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Molecular indicators of redox and marine photoautotroph composition in the late Middle Ordovician of Iowa, U.S.A.

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Abstract—Saturated and aromatic hydrocarbons were used to evaluate depositional redox conditions and marine photoautotroph contributions to Middle Caradocian strata of the central United States (IA). At the base of the Spechts Ferry Member of the Decorah Formation, ^{13}C-enriched aryl isoprenoids, derivatives of green sulfur bacteria, become abundant, indicating the development of photic-zone anoxia. This is coincident with the disappearance of the organic-walled microfossil *Gloeocapsomorpha prisca* and a marked decrease in the relative abundances of cyanobacterial biomarkers. The development of dysoxic to anoxic conditions and/or associated changes in basin circulation potentially affected the distributions and abundances of these organisms. In the overlying Guttenberg Member, *G. prisca*-derived organic matter becomes dominant, but relative cyanobacteria abundances remain low. In addition, the percentage total organic carbon is greater than 20%, even though selected biomarker ratios (pristane/phytane ratios greater than 3, and homohopane indices less than 0.5) and the presence of bioturbation indicate that bottom waters were oxygenated. It is suggested that deposition of *G. prisca* affected both organic matter preservation and depositional redox conditions. Observed variations in redox indicators and marine photoautotroph contributions are associated with changes in siliciclastic deposition, reported macrofauna turnover and with evidence for oceanic cooling and a change in circulation patterns documented in the eastern United States.

Key words—biomarkers, *Gloeocapsomorpha prisca*, methylhopanes, cyanobacteria, aryl isoprenoids, Ordovician, green sulfur bacteria, carbon-isotope excursion

INTRODUCTION

The late Middle Ordovician (*P. undatus* zone) of the eastern United States contains significant evidence for macrofaunal turnover (Patzkowsky and Holland, 1993, 1996, 1997; Frey, 1995). These authors suggested that a tectonically driven change in basin circulation and/or increased upwelling caused cool, oxygen-poor waters to spread through the Taconic foreland basin, resulting in the extinction of fauna in the eastern United States (Patzkowsky and Holland, 1996). Evidence for profound variation in basin circulation in this interval includes a transition from tropical- to temperate-type carbonates, a decline in the abundances of calcareous green algae and cyanobacterial mats and an increase in phosphorite deposits (Patzkowsky and Holland, 1993; Holland and Patzkowsky, 1996, 1997). A pronounced positive carbon-isotope excursion in both carbonate (~3‰) and bulk organic matter (3–7‰) spans the interval of faunal change (Hatch *et al.*, 1987; Ludvigson *et al.*, 1996; Patzkowsky *et al.*, 1997) and offers further evidence of regional and possibly global changes in carbon cycling.

During the same interval, a significant local extinction occurs in strata from the upper Mississippi valley (Sloan, 1987, Sloan and Alexander, 1997), suggesting that oceanographic processes similar to those of the eastern United States affected biota in the central United States. Indeed, in correlative units in eastern Wisconson Saylor *et al.* (1997) find a lithofacies shift to cool-water-type carbonates similar to those observed in the eastern U.S. However, Sloan (1987) invoked deposition of a widespread volcanic ash (the Deicke K-bentonite) rather than paleoceanographic processes as the cause of extinction.

Here, we use molecular indicators to examine the timing and magnitude of redox variations related to these oceanographic changes in a single continuous core from Iowa.

Specifically, we evaluate whether redox variations are associated with published evidence for bioturba-

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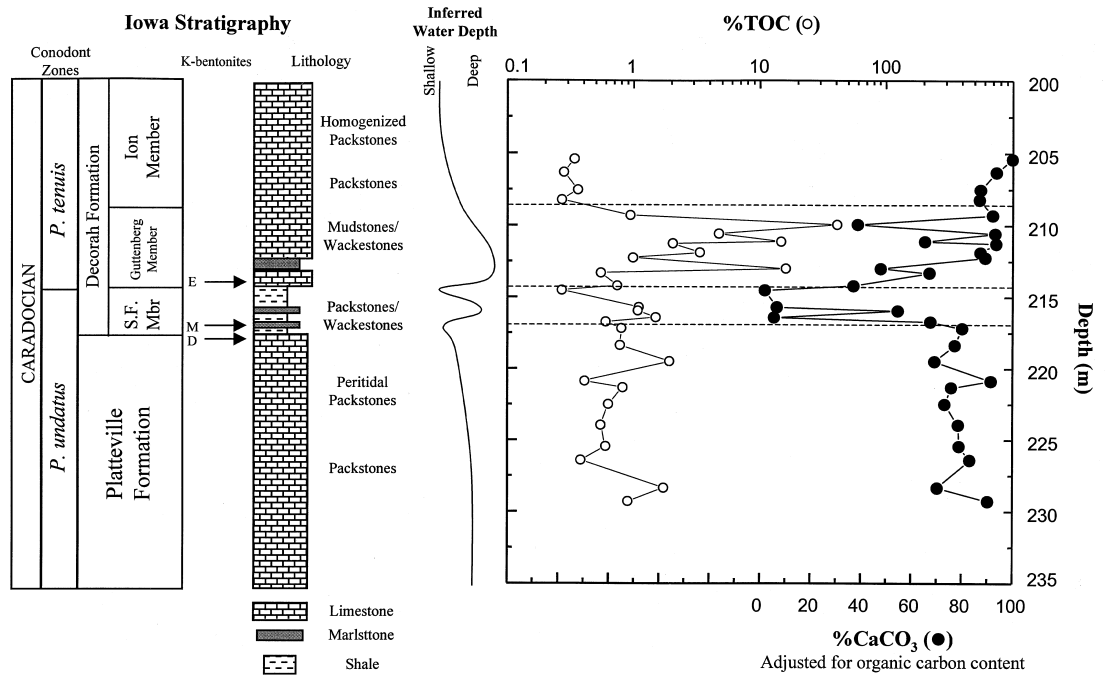

Fig. 1. Lithostratigraphy of the Platteville and Decorah Formations, Cominco SS-9 core, Millbrook Farms, Jackson, Co., IA. *P. undatus–P. tenuis* boundary based upon Sweet (1984), and references for inferred water depth are given in the text. Note the log-scale used to plot %TOC. Arrows denote in stratigraphic succession upsection the Deicke (D), Millbrig (M) and Elkport (E) K-bentonites, and horizontal dashed lines represent lithostratigraphic boundaries. S.F. Mbr. means Spechts Ferry Member.

tion, lithofacies variations and inferred water depth. A second goal is to evaluate changes in the organic materials derived from photosynthetic organisms using molecular markers and to determine if those changes track sedimentological evidence for redox or water-depth variations. In particular, the contributions from cyanobacteria, anoxygenic photosynthetic bacteria, and *Gloeocapsomorpha prisca* are evaluated using lipid biomarkers. To achieve these goals, we performed molecular and isotopic analyses on saturated and aromatic hydrocarbons isolated from a continuous core of the upper Platteville and Decorah Formations.

ANALYTICAL TECHNIQUES

Sample preparation

Approximately 50 g of rock were collected from thirty horizons in the Cominco SS-9 core from Millbrook Farms in Jackson County, IA (currently archived at the Iowa State Geological Survey). The sampled interval spans the upper Platteville Formation through the lower Ion Member of the Decorah Formation (Fig. 1). Samples were gently washed with methanol to remove handling and storage contamination, ground with mortar and pestle and powdered with a ball mill device. The powdered samples were Soxhlet extracted with a 2:1 dichloromethane:methanol azeotrope for at least 24 h. The total organic extract was separated by column chromatography into saturated hydrocarbon, aromatic hydrocarbon and polar fractions by passing sequentially 20 ml of hexane, toluene and methanol through 8 g of activated silica gel.

The hydrocarbon fraction was further divided into *n*-alkanes and branched/cyclic hydrocarbons by adduction with urea (Michalczyk, 1985). Samples were dissolved in methanol saturated with urea, pentane and acetone (200 μl each) and refrigerated for 30 min. Samples were evaporated under N_2 and the resulting urea crystals were extracted with hexane to yield branched/cyclic fractions. Urea crystals were dissolved by addition of 500 μl of extracted H_2O and the solution was extracted with hexane to yield the *n*-alkane fraction.

Isotope-ratio-monitoring gas chromatography–mass spectrometry (irmGC–MS)

Carbon-isotopic ratios of individual compounds were determined by irmGC–MS (Merritt *et al.*, 1995). Samples passed through a DB-1 methylsilicone phase stationary column (60 m length, 0.32 mm inner diameter and 0.25 μm film thickness) programmed from 60°C to 140°C at 10°C/min and to 320°C (held for 15 min) at 2°C/min. Compounds eluting from the GC were converted to CO_2 by combustion at 1000°C over nickel and platinum with a trace O_2 stream. Water was removed by a selectively permeable membrane, flushed by an external helium stream. Isotopic compositions were

Table 1. Biomarker redox indicators in the SS-9 core

Unit	Depth (ft)	%$CaCO_3^{\dagger}$	%TOC	Pr/Ph ratio	Homohopane Index	Gammacerane index
Ion Member	205.4	99.9	0.34	0.83	0.073	0.03
	206.3	93.6	0.28	1.07	0.090	0.03
	207.5	87.4	0.36	1.20	0.102	0.03
	208.2	87.0	0.27	1.57	0.103	0.03
Guttenberg Member	209.3	92.2	0.94	1.51	0.067	0.03
	209.9	38.8	40.83	3.29	0.059	0.02
	210.6	93.1	4.75	2.26	0.070	0.03
	211.1	65.5	14.65	3.28	0.050	0.02
	211.3	93.4	2.05	1.99	0.053	0.02
	211.9	87.4	3.36	–	–	–
	212.2	89.2	0.99	1.42	0.053	0.02
	213.0	48.0	15.99	2.77	0.056	0.02
	213.3	67.3	0.55	2.09	0.104	0.02
	214.2	37.1	0.74	1.46	0.100	0.05
Spechts Ferry Member	214.5	2.0	0.27	1.46	0.080	0.05
	215.7	6.7	1.10	2.20	0.099	0.04
	216.0	54.8	1.08	–	–	–
	216.4	5.6	1.50	1.83	–	0.09
	216.7	67.6	0.60	1.37	0.104	0.15
Platteville Formation	217.2	80.2	0.80	–	0.099	0.03
	218.4	77.3	0.78	1.65	0.095	0.02
	219.5	69.3	1.93	1.80	0.081	0.03
	220.9	91.6	0.41	–	0.090	0.02
	221.3	75.9	0.82	1.83	0.081	0.01
	222.5	73.3	0.63	1.89	0.080	0.02
	224.0	78.7	0.55	1.70	0.082	0.02
	225.5	79.1	0.60	1.60	0.079	0.02
	226.4	83.2	0.38	1.39	0.072	0.02
	228.3	70.4	1.73	1.99	0.068	0.03
	229.3	90.2	0.90	1.42	0.065	0.02

†%$CaCO_3$ has been adjusted for organic content as described in the methods section.

measured on a stable-isotope mass spectrometer (Finnigan MAT 252), and δ-values relative to PDB were calculated by comparison against a calibrated CO_2 gas introduced by a second capillary: $\delta^{13}C = (^{13}R_{SA}/^{13}R_{PDB}\text{-}1) \times 10^3$, where $^{13}R_{SA}$ and $^{13}R_{PDB}$ represent the $^{13}C/^{12}C$ abundance ratio for the sample and the PDB standard, respectively (Ricci *et al.*, 1994). The working standard was calibrated against NBS-19. Analytical precision, determined using co-injected standards, is $\pm 0.5‰$ for cyclic compounds and $\pm 0.6‰$ for aryl isoprenoids.

Gas chromatography–mass spectrometry (GC–MS)

Samples were injected via autosampler into a Hewlett Packard 6890 gas chromatograph and passed through a DB-1 column with a methylsilicone-phase (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness) programmed from 35°C (2 min) to 310°C (held at 70.5 min) at 2°C/min. Eluting compounds passed into a Hewlett Packard 5972MSD that operated in selective ion monitoring (SIM) mode. Several additional full scan analyses were made to confirm compound identifications. Abundances were calculated by comparison to internal standards, *o*-terphenyl (aromatic fractions) and 5β-cholane (saturate fractions). Response factors of aryl isoprenoids and methylhopanes were not determined; reported abundances are normalized to the internal standard and to the weight of rock extracted.

Total organic carbon (%TOC) and whole rock carbonate analyses

CO_2 from carbonate and total carbon was liberated by immersion in phosphoric acid and combustion at 1200°C, respectively, and quantified by coulometry. Percentage total organic carbon (%TOC) was determined by difference. Based upon analysis of standards, error is typically less than 5% of the measured value. $CaCO_3$ contents in Table 1 and Fig. 1 were adjusted to show $CaCO_3$ contents independent of TOC variations: $\%CaCO_{3reported} = 100 \times \%CaCO_{3measured}/(100\% - \%TOC)$.

Carbonate $\delta^{13}C$ values were determined by dissolving samples in phosphoric acid and analyzing liberated CO_2 on a Finnigan MAT 252 stable isotope mass spectrometer. Prior to measurement, samples were heated for 1 h under vacuum at 380°C to remove volatile organic material. TOC $\delta^{13}C$ values were determined by heating decalcified samples at 800°C with excess cupric oxide for 5 h; liberated

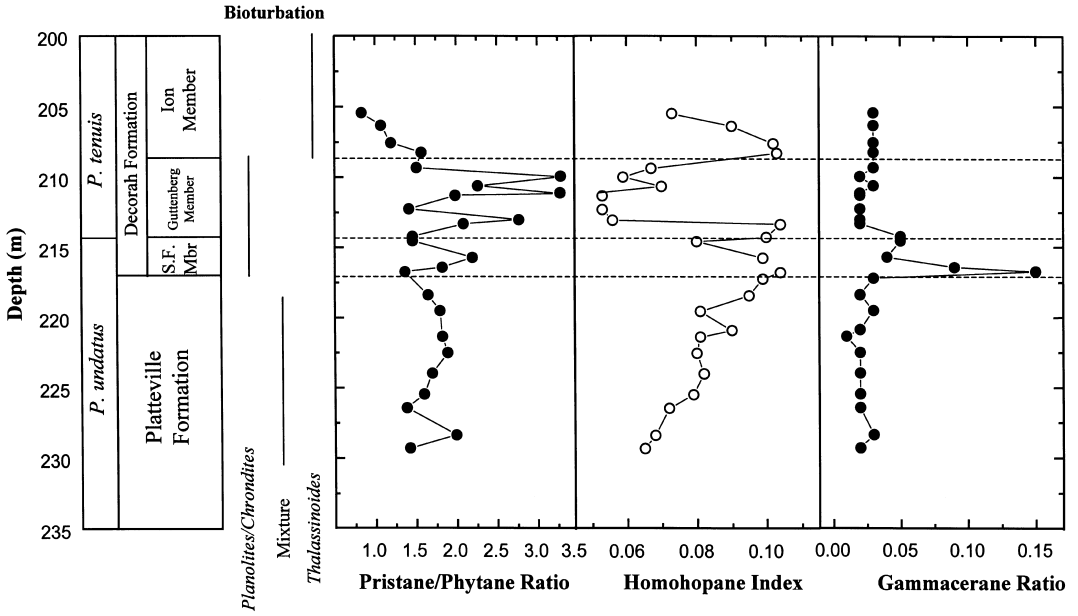

Fig. 2. Biomarker proxies for redox conditions. Pristane/phytane ratios, homohopane index and gammacerane index (the ratio of gammacerane to [22*S* + 22*R*)-17α(H),21β(H)-29-homohopane] are shown. Vertical lines represent dominant ichnofacies in a given horizon. Horizontal dashed lines represent lithostratigraphic boundaries.

CO_2 was cryogenically purified in a glass vacuum system and introduced to the stable-isotope mass spectrometer via the dual-inlet system.

Petrographic analyses

We examined bed-parallel and bed-perpendicular fragments from all samples for dominant macerals (excepting shales 214.5, 215.7 and 216.4 m). Rock fragments were suspended in resin and polished using successively 400 grit paper, 600 grit paper, 0.3 μm alumina on Texmet cloth and 0.05 μm alumina. Samples were viewed and examined under white light and using fluorescence emission upon blue-light excitation (Davis *et al.*, 1990).

LITHOLOGY AND PALEOBATHYMETRY

The Platteville Formation is predominantly carbonate mudstone with interbedded fossiliferous packstone lenses. These lenses are similar to those observed in overlying formations, that have been attributed to tempestites (Ludvigson *et al.*, 1996). In general, the Platteville Formation is bioturbated and contains abundant *Planolites*, *Chondrites* and *Thalassinoides* burrows (Byers, 1983; Dokken, 1987). $CaCO_3$ contents range from 70 to 90% in the Platteville Formation (Table 1 and Fig. 1), and TOC contents are generally less than 1.0%. Although interrupted by smaller-scale cycles, the upper Platteville Formation (McGregor Member) represents a shallowing-upward interval, shifting from open marine limestones at its base to peritidal carbonates in the uppermost units (Witzke and Bunker, 1996). The extinction described by Sloan (1987) and Sloan and Alexander (1997) occurs at the Deicke K-bentonite, which in the SS-9 core, is located in the uppermost meter of the Platteville Formation (D. Kolata, pers. comm.).

The Spechts Ferry Member of the Decorah Formation is a gray–green shale with minor interbeds of siliceous limestones (predominantly wackestones to packstones). The Spechts Ferry Member is mildly bioturbated by *Chondrites* and *Planolites* burrows in some intervals (Ludvigson *et al.*, 1996). The packstone intervals contain abundant bryozoan, brachiopod and echinoderm fossil debris and have been interpreted as proximal tempestites. $CaCO_3$ contents are low, even in the packstone beds, but the abundance and thickness of carbonate beds increase through the Spechts Ferry Member and the lowermost Guttenberg Member. %TOC values range from 0.3 to 1.6%. The Spechts Ferry Member represents a transgressive–regressive cycle (Witzke and Bunker, 1996), and tempestite thicknesses and abundances suggest shallow, subtidal depositional conditions (ca. 20–40 m water-depth; Ludvigson *et al.*, 1996).

The Guttenberg Member is composed predominantly of carbonate mudstones with occasional skeletal wackestone and packstone lenses interpreted by Ludvigson *et al.* (1996) as tempestite beds. In general, $CaCO_3$ contents increase from ca. 40% at the Spechts Ferry–Guttenberg boundary to values greater than 80% in the upper Guttenberg Member. In addition, thin (ca. 1 cm), brown-colored shale partings are common and associated with high

TOC contents (up to 50%; Hatch *et al*., 1987). These organic-rich layers are associated with the presence of the organic-walled microfossil *G. prisca* (Jacobson *et al*., 1988). Values for %TOC in the Guttenberg Member are highly variable and range from 0.5 to 40% in our samples. Like the Spechts Ferry, bioturbation consists primarily of *Chondrites* and *Planolites* burrows (Ludvigson *et al*., 1996). Witzke and Bunker (1996) also interpreted the Guttenberg Member as a transgressive–regressive cycle, and Ludvigson *et al*. (1996) argued that the water depths ranged from 40 to 100 m during deposition of this interval.

The Ion Member of the Decorah Formation is composed of skeletal wackestones and packstones, and $CaCO_3$ contents range from 87 to 99%. Correspondingly, TOC contents are low, ranging from 0.25 to 0.35%. In the upper portion of the section (above 207 m), individual packstone beds are not distinguishable, which Ludvigson *et al*. (1996) attributed to homogenization by *Thalassinoides* burrows. Ludvigson *et al*. (1996) suggest that water depths continued to decrease through deposition of the Ion Member and that sediments were deposited above storm wave base (*ca*. 20 to 40 m water depth).

BIOMARKER REDOX INDICATORS

Many biomarker redox proxies are affected by thermal maturity and clay contents of the mineral matrix (Peters and Moldowan, 1993). Because sampling is confined to a narrow stratigraphic interval from a single core, maturity variations are unlikely to influence biomarker proxies. However, the relative abundance of clay varies significantly in this interval (the noncarbonate fractions are composed predominantly of illite and kaolinite clays; Ludvigson *et al*., 1996), and some molecular transformations were likely catalyzed by clays, such that they cannot serve as accurate redox indicators. Specifically, we exclude discussion and interpretation of diasterane/(diasterane + regular sterane) and C_{30} diahopane/C_{29}Ts ratios.

Pristane/phytane ratio

The pristane/phytane ratio can be used as an indicator of redox conditions in ancient sediments (Didyk *et al*., 1978; Hughes *et al*., 1995). Values above 3.0 are considered to indicate dysoxic to oxic sediments, values below 1.0 indicate anoxic conditions, and values between 1.0 and 3.0 suggest intermediate conditions. More recently, ten Haven *et al*. (1987) noted that the utility of this indicator is compromised by several factors, and challenged the assumption that both compounds are derived from a common source. In particular, there is strong evidence which suggests the phytol moiety of eukaryotic chlorophylls is not the sole source for both compounds in some sediments (Chappe *et al*., 1982; Goosens *et al*., 1984; Freeman *et al*., 1990). However, in our samples, pristane and phytane have similar carbon-isotope compositions, and this is consistent with their derivation from a single source (Hayes *et al*., 1990). Although we cannot exclude multiple sources, pristane/phytane ratios are reasonably consistent with other molecular redox indicators (Fig. 2).

Ratios range from ~1.1 to 2 in the Platteville Formation and the Spechts Ferry Member of the Decorah Formation (Fig. 2). A trend towards lower values occurs in the uppermost Platteville and terminates as a minimum in the lower Spechts Ferry Member, but in general, differences between the two units are small. Ratios are variable and higher in the Guttenberg Member, with highest values of approximately 3.4. In the Ion Member, pristane/phytane ratios are again low, with the lowest value in the section (ca. 0.8) observed in the uppermost sample.

Homohopane index

The homohopane index is defined as the ratio of C_{35}/C_{31-35} homohopanes (17α(H),21β(H), 22*S* + 22*R*), and is usually high in sulfide-rich and anoxic sediments, where conversion of bacteriohopanetetrol to lower molecular-weight homologues is inhibited (Peters and Moldowan, 1991). Recent work indicates that reaction of reduced sulfur with bacteriohopanetetrol could also be an important control on the preservation of higher molecular-weight homohopane homologues (Sinninghe Damsté *et al*., 1995a). For a suite of bitumens and oils Peters and Moldowan (1991) reported values less than 0.06 when bottom-waters and/or sediments contain oxygen and greater than 0.1 when bottom-waters and/or sediments are anoxic. However, thermal maturation and organic matter sources influence the index and ranges should be used as qualitative rather than absolute guides to interpretation.

In our samples, the lowest values (0.05–0.06) are observed in rocks from the middle and upper Guttenberg Member (Fig. 2). Samples from the uppermost Platteville Formation and Spechts Ferry Member yielded the highest homohopane indices (up to 0.12). In general homohopane indices increase through the Platteville Formation and achieve maximum values in the Spechts Ferry Member. The transition from relatively high values in the Spechts Ferry to lower values in the upper Guttenberg is sharp and occurs approximately 1.5 m above the Elkport K-bentonite, located at or near the inferred base of the Guttenberg (Kolata *et al*., 1996).

Gammacerane

Gammacerane is derived from tetrahymanol (ten Haven *et al*., 1989), a compound synthesized by

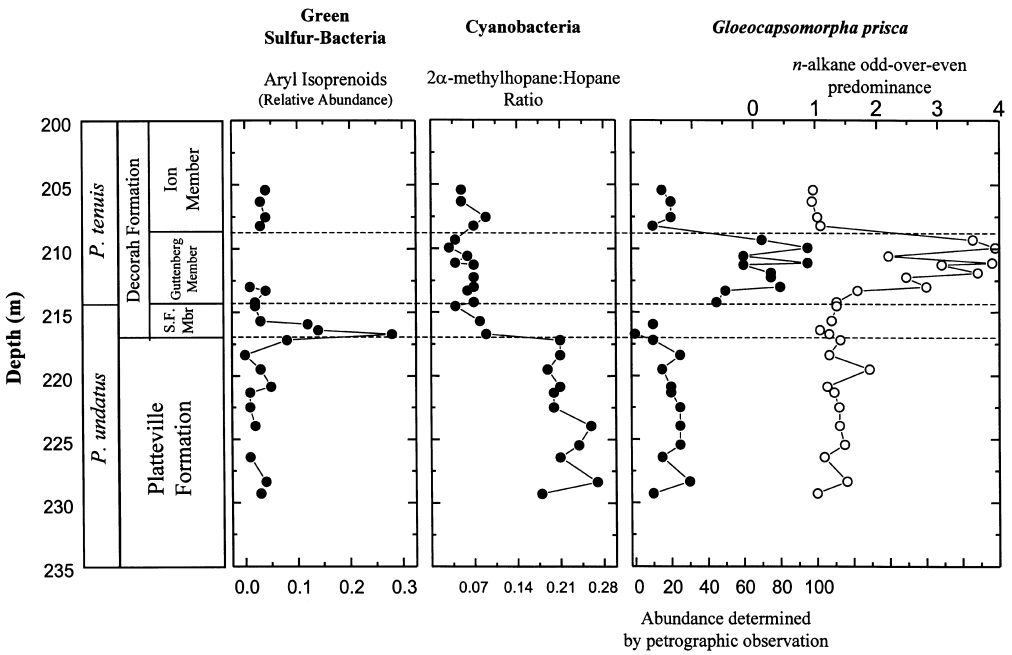

Fig. 3. Relative abundances of aryl isoprenoids ($C_{18}+C_{19}$), 2α(CH_3)-hopanes and *G. prisca*. Aryl isoprenoid abundances were determined as described in the methods section and normalized to %TOC. 2α(CH_3)-hopanes are reported as the abundances of (22*S* + 22*R*)-2α(CH_3),17α(H),21β(H)-29-homohopanes (*m*/*z* 205) normalized to the abundances of (22*S* + 22*R*)-17α(H),21β(H)-29-homohopanes (*m*/*z* 191). *G. prisca* percent abundances were determined by petrographic observations and proxied by the ratio of odd-over-even low molecular-weight *n*-alkanes [$(C_{17}+C_{19})/2 \times C_{18}$]. Horizontal dashed lines represent lithostratigraphic boundaries.

heterotrophic ciliates found at the chemocline in modern environments (Fenchel *et al.*, 1990, Zubkov *et al.*, 1992). Relatively high gammacerane abundances are typically interpreted as evidence of a stratified, anoxic water column (Schoell *et al.*, 1994; Sinninghe Damsté *et al.*, 1995b; Kenig *et al.*, 1995; Collister and Wavrek, 1996), which can be associated with hypersaline conditions. In our samples, gammacerane indices (the ratio of gammacerane to 17α(H),21β(H), 22*S* + 22*R* C_{31} homohopane) are low through most of the section and slightly higher in samples from the Spechts Ferry Member (Fig. 2). In two Spechts Ferry samples gammacerane indices are approximately 6× greater than that observed elsewhere in this interval.

MOLECULAR INDICATORS OF ORGANIC MATTER SOURCES

Green sulfur bacteria

Aryl isoprenoids are presumed degradation products of isorenieratene (Summons and Powell, 1987), a diaromatic carotenoid present in green sulfur bacteria (*Chlorobiaceae*, Liaaen-Jensen, 1978). Recent work indicates that in some depositional environments, aromatization of β-carotane can also be a significant source of aryl isoprenoids (Koopmans *et al.*, 1996b). Compound-specific isotope analyses are therefore required to verify green sulfur bacteria as the exclusive source of aryl isoprenoids, since these organisms assimilate carbon via the reverse tricarboxylic acid cycle and are typically ^{13}C-enriched relative to oxygenic phytoplankton (Quandt *et al.*, 1977; Sirevag *et al.*, 1977).

Aryl isoprenoids are present in at least trace abundances through this section [Fig. 3 and 4(a)], except in the Guttenberg Member where they were not detected. They are most abundant in samples from the Spechts Ferry Member, and we determined their $\delta^{13}C$ values in samples from this interval. The $\delta^{13}C$ values of the C_{16} aryl isoprenoid are −20 and −18‰ in samples 216.7 and 216.4 m, respectively. These values are enriched in ^{13}C by approximately 10‰ relative to pristane and phytane, and are consistent with a green sulfur bacteria source. Further, isorenieratane and multiple polyaromatic degradation products that can serve as indicators of green sulfur bacterial contributions (Koopmans *et al.*, 1996a) are present in samples from the Spechts Ferry Member [Fig. 4(a) and (b)]. Among the compounds observed are C_{32} and C_{33} diaryl isoprenoids and diaryl isoprenoids with either one additional benzene ring, two additional benzene rings, or a napthalene moiety (Koopmans *et al.*, 1996a). In contrast, in the Platteville Formation and the Ion Member, such compounds were not observed, and concentrations of aryl isoprenoids are approximately 5× lower than in the Spechts

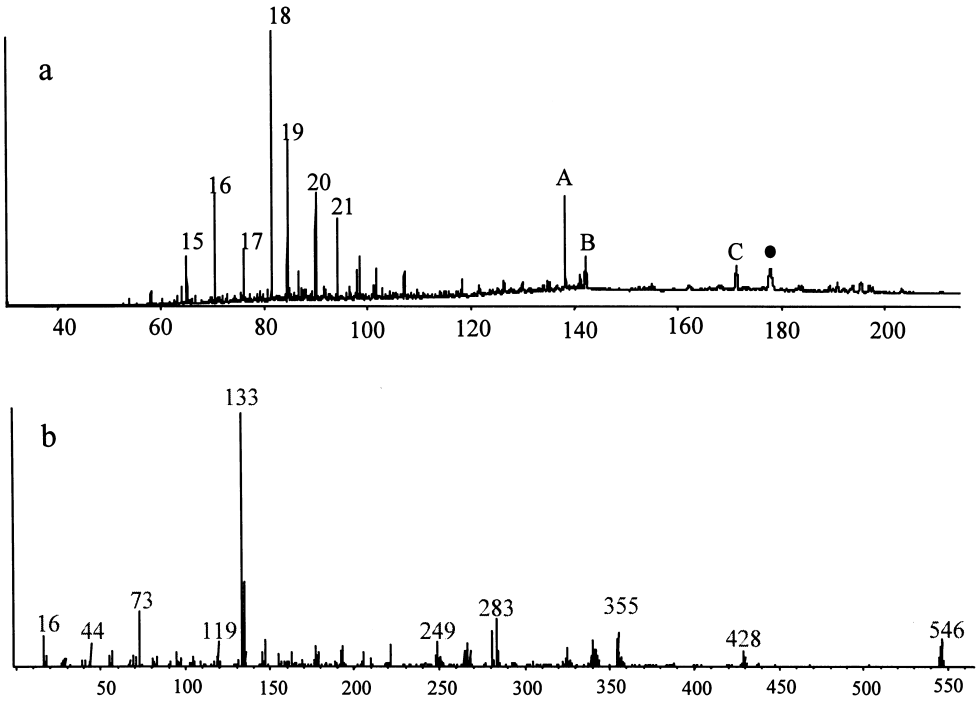

Fig. 4. Mass chromatogram (a) of m/z 133 showing homologous series of aryl isoprenoids (numbers, representing the number of carbon atoms in individual homologues) and diaryl isoprenoids. A indicates a C_{32} diaryl isoprenoid with an extra benzene moiety, B a C_{33} diaryl isoprenoid, C a C_{40} diaryl isoprenoid with an extra benzene moiety and (●) indicates isorenieratane for which the mass spectrum is shown in (b).

Ferry Member and are too low for isotopic analysis.

Cyanobacteria

Samples from the SS-9 core contain abundant homologous series of A-ring methylated hopanes (Fig. 5, Table 3). Methylhopanes can be derived from a variety of prokaryotes, including cyanobacteria, methylotrophic bacteria and acetobacteria (Zundel and Rohmer, 1985; Bisseret *et al.*, 1985). Carbon-isotopic evidence suggests that $3\beta(CH_3)$-hopanes in the Green River shale derive primarily from methylotrophic bacteria (Collister *et al.*, 1992). Culture studies strongly suggest that cyanobacteria are an important, if not primary, source of $2\alpha(CH_3)$-hopanes to sediments (Summons *et al.*, 1996). Based on retention times and mass spectra, we identified homologous series of both $2\alpha(CH_3)$- and $3\beta(CH_3)$-hopanes (Summons and Jahnke, 1990, 1992; Fig. 5).

Methylotrophic bacteria primarily utilize methane as a carbon source and are commonly associated with redox boundaries in aquatic depositional environments. In ancient sediments, their contributions can be recognized by abundant ^{13}C-depleted hopanes (–40– – 85‰; Freeman *et al.*, 1990; Collister *et al.*, 1992; Summons *et al.*, 1994; Schoell *et al.*, 1994). Here, abundances of methylhopanes do not correlate with redox variations inferred from either lithologic or biomarker indicators, and $\delta^{13}C$ values of all hopanes range from −32 to −28‰ (unpublished data) which are similar to values for plankton-derived compounds such as pristane and phytane. We conclude that the abundant methylhopanes in these samples are not derived from methylotrophic bacteria and derive primarily from cyanobacterial sources.

22*S* and 22*R* $2\alpha(CH_3)$-29-homohopane abundances normalized to 22*S* + 22*R* 17α(H),21β(H)-29-homohopane abundances (Fig. 3, Table 2) decrease by a factor of four across the Platteville–Spechts Ferry boundary. 22*S* and 22*R* $2\alpha(CH_3)$-29-homohopane concentrations normalized to TOC contents (data not shown) exhibit similar behavior, suggesting the shift records a decrease in cyanobacterial contributions rather than changes in methylhopane preservation. This shift is coincident with the increase in aryl isoprenoid abundances and inferred development of photic-zone anoxia, a change from calcareous to siliciclastic lithology, and an inferred increase in water depth.

Gloeocapsomorpha prisca

Petrographic and geochemical analyses reveal that *G. prisca* is present throughout the sampled interval (see also Jacobson *et al.*, 1988). *G. prisca* fossils observed in these samples are the "open (phenol-poor)" morphotype described by Derenne

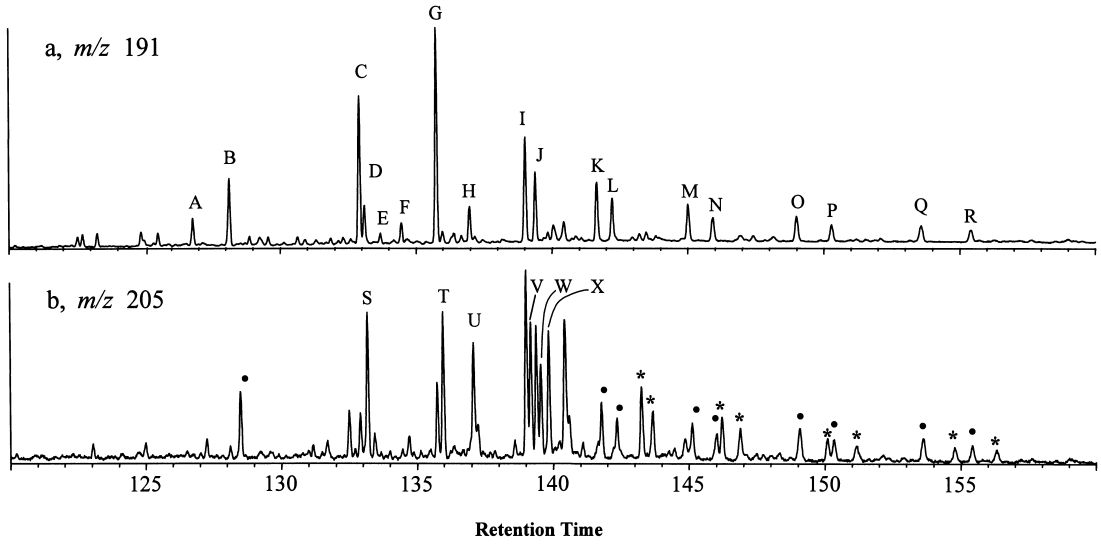

Fig. 5. Mass chromatograms of m/z 191 and 205 showing hopane and methylhopane distribution, respectively, in a sample from the uppermost Platteville (697.2′). Hopane and methylhopane identifications are provided in Table 3. In addition, (●)s and (*)s denote tentatively identified homologous series of $2\alpha(CH_3)$-hopanes and $3\beta(CH_3)$-hopanes, respectively.

Table 2. Compound abundances in the SS-9 core

Unit	Depth (ft)	Aryl isoprenoid abundance[†]	Methylhopane abundance[†]	*G. prisca* abundance (%)[‡]	*n*-Alkane distribution[§]
Ion Member	205.4	0.04	0.05	15	0.97
	206.3	0.03	0.05	20	0.95
	207.5	0.04	0.09	20	1.04
	208.2	0.03	0.07	< 10	1.09
Guttenberg Member	209.3	Tr	0.04	70	3.58
	209.9	Tr	0.03	> 95	3.94
	210.6	Tr	0.06	60	2.20
	211.1	Tr	0.04	> 95	3.89
	211.3	Tr	0.07	60	3.07
	211.9	Tr	n.d.[¶]	75	3.66
	212.2	Tr	0.07	75	2.49
	213.0	0.01	0.07	80	2.82
	213.3	0.04	0.06	50	1.69
	214.2	0.02	0.07	45	1.35
Spechts Ferry Member	214.5	0.02	0.04	n.m.[‖]	1.35
	215.7	0.03	0.08	n.m.	1.27
	216.0	0.12	n.d.	< 10	–
	216.4	0.14	n.d.	n.m.	1.08
	216.7	0.28	0.09	absent	1.23
Platteville Formation	217.2	0.08	0.21	< 10	1.41
	218.4	0.00	0.21	25	1.23
	219.5	0.03	0.19	15	1.89
	220.9	0.05	0.21	20	1.20
	221.3	0.01	0.20	20	1.31
	222.5	0.01	0.20	25	1.39
	224.0	0.02	0.26	25	1.40
	225.5	–	0.24	25	1.48
	226.4	0.01	0.21	15	1.15
	228.3	0.04	0.27	30	1.52
	229.3	0.03	0.18	10	1.03

[†]Abundances were calculated as described in Fig. 3.[‡]Vol% *G. prisca* of total kerogen based on petrographic observations of polished rock surfaces under blue light fluorescence; error for measurements is ±10%.[§]Odd-over-even *n*-alkane distribution as described in Fig. 3.[¶]n.d. means not determined.[‖]shale sample; *G. prisca* abundances not determined.

Table 3. Hopane identifications for Fig. 5

Peak number	Compound name
A	22,29,30-trinorneohopane (Ts)
B	22,29,30-trinorhopane (Tm)
C	17α(H),21β(H)-30-norhopane
D	18α(H)-30-norneohopane (C_{29}Ts)
E	17α(H)-diahopane
F	17β(H),21α(H)-30-norhopane
G	17α(H),21β(H)-hopane
H	17β(H),21α(H)-hopane
I	(22*S*)-17α(H),21β(H)-29-homohopane
J	(22*R*)-17α(H),21β(H)-29-homohopane
K	(22*S*)-17α(H),21β(H)-29-dihomohopane
L	(22*R*)-17α(H),21β(H)-29-dihomohopane
M	(22*S*)-17α(H),21β(H)-29-trihomohopane
N	(22*R*)-17α(H),21β(H)-29-trihomohopane
O	(22*S*)-17α(H),21β(H)-29-tetrahomohopane
P	(22*R*)-17α(H),21β(H)-29-tetrahomohopane
Q	(22*S*)-17α(H),21β(H)-29-pentahomohopane
R	(22*R*)-17α(H),21β(H)-29-pentahomohopane
S	2α(CH_3),17β(H),21α(H)-30-norhopane
T	2α(CH_3),17α(H),21β(H)-hopane
U	3β(CH_3),17α(H),21β(H)-30-norhopane
V	(22*S*)-2α(CH_3),17α(H),21β(H)-29-homohopane
W	(22*R*)-2α(CH_3),17α(H),21β(H)-29-homohopane
X	2β(CH_3),17α(H),21β(H)-hopane

et al. (1992). In the Platteville and Ion units, *G. prisca* occurs as the disseminated A maceral in the classification scheme of Stasiuk *et al*. (1993). In the Guttenberg, *G. prisca* organic matter is represented by both the stromatolitic maceral as well as the disseminated A maceral. We did not observe the *G. prisca* "closed (phenol-rich)" morphotype (Derenne *et al*., 1992) or disseminated B maceral (Stasiuk *et al*., 1993) in any of our samples.

In the SS-9 core, *n*-alkane distributions vary with the proportional abundances of *G. prisca* determined by petrographic techniques. In particular, *n*-alkanes with less than 20 C-atoms are most abundant relative to higher molecular weight homologues and exhibit strongest odd-over-even predominance in *G. prisca*-rich units. Thus, we use *n*-alkane distributions to complement petrographic interpretation of *G. prisca* abundance (Table 2; Fig. 5). *n*-Alkane distributions and petrographic observations indicate that *G. prisca* abundances are greatest in the Guttenberg Member with markedly lower and variable concentrations in the lower Platteville Formation. In samples from the Spechts Ferry and Ion Members and the upper Platteville Formation, *n*-alkane distributions and petrographic observations indicate that *G. prisca* is present in very low abundances. We observed minimal *G. prisca*-derived organic matter during petrographic examination of Spechts Ferry Member samples.

PALEOCEANOGRAPHIC INTERPRETATIONS

Redox variations

The presence of benthic macrofossils and bioturbation indicates that deposition throughout the Middle Caradocian of IA occurred under a relatively oxidizing water column. Ludvigson *et al*. (1996) argued that the lack of deep burrowing fabrics (i.e. *Thalassinoides*) in the Spechts Ferry and Guttenberg Members indicated that bottom waters were intermittently dysoxic during deposition of those units. Biomarker data do not entirely support this interpretation, and these apparently conflicting observations are discussed below.

Platteville formation. Rising homohopane indices suggest oxygenation declined throughout deposition of the Platteville Formation. Macrofossil and ichnofossil data suggest that a decrease in oxygen did not impact benthic organisms and low gammacerane indices suggest water-column stratification did not occur during this time. Pristane/phytane ratios in this interval are intermediate and consistent with either explanation. Aryl isoprenoids are present, but in trace abundances that are too low for compound-specific isotope analyses. From these observations, we suggest bottom waters were oxic during deposition of the Platteville Formation and that the trend in homohopane indices reflects a change in redox conditions within the sediments and not in the overlying waters.

Spechts Ferry Member. The discrepancy between lithologic and biomarker redox indicators in the Spechts Ferry is more dramatic. High homohopane indices (>0.10) suggest dysoxic or anoxic conditions, and relatively high gammacerane indices suggest at least intermittent water-column stratification. The presence of abundant, ^{13}C-enriched aryl isoprenoids indicates that green sulfur bacteria also were present in this interval and provides evidence for photic-zone anoxia. However, waters were relatively shallow during this time, and the photic zone could have reached the sediment–water interface. The lack of *Thalassinoides* burrows (Fig. 2) suggests that conditions were more reducing during deposition of the Spechts Ferry Member than during Platteville Formation deposition (Bromley and Ekdale, 1984; Arthur and Sageman, 1994; Ludvigson *et al*., 1996). However, the presence of macrofossils and, in particular, *Chondrites* and *Planolites* burrows is inconsistent with water-column anoxia. We suggest bottom waters were largely dysoxic during this interval and sediments were anoxic below the surface burrows. The presence of aryl isoprenoids could have resulted from intermittent photic-zone anoxia, which, when present, allowed green sulfur bacteria to thrive and contribute organic matter to the sediments.

Guttenberg member. Relatively high pristane/phytane ratios (>3), low gammacerane indices and low homohopane indices (~0.05–0.06), suggest that bottom-waters were oxic during deposition of the Guttenberg Member. This interpretation is largely consistent with the presence of both benthic macrofossils and bioturbation in this unit, although abundant *Planolites* and *Chondrites* burrows suggest

dysoxic conditions prevailed. It is also consistent with the absence of the *G. prisca* disseminated B maceral, which is suggested to be derived from a precursor that thrived below the halocline in a salinity-stratified water column (Stasiuk *et al.*, 1993).

Although both biomarker and sedimentary indicators of benthic conditions are consistent with oxic sediments and bottom-waters during deposition of the Guttenberg Member, the picture is less clear when data from the other units are compared. Specifically, pristane/phytane ratios are significantly lower and homohopane indices are significantly higher in the Platteville and Ion units than in the Guttenberg Member, suggesting that sediments were more oxic during deposition of the Guttenberg Member. Yet, bioturbation is much more extensive and characteristic of more oxygenated sediments in the Platteville and Ion units (*Thalassinoides vs. Chondrites* burrows; Ludvigson *et al.*, 1996). We suggest this discrepancy indicates that *G. prisca*-derived organic matter exerted an important control on sedimentary conditions. Specifically, the deposition of abundant, refractory cellular material limited diffusion of electron acceptors such as oxygen and sulfate into the sediments. The resulting reducing conditions could have served to restrict bioturbation of the sediments. This mechanism could have also limited the production of sedimentary HS^-, which can facilitate phytol (Kohnen *et al.*, 1991) and bacteriohopanetetrol (Sinninghe Damsté *et al.*, 1995a) preservation, and thereby explain elevated pristane/phytane ratios and decreased homohopane indices in this unit. Indeed, in this section framboidal pyrite is commonly associated with amorphous organic matter but is rare in *G. prisca*-rich intervals (Jacobson *et al.*, 1988). Moreover, Bauld *et al.* (1979) reported that *in situ* bacterial sulfate reduction was not supported in mats of *Entophysalis major*, a cyanobacteria that has been proposed as a modern analogue for *G. prisca* (Foster *et al.*, 1989).

Oxygenated bottom waters and surface sediments also seem inconsistent with the high TOC contents (as high as 40%) observed in Guttenberg Member samples. *G. prisca* is typically associated with high TOC contents (e.g. Estonian kukersite and other units; Foster *et al.*, 1989 and references cited therein), and Derenne *et al.* (1990) proposed that high organic contents result from selective preservation of a resistant aliphatic biopolymer that composes the *G. prisca* cell wall. Additionally, high %TOC values could arise if *G. prisca* grew in either blooms that sedimented rapidly (Hoffman *et al.*, 1987) or as benthic mats that were rapidly buried by sediments (Reed *et al.*, 1986). Such mechanisms could result in discrete, organic-rich horizons, and indeed, the most organic-rich samples do occur in layers approximately 1–2 cm thick.

Ion member. Biomarkers and lithologic redox indicators generally agree in the Ion Member. The presence of *Thalassinoides* burrows and abundant benthic fossil material strongly suggests that bottom waters and sediments were oxygenated during deposition of this unit. Although pristane/phytane ratios are lower in the Ion member than elsewhere in the sampled interval, the other biomarker indices are consistent with this interpretation.

Causes of redox variations. Previous workers (Witzke and Bunker, 1996; Ludvigson *et al.*, 1996) have invoked increased water depth and decreased vertical mixing as a primary control on anoxia in the midcontinent during the Ordovician. Indeed, in the Late Ordovician Maquoketa Formation, ^{13}C-enriched aryl isoprenoids are present in rocks deposited under deep subtidal conditions but are present in low abundances or absent in intervals deposited under shallower conditions (Guthrie, 1996).

That pattern does not prevail in our samples. Lithologic data indicate that bottom waters were dysoxic during deposition of the Guttenberg Member — coincident with the greatest water depths in this interval (up to 100 m; Ludvigson *et al.*, 1996). However, evidence for intermittent photic-zone anoxia is observed only in Spechts Ferry Member samples, a unit deposited in waters approximately 40 m deep (sic.). Therefore, in samples from the SS-9 core, the development of anoxic depositional conditions is not solely governed by water depth, and we must consider alternative mechanisms for the development of water-column anoxia during deposition of the Spechts Ferry Member.

One possibility is that enhanced inputs of freshwater from the transcontinental arch resulted in intermittent water-column stratification. Although this is consistent with the greater abundance of fine-grained siliciclastic materials in the Spechts Ferry, carbonate oxygen-isotope abundances do not vary through this interval (Ludvigson *et al.*, 1996), as would be expected if freshwater inputs were significant (Arthur *et al.*, 1985). Elevated productivity could have also caused bottom-waters to become anoxic (Pedersen and Calvert, 1990). This seems unlikely; a combination of increased productivity and photic-zone anoxia would be expected to result in higher TOC contents, but this is not observed. We note that this interval is associated with the onset of black shale deposition across eastern North America (Hay and Cisne, 1988), and mechanism(s) leading to anoxia at this time could have been important on a broad geographic scale.

Variations in inferred redox, water depth and phytoplankton contributions

Aryl isoprenoids record significant changes in water-column redox conditions and their abundance

patterns suggest intermittent photic-zone anoxia during deposition of the Spechts Ferrry Member. Methylhopane indicators of cyanobacterial inputs decrease markedly at the Platteville–Spechts Ferry boundary, coincident with the molecular evidence for photic-zone anoxia, a change from calcareous to siliciclastic lithology and an inferred increase in water depth (Fig. 1). Higher in the core, methylhopane concentrations remain low, despite evidence for a return to oxic conditions, resumed deposition of calcarareous sediments and an inferred increase in water depth. Moreover, methylhopane abundances are not higher above the Elkport K-bentonite, even though benthic macrofaunal data show that genera presumably affected by the Deicke K-bentonite had returned by the time the Elkport K-bentonite was deposited (Sloan, 1987).

Regional circulation changes likely affected cyanobacteria distributions at or following deposition of the Spechts Ferry Member. Indeed, several workers (Patzkowsky and Holland, 1993; Lavoie, 1995; Patzkowsky and Holland, 1996, 1997; Holland and Patzkowsky, 1997; Pope and Read, 1997) have argued that an eustatic sea-level rise and the Taconic orogeny resulted in the spread of cool, nutrient-rich waters across eastern North America during the *P. tenuis* conodont zone. These oceanographic changes resulted in a switch from tropical-type to temperate-type carbonates and are characterized by decreased abundances of cyanobacterial mats and green algae fossils above the base of the *P. tenuis* zone in the eastern United States (Patzkowsky and Holland, 1993). A similar and essentially correlative shift to temperate-type carbonates is reported for the Galena Formation in eastern Wisconsin (Saylor *et al.*, 1997). Cyanobacterial biomarker distributions in the SS-9 core were likely impacted by related events, and could reflect a wide-scale change in photic-zone conditions.

G. prisca abundances are low in the upper Platteville Formation and the Ion Member, both deposited in waters 20–40 m deep (Ludvigson *et al.*, 1996), and highest abundances occur in the Guttenberg Member, which was presumably deposited in waters 40–100 m deep. Thus, in this setting *G. prisca* is generally more abundant in relatively deeper waters. The lack of *G. prisca* fossils in the Spechts Ferry Member — deposited in waters of intermediate depth — suggests that either photic-zone anoxia or siliciclastic inputs were also important in determining the habitat of this organism.

CONCLUSIONS

We examined molecular indicators for organic-matter sources and depositional redox conditions during the Middle Caradocian from a single, continuous core from Jackson County, IA. Our molecular data and published sedimentological, ichnofossil and benthic macrofaunal data indicate oxic conditions prevailed throughout deposition of the Platteville Formation and the Ion Member of the Decorah Formation. Trace fossils are more restricted in the Spechts Ferry and Guttenburg Members of the Decorah Formation, suggesting dysoxic conditions during deposition of these units. Molecular indices for redox conditions suggest that the Spechts Ferry was generally characterized by anoxic sediments below the zone of surface burrows, and experienced intermittent photic-zone anoxia as indicated by contributions from green sulfur bacteria. In contrast, molecular data indicate the Guttenburg Member was deposited under oxic conditions. This unit contains abundant organic remains of *G. prisca*, and we suggest the deposition of this material served to restrict bioturbation by limiting diffusion of oxidants to the sediments. Combined sedimentological, fossil and molecular data lead to a more refined picture of redox conditions during deposition of these units, and this work demonstrates the utility of multidisciplinary lines of evidence in paleoceanographic studies.

At the base of the Spechts Ferry Member, methylhopane indicators of cyanobacterial inputs diminish, suggesting the onset of shale deposition was accompanied by a significant change in the phytoplankton community. While evidence for *G. prisca* contributions is found in trace levels throughout most of the core, molecular and petrographic evidence for *G. prisca* increase dramatically in the Guttenburg Member. We suggest these two fundamental changes in the dominant phototrophic sources of organic matter were associated with a shift to siliciclastic lithofacies, possibly linked to wide-spread changes in ocean circulation and general oceanic cooling documented to the northeast of the core site (WI), and throughout the eastern United States.

NOTE ADDED IN PROOF

Methylhopane identifications were confirmed by GC-MS/MS analyses performed at the Netherlands Institute for Sea Reseach.

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