

Lipid biomarkers record fundamental changes in the microbial community structure of tropical seas during the Late Ordovician Hirnantian glaciation

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ABSTRACT

The Late Ordovician mass extinction was linked to climate cooling and glaciation of Gondwana during the terminal Ordovician Hirnantian Age (444.7–443.4 Ma). Extinction patterns have been well described for many marine taxa, but much less is known about marine microbial communities through this interval. To elucidate the structure of microbial communities in tropical marine basins through the Late Ordovician, we analyzed lipid biomarkers in thermally well preserved strata from the Taconic foreland (Anticosti Island, Canada), the Cincinnati Arch (midwestern United States), and the western continental margin (Vinini Formation, Nevada, United States). Despite clear oceanographic differences, lipid biomarker profiles show similarities between these three localities. Major shifts in biomarker distributions of Anticosti Island and the Vinini Formation, mainly hopane/sterane ratios, record changes in the balance of bacterial versus algal primary production. Bacterial contributions to sedimentary organic matter were highest during warm intervals, both before and after Hirnantian cooling. In particular, 3 β -methylhopanes, likely sourced from aerobic methanotrophic bacteria, occur in high relative abundance (many times the Phanerozoic average) across Laurentia throughout most of the interval studied. 3 β -methylhopane abundances also reveal an overall positive relationship with paleotemperature proxies, implying increased methane cycling during warm intervals. These results suggest that enhanced methane cycling could have provided an important positive feedback on climate during extended intervals of early Paleozoic time.

INTRODUCTION

Near the end of Late Ordovician time, climatic and environmental changes drove one of the most severe mass extinctions of the Phanerozoic Eon. Atmospheric $p\text{CO}_2$ was perhaps 8–16 times preindustrial levels (Berner and Kothavala, 2001), and predominantly warm surface seawater temperatures appear to have characterized much of Ordovician time. This warm climate state was interrupted by Late Ordovician cooling, the magnitude and timing of which remain subject to debate (e.g., Pope and Steffen, 2003; Brenchley et al., 1994; Finnegan et al., 2011). Expansion and retreat of continental ice sheets at high southern latitudes in the Hirnantian stage (ca. 444.68–443.41 Ma) were accompanied by a perturbation to the global carbon cycle manifest as a 3‰–6‰ positive carbon isotope excursion (Brenchley et al., 1994).

Global reconstructions suggest that eustatic sea level was at or near Phanerozoic highstand during much of Late Ordovician time (e.g., Hallam, 1992), and many continents were inundated by epeiric seas. These warm, shallow seas often hosted diverse faunas but may have had idiosyncratic circulation patterns in which oxygen minimum zones (OMZs) would expand to influence large areas of epicontinental seafloor

(Witzke, 1987; Finney et al., 2007; LaPorte et al., 2009). The broad distribution of epeiric sea habitats and their sensitivity to both record bias and environmental forcings (e.g., eustatic sea level, temperature, bottom-water O_2 concentrations) have been implicated in the common-cause driver (Finnegan et al., 2012) and two-phased expression of the Late Ordovician mass extinction (Sheehan, 2001).

Although there has been progress in understanding patterns of faunal extinction through Late Ordovician time, far less is known about the microbial community dynamics that underpinned food webs and catalyzed biogeochemical cycles. Lipid biomarkers track important evolutionary, microbial, and environmental transitions associated with mass extinctions (e.g., Cao et al., 2009), including the response of microbial communities to environmental change during earlier Ordovician events (Pancost et al., 1998). Previous studies have noted that high hopane/sterane ratios and large amounts of methylhopanes are typical of Ordovician oils and source rocks (e.g., Reed et al., 1986; Summons and Jahnke, 1990)—these features have yet to be investigated in stratigraphic framework or integrated with independent proxy information to understand their paleoenvironmental significance.

Here we present a lipid biomarker profile from western Anticosti Island, Quebec, Canada,

to construct a record of marine microbial community structure through the Hirnantian interval in a tropical carbonate ramp setting (see the GSA Data Repository¹). Additional stratigraphic data from the United States midcontinent (Cincinnati region) and from the western margin of Laurentia (Vinini Formation at Vinini Creek, Nevada, United States) were studied to assess the temporal, environmental, and spatial extent of the patterns observed on Anticosti Island (Fig. 1).

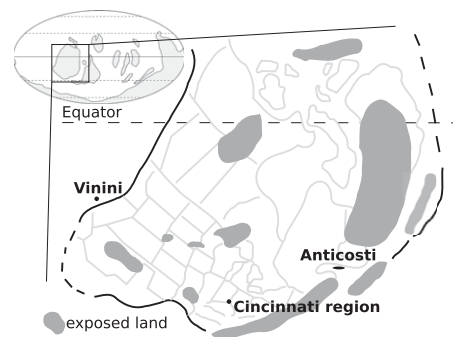


Figure 1. Late Ordovician paleogeography and locations of studied Laurentian sections. Gray lines are approximate modern-day boundaries of states and provinces in the United States and Canada, respectively. Paleogeography modified from Cocks and Torsvik (2002). Laurentian map modified from Raatz and Ludvigson (1996).

Strata exposed in outcrop on Anticosti Island record deposition of a storm-influenced tropical carbonate ramp in the rapidly subsiding Taconic Foreland Basin (Long, 2007), and provide one of the most complete records of the Hirnantian interval on Laurentia. Detailed investigations of Anticosti Island sedimentary geology, biostratigraphy, paleontology (e.g., Long, 2007; Desrochers et al., 2010; Delabroye et al., 2011; Achab et al., 2011; Copper, 2001), and chemostratigraphy (e.g., Long, 1993; Jones et al., 2011; Young

¹GSA Data Repository item 2013031, supplemental information, is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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et al., 2010) provide excellent context for lipid biomarker study. Most importantly, surface outcrops on western Anticosti Island have telinite reflectance values (0.8%–1.0%) indicative of organic thermal maturities in the early to mid oil window (Bertrand, 1990). The Katian-age Whitewater, Liberty, and Waynesville Formations of the Cincinnati region of the United States (e.g., Holland, 1993) were deposited on a shallow mixed carbonate/clastic ramp in an epeiric sea setting. Contemporaneous collection of samples for biomarker analysis with samples for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses on Anticosti Island (Jones et al., 2011) and for clumped isotope paleothermometry on Anticosti Island and in the Cincinnati region (Finnegan et al., 2011) allow direct examination of stratigraphic relationships between lipid biomarker data and these independent proxies. The Katian- to Hirnantian-age Vinini Formation (exposed in the Roberts Mountains of Nevada) was deposited on the passive margin of western Laurentia in a putative upwelling zone (Finney et al., 1999).

Biostratigraphic and chemostratigraphic data presently offer several non-unique correlations between Anticosti Island and the Vinini Formation. Under either correlation scenario—biostratigraphic (Fig. 2) or chemostratigraphic (Fig. DR1 in the Data Repository)—the lipid biomarker results show restructuring of microbial communities and carbon cycling pathways during Late Ordovician cooling.

RESULTS AND DISCUSSION

Microbial Community Structure Prior to Hirnantian Cooling

The ratio of (C_{27} – C_{35}) hopanes to (C_{27} – C_{29}) steranes provides a basic but informative measure of the relative contributions of bacteria and eukaryotes to sedimentary organic matter. Hopanes are the hydrocarbon fossil products of biohopanoids produced by diverse groups of bacteria, while steranes are derived from sterols common to all eukaryotes and absent in all but a very few bacteria (e.g., Summons et al., 2006).

Prior to the positive $\delta^{13}\text{C}$ excursion and glacial maximum, Anticosti- and Cincinnati-region bitumens yield hopane/sterane (H/St) ratios around an average baseline of ~4.0–6.0 (Fig. 2; Table DR1 in the Data Repository), significantly elevated above the Phanerozoic marine average range of 0.5–2.0 (Peters et al., 2003). Such elevated H/St ratios are commonly attributed to high levels of bacterial versus eukaryotic productivity, and have been associated with significant environmental perturbations, such as the Permian-Triassic mass extinction (Cao et al., 2009). Here, the high H/St background values of pre- $\delta^{13}\text{C}$ excursion Anticosti- and Cincinnati-region bitumens (Fig. 2) reflect enhanced bacterial contribution to total primary productivity in warm, oligotrophic marine basins and

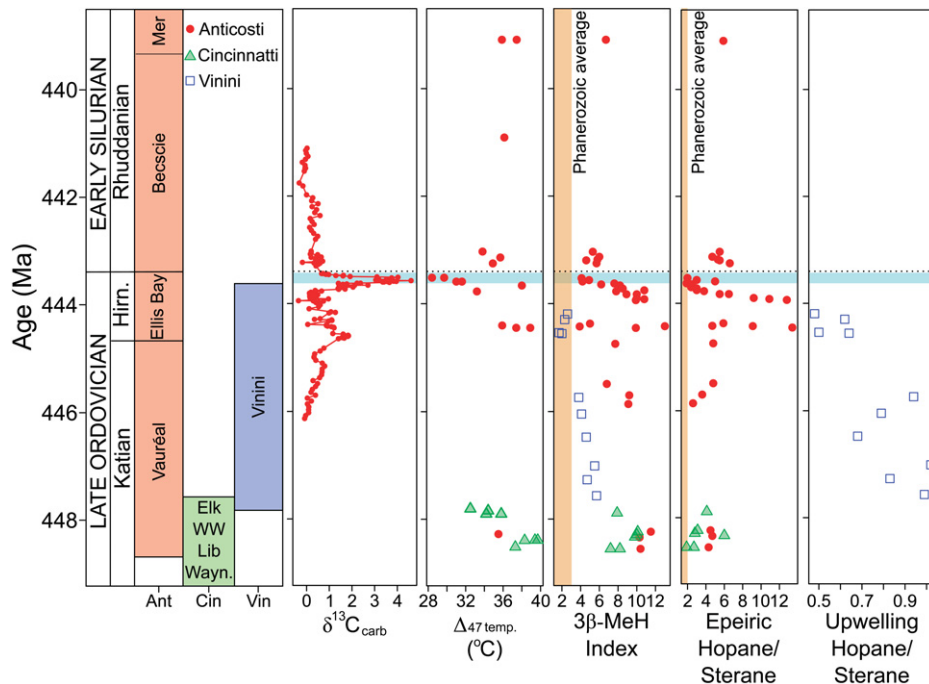


Figure 2. Lipid biomarker stratigraphic records from Western Anticosti Island (Canada), the Cincinnati region of the United States, and the Vinini Formation of Nevada (United States) plotted with a stable carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) profile from Anticosti Island (Jones et al., 2011) and clumped isotope paleothermometry estimates of sea-surface temperatures (Finnegan et al., 2011). Vertical bars indicate the Phanerozoic marine averages for hopane/sterane and 3 β -methylhopane index [C_{31} 3 β -methylhopane / (C_{30} $\alpha\beta$ hopane + C_{31} 3 β -methylhopane) \times 100]. Relationships shown here were primarily based on graptolite (Finney et al., 1999; Sadler et al., 2009; Loydell, 2012), chitinozoan (Delabroye et al., 2011), and brachiopod (Copper, 2001) biostratigraphy. Biomarker stratigraphies correlated on the basis of carbon isotope data are presented in Figures DR1 and DR3 (see footnote 1), but either scheme highlights the same salient relationships between biomarker data and estimates of paleotemperature. Hirn.—Hirnantian; Mer—Merrimack; Elk—Elkhorn; WW—Whitewater; Lib—Liberty; Wayn.—Waynesville; MeH—methylhopane.

epeiric seas, consistent with limitation of algal production due to extensive denitrification in OMZs (LaPorte et al., 2009). Under these conditions, recycled ammonium, rather than nitrate, would have likely provided a primary nitrogen source (e.g., Higgins et al., 2012). Substantially lower H/St ratios from Vinini Formation bitumens indicate larger amounts of algal production along the northwestern margin of Laurentia, consistent with upwelling of nutrient-rich waters driven by western boundary current circulation (Finney et al., 1999).

Anticosti Island bitumens also contain unusually high amounts of a series of C_{30} – C_{36} 3 β -methylhopanes (3-MeH; Fig. 2)—molecules thought to derive primarily from microaerophilic type 1 methanotrophic proteobacteria, as well as some acetic acid bacteria (Farrimond et al., 2004). Ecological considerations likely preclude acetic acid bacteria as significant sources of 3-MeH in marine environments. Methanotroph origins for 3-MeH are further supported by the identification of ^{13}C -depleted hopanes and high 3-MeH indices in some ancient rocks (e.g., Ruble et al., 1994). While 3-MeH can be detected in nearly all rock samples of any age, they are rarely as abundant as observed in our sections.

Results from our Laurentian locations suggest that elevated 3-MeH abundances were a widespread phenomenon in Ordovician seas. 3-MeH indices are 4%–12% (Fig. 2) in Anticosti extracts and are >7.2% in Cincinnati-region bitumens, more than 2000 km away; in the absence of any evidence of seep structures that might indicate localized methane sources, these values signify enhanced methane cycling on a regional scale. Although not as high, Vinini Formation 3-MeH indices (1.7%–5.7%) also reach values well above the Phanerozoic average (1%–3%; Cao et al., 2009), and highlight the widespread nature of the signal (Fig. 2; Table DR1).

We hypothesize that high 3-MeH abundances were a consequence of warm temperatures in Late Ordovician tropical surface seawater (e.g., Finnegan et al., 2011). High temperatures would have decreased the solubility of O_2 in seawater, and perhaps along with more limited supply of electron acceptors like nitrate and sulfate (e.g., Gill et al., 2007; LaPorte et al., 2009; Hammarlund et al., 2012), promoted greater fermentative recycling of organic matter and an enhanced methane cycle (Luo et al., 2010).

Sterane carbon-number distributions provide useful insight into changes in algal primary

production across Phanerozoic time (Grantham and Wakefield, 1988; Schwark and Emt, 2006). The C_{27} – C_{30} steranes in Anticosti Island, Cincinnati region, and Vinini Formation bitumens are dominated by C_{29} isomers (Table DR1), biomarkers characteristic of green algae (Volkman, 1986) and typical of lower Paleozoic marine settings (Grantham and Wakefield, 1988). The small cell size and ability to grow on a variety of nitrogen species possessed by many green algal clades suits them to oligotrophic marine conditions (Parker et al., 2008).

Responses to Hirnantian Cooling

Broad changes in microbial communities and methane cycling took place during Hirnantian time and through the mass extinction intervals (Copper, 2001) and carbon isotope excursion on Anticosti Island (Fig. 2). We observe a large excursion in H/St from an average H/St of ~4 in the Vauréal Formation to an H/St of 12.8 in the Lousy Cove Member of the Ellis Bay Formation, followed by a decline to lower values, all prior to the $\delta^{13}C$ excursion. The initiation of the H/St excursion is poorly constrained due to lack of outcrop, but the decline to H/St values less than those of the Vauréal Formation is clearly defined (Fig. 2; Fig. DR3). The decrease in H/St is not coupled to a significant change in lithofacies, as the trajectory stabilizes before deposition of the basal portion of the bioherm-bearing Laframboise Member of the Ellis Bay Formation and is not accompanied by a trend in either carbonate or organic carbon content (see the Data Repository; Jones et al., 2011). This decline in H/St occurs during a reduction in acritarch diversity (Delabroye et al., 2011), possibly reflecting emergence of a lower-diversity, higher-abundance (bloom-like) algal ecosystem. The lowest H/St values observed on Anticosti Island occur during a glacial maximum recognized from both sedimentary (Desrochers et al., 2010) and paleoclimate proxy data (Finnegan et al., 2011).

Absolute concentrations of steranes, hopanes, and methylhopanes relative to total organic carbon reveal that all compound classes increase in yield during the decline in H/St and prior to the $\delta^{13}C$ excursion (Table DR2 and Fig. DR3). The increase in yields of these cyclic hydrocarbons could reflect release from kerogen during early-oil-window catagenesis (Farrimond et al., 1998) and/or the preferential enrichment of recalcitrant polycyclic alkanes versus linear and branched hydrocarbons during more oxic diagenetic conditions. In either case, the observed rate of change in sterane abundance is significantly higher than for hopanes as H/St declines (Fig. DR3 and Table DR2). Therefore a changing eukaryotic (algal) sterane contribution is the major control on the observed H/St ratios. The relative increase in algal production, and hence lower H/St, during the glacial maximum may have been supported by waning of fixed-

nitrogen limitation due to contraction of denitrifying OMZs (LaPorte et al., 2009).

Sterane distributions generally remain very stable throughout the studied interval and show a C_{29} sterane dominance during both warm and cool intervals (Table DR1). By contrast, microfossil analyses demonstrate that plankton experienced conspicuous extinction over this interval (Delabroye et al., 2011); this apparent discordance is likely due to the differential sensitivity of the morphological and molecular fossil records to taxonomic level and uncertainties in Paleozoic microfossil phylogenetic affinities (Delabroye et al., 2011). The relative stability of sterane carbon-number patterns through our time series, and dominance of C_{29} steranes, reveals that despite clear plankton extinctions, eukaryotic primary production was dominated by green algal clades throughout the glaciation and carbon-cycle perturbation.

The decline in H/St ratio is followed by a decrease in 3-MeH index from 8%–11% to 4%–6% (Fig. 2). This decrease initiates in the Lousy Cove Member, with a drop in the basal Laframboise Member that corresponds to both a significant facies (and eustatic sea level) change (Copper, 2001; Desrochers et al., 2010) and declining sea-surface temperature estimates (Finnegan et al., 2011). A similar, though somewhat smaller, trend in 3-MeH index is observed in the Vinini Formation, which declines from 5.7% to 2.6% (Fig. 2). We interpret this pattern as a reduction in methanogenesis and concomitant methanotrophy due to cooling-driven increases in seawater O_2 concentrations with resultant OMZ contraction (LaPorte et al., 2009) and increased oxidant budgets in shallow sediments. In this fashion, a reduction in methane cycling would have added an important positive feedback on Hirnantian cooling.

Silurian Recovery

Lipid biomarker profiles in the lowermost Silurian Becscie Formation on Anticosti Island reflect a return to microbial communities similar to those preceding the Hirnantian glacial maximum (Fig. 2). Although our Silurian sample coverage is not extensive due to more-prevalent grainstone lithologies, a H/St ratio of 5.6 in a sample from the Aeronion Merrimack Formation suggests that bacteria once again made a significantly higher contribution to primary productivity relative to algae compared with typical Phanerozoic marine rocks and oils. The Silurian bitumens also record high 3-MeH indices, implying that methane cycling was again enhanced during the warm period (Finnegan et al., 2011) that followed the Hirnantian glacial maximum (Fig. 2).

CONCLUSIONS

Biomarker patterns in tropical shallow marine basins through the Hirnantian stage capture a fun-

damental restructuring of marine microbial communities during this interval of climate change. Bacterial primary production was favored during warm, greenhouse climates and low-oxidant, expanded OMZ conditions; eukaryotic production (mainly by green algae) was tied to regions and intervals of cooler ocean temperatures and contracted OMZ conditions. The coupling of lipid biomarkers with independent paleoenvironmental proxies provides a framework for interpreting systematic changes in $\beta\beta$ -methylhopane abundances, a widespread but previously enigmatic characteristic of Ordovician-aged source rocks. High $\beta\beta$ -methylhopane indices imply enhanced methane cycling under warm, lower-oxidant environmental conditions, and outline the existence and mechanics of a positive climate feedback that would have both promoted warm climates, maintaining the expanded OMZs observed in Late Ordovician marine basins, as well as amplified cooling during the Hirnantian glacial maximum.

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