight homologues is inhibited. The abundance ratio of the acyclic isoprenoids, pristane to phytane, shifts from about 2 in the lower unit to 4.5 in the upper, organic carbon-rich facies. In addition, the abundance of gammacerane normalized to that of 21 $\beta$ (H),22R+22S C<sub>31</sub>

homohopane declines from 0.15 to 0.02 across this interval. Although individual molecular proxies are difficult to interpret in terms of absolute levels of oxygen in the depositional environment, taken together, these data suggest strongly reducing conditions gave way to relatively less reducing conditions across this interval, coincident with the increased contributions from *G. prisca*. Likewise, biomarkers from phytoplankton also show significant change during this time. Specifically, decreasing abundances of C<sub>29</sub> sterane, C<sub>28</sub> triaromatic steroids and methylhopanes suggest that relative contributions from eukaryotic algae and cyanobacteria declined.

## Implications for late-middle Ordovician palaeoceanography

Biomarker and isotopic analyses reveal contributions from *G. prisca* strongly influenced the  $\delta^{13}\text{C}_{\text{TOC}}$  record in the Iowa section, and to a lesser degree, in the Ontario section. When  $\Delta^{13}\text{C}$  is reevaluated using *n*-C<sub>28</sub>, we observe a similar pattern in all three localities, and, specifically, values for  $\Delta^{13}\text{C}$  decline by 2 ‰ across the interval of interest. This indicates that the geographic variations in  $\Delta^{13}\text{C}$  values previously determined from bulk organic carbon were a result of small contributions from *G. prisca* to organic matter in Ontario samples and significant contributions of this microfossil in the samples from Iowa. The similar timing and magnitude of the shift is noteworthy, and a possible cause for this includes widespread increased availability of nutrients in the photic zone, which elevated cellular growth rates and thereby decreased phytoplankton fractionation (Laws *et al.*, 1995). This explanation is fortified by the observed changes in environmental redox: the molecular patterns are consistent with a major reorganization of oceanographic circulation inferred from the lithologic patterns. Alternatively, the widespread and coincident decline in  $\delta^{13}\text{C}$  could reflect a decrease in global atmospheric CO<sub>2</sub> levels, although this would require that levels at this time were significantly lower than those estimated from geochemical models (Patzkowsky *et al.*, 1997) in order for a CO<sub>2</sub> decline to influence algal isotopic fractionation. It is possible that both mechanisms were important at this time, since a drop in CO<sub>2</sub> levels is consistent with both the inorganic isotopic evidence for increased organic carbon burial, and the widespread cooling of ocean waters during this time. The relative importance of nutrient vs. CO<sub>2</sub> changes can be tested by employing isotopic analyses of bulk phases and biomarker and compound-specific isotope analyses in coeval units deposited on other continents.