

Stable isotope (C, S, N) and molecular studies on the Precambrian Nonesuch Shale (Wisconsin–Michigan, U.S.A.): Evidence for differential preservation rates, depositional environment and hydrothermal influence

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ABSTRACT

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The organic-rich, Middle Proterozoic Nonesuch Formation is part of a thick volcanoclastic rift-fill sequence (Mid-Continent Rift System, northern Wisconsin and Upper Peninsula Michigan) with a mild thermal history. Despite stratigraphic/sedimentologic similarities between the east (Michigan) and west (Wisconsin) study areas, distinctions in organic petrologic, elemental and stable isotopic parameters are noted. Geologic arguments and predictable relationships among organic carbon content, bulk and molecular pyrolysate composition and petrologic parameters are sufficient to invoke differential preservation of the same (or similar) primary producers as the principal cause of variability. Isotopic signals indicating precipitation of calcite via intense organic production (planktonic blooms) is evident among carbonate laminites. Incorporation or concentration of organic degradation by-products is evident, particularly in the west, from carbon and nitrogen stable isotope data. It is proposed that whereas preservation of organic productivity of a particular organism may be nearly complete in one organic facies in the east and west, organic remains in other intervals in the west were subject to extensive degradation and reconstitution to form protokerogens. Implications of the study include establishing parameters for recognizing pre-Devonian lacustrine vs. marine euxinic systems, clues to the complexity of Middle Proterozoic aquatic systems and in recognizing the input of hydrothermal fluids to water bodies and early sediments.

1. Introduction

A broad framework incorporating benchmarks in the physical, chemical and biological evolution of the Earth is now in place (e.g., Schopf et al., 1983; Windley, 1984; Walter, 1987; Veizer, 1988). Traditionally, the vulnerability of Precambrian organic matter to de-

struction by metamorphism and contamination by mobile fluids has relegated organic geochemistry to a secondary role in constructing this framework. However, recognition and circumvention of these pitfalls (e.g., McKirdy, 1974) and the application of innovative preparation and analytical techniques (e.g., Summons et al., 1988a, b) will permit a more refined geochemical assessment of the biogeochemical history of the Earth. For such an effort to succeed, clues to the origin of geo-

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chemical variability in various Precambrian sedimentary settings must be sought using diverse lines of geologic and geochemical data.

The present study seeks to establish the range of geochemical variability for a single Precambrian sedimentary unit — the Middle Proterozoic Nonesuch Formation (Keweenaw Oronto Group) of the North American Mid-Continent Rift System. Applying a framework based on the geographic and stratigraphic distribution of organic facies comprising the Nonesuch Formation, an attempt is made to delineate biologic, sedimentologic, diagenetic and post-diagenetic factors responsible for the variability in a host of organic and inorganic geochemical parameters. The Nonesuch Formation is a particularly promising unit on which to apply this approach as it exhibits significant organic enrichment levels and has had a mild thermal history (Imbus et al., 1988, 1990). Although geochemical data have recently been proposed to suggest a marine origin (Pratt et al., 1991), there is substantial stratigraphic and sedimentologic evidence for a lacustrine (thermally stratified) rift deposit origin for the Nonesuch Formation (Elmore, 1981; Milavec, 1986; Elmore et al., 1989). Greater geochemical variability is reasonably expected for organic materials from lacustrine, as opposed to marine settings, because smaller water volume and greater exposure to land-derived processes ensures more rapid response to changes in climate and hydrology. Furthermore, volcanism associated with developing rifts, enhances the likelihood that the ancient Nonesuch waters were more strongly influenced by mineralizing fluids than would be expected in lakes formed in other settings.

The size and diversity of the data set generated for the present study affords an opportunity to address a number of issues related to biogeochemical processes in the ancient Nonesuch water body. The approach applied may be useful in focussing future studies concerned with the origin of geochemical variability through Earth's history (secular trends) and in

evaluating parameters of potential utility in distinguishing between marine and lacustrine pre-Devonian settings.

2. Samples and procedures

Nonesuch Formation samples used in the present study were collected from among eight core sections and from four outcrop sections in Wisconsin and Michigan (Milavec, 1986; Imbus, 1990; see Fig. 1 for sample locations). Details of sample selection for organic geochemistry, which was done in conjunction with detailed stratigraphic/sedimentologic assessment (Milavec, 1986), are given in Imbus (1990).

A total of 218 bitumen-free Nonesuch Formation samples were analyzed for organic carbon (referred to as TOC) and kerogen stable carbon isotope composition ($\delta^{13}\text{C}_{\text{KER}}$). The $\delta^{13}\text{C}_{\text{KER}}$ analyses were performed on decarbonated whole-rock specimens (Imbus, 1990). Selected samples were analyzed for: (1) total sulfur and Rock Eval[®] pyrolysis in accordance with standard techniques at Texaco EPTD, Houston, Texas; (2) nitrogen elemental (C/N) and $\delta^{15}\text{N}$ (Macko et al., 1982); (3) sulfide $\delta^{34}\text{S}$, performed by Coastal Laboratories, Austin, Texas; (4) pyrolysis–flame ionization detection (PY–FID) and pyrolysis–gas chromatography–mass spectrometry (PY–GC–MS) on whole-rock specimens; and (5) carbonate stable carbon and oxygen isotopes (procedure of McCrea, 1950). Details of the sample selection criteria, sample preparation and analytical techniques are given in Imbus (1990).

3. Results and discussion

3.1. Stratigraphic/sedimentologic framework applied

The Nonesuch Formation, averaging 167 m in thickness where it occurs in Upper Peninsula Michigan and northern Wisconsin (Fig. 1), is situated near the center of the Middle

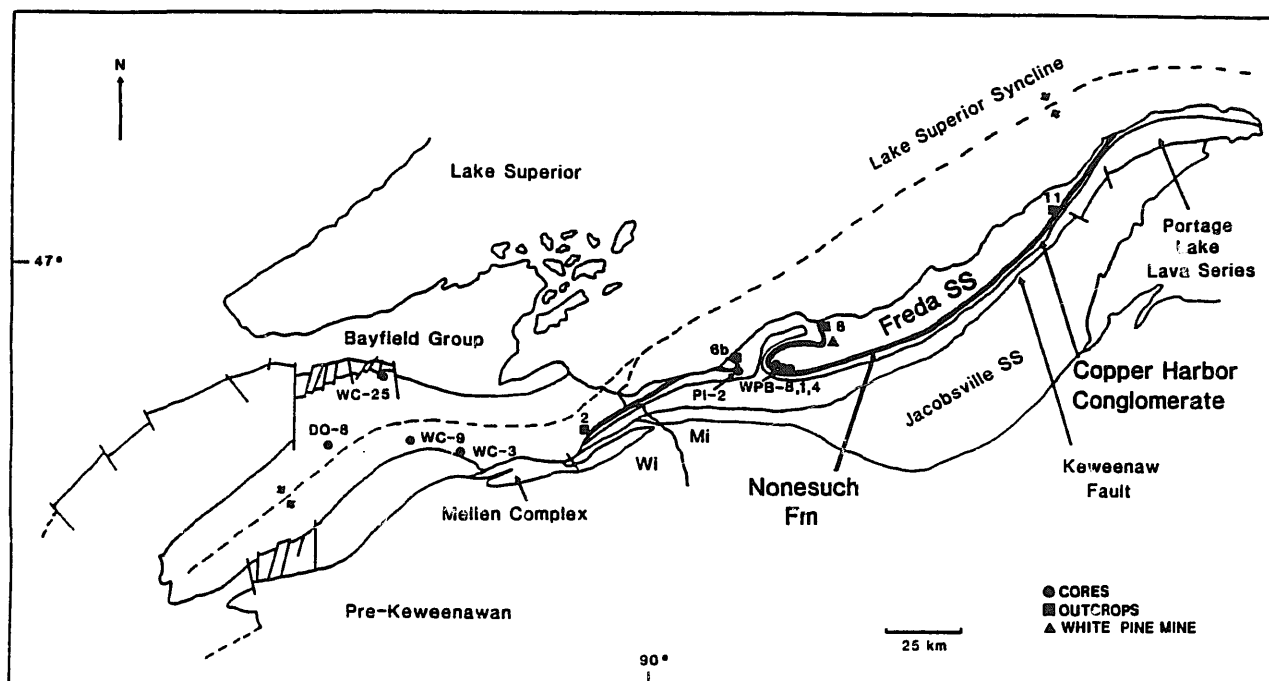


Fig. 1. Geologic map showing core and outcrop section locations sampled for organic petrologic and geochemical analyses (from Imbus et al., 1988; used with permission, Pergamon Press, Oxford).

Proterozoic (Keweenaw) Oronto Group (Fig. 2a). The Oronto Group is a thick volcanic and clastic basin-filling deposit occupying the Keweenaw Trough of the Mid-Continent Rift System (northern sector, cf. Dickas, 1986). Studies by Elmore (1981) and Milavec (1986), involving detailed analysis of entire core and outcrop sections reveal that the euxinic silts and shales of the Nonesuch Formation likely represent a lacustrine setting that evolved from marginal lacustrine to lacustrine to fluvial-lacustrine environments (Fig. 2b). According to Elmore et al. (1989), interactions among rates of subsidence, possible changes in climate and differences in tectonic setting controlled sedimentation in the Nonesuch lake, resulting in variable vertical facies sequences.

With the exception of the shale facies of the lacustrine facies assemblage, individual organic-rich facies are difficult to correlate region-wide. Based on a relatively abundant and uniform distribution of samples representative of stratigraphic and "organic facies" inter-

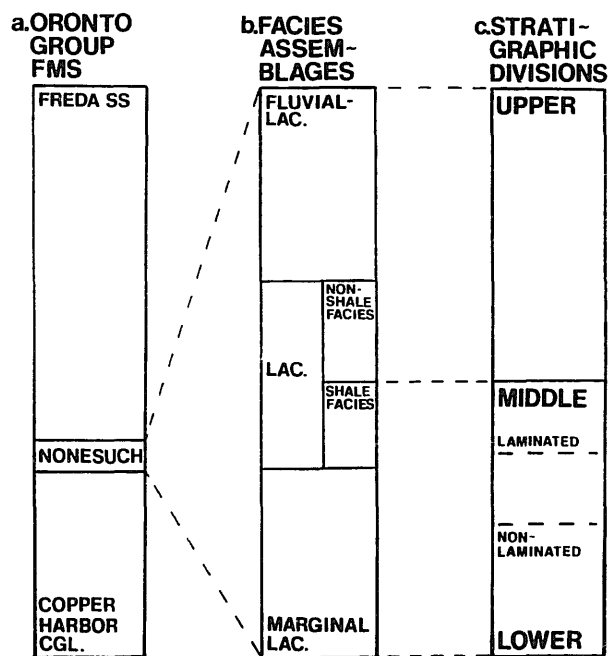


Fig. 2. Stratigraphic relationships: (a) between the Nonesuch Formation and the Middle Proterozoic Oronto Group; (b) generalized within the Nonesuch Formation (after Milavec, 1986); and (c) stratigraphic/sedimentologic scheme applied in the present study.

vals, a modified stratigraphic/sedimentologic scheme is used to compile geochemical data in the present study (Fig. 2c). In general, compilations incorporating this framework and applied over the east (Michigan) and west (Wisconsin) study areas result in a six-part "geographic/stratigraphic" division (i.e. east and west: lower, middle and upper).

3.2. Distribution of organic carbon

Fig. 3 depicts the results of TOC analyses for four core sections sampled at regular intervals, and is definitive in documenting overall trends in organic carbon distribution in the Nonesuch

Formation. In general, TOC values are higher in the east (PI-2, WPB-8) than in the west (DO-8, WC-9). A ~30-m unit, lying 46–91 m above the base of the Nonesuch Formation, is correlatable on the basis of TOC. This unit corresponds to the shale facies of the lacustrine facies assemblage (middle division). Substantial organic enrichment is also noted in portions of the lower division (mudstone facies of the marginal lacustrine facies assemblage) and sporadically in the upper division (exclusive of the shale facies of the lacustrine facies assemblage) and in the fluvial-lacustrine facies assemblage and associated Freda Sandstone. Substantial thickening of the east-

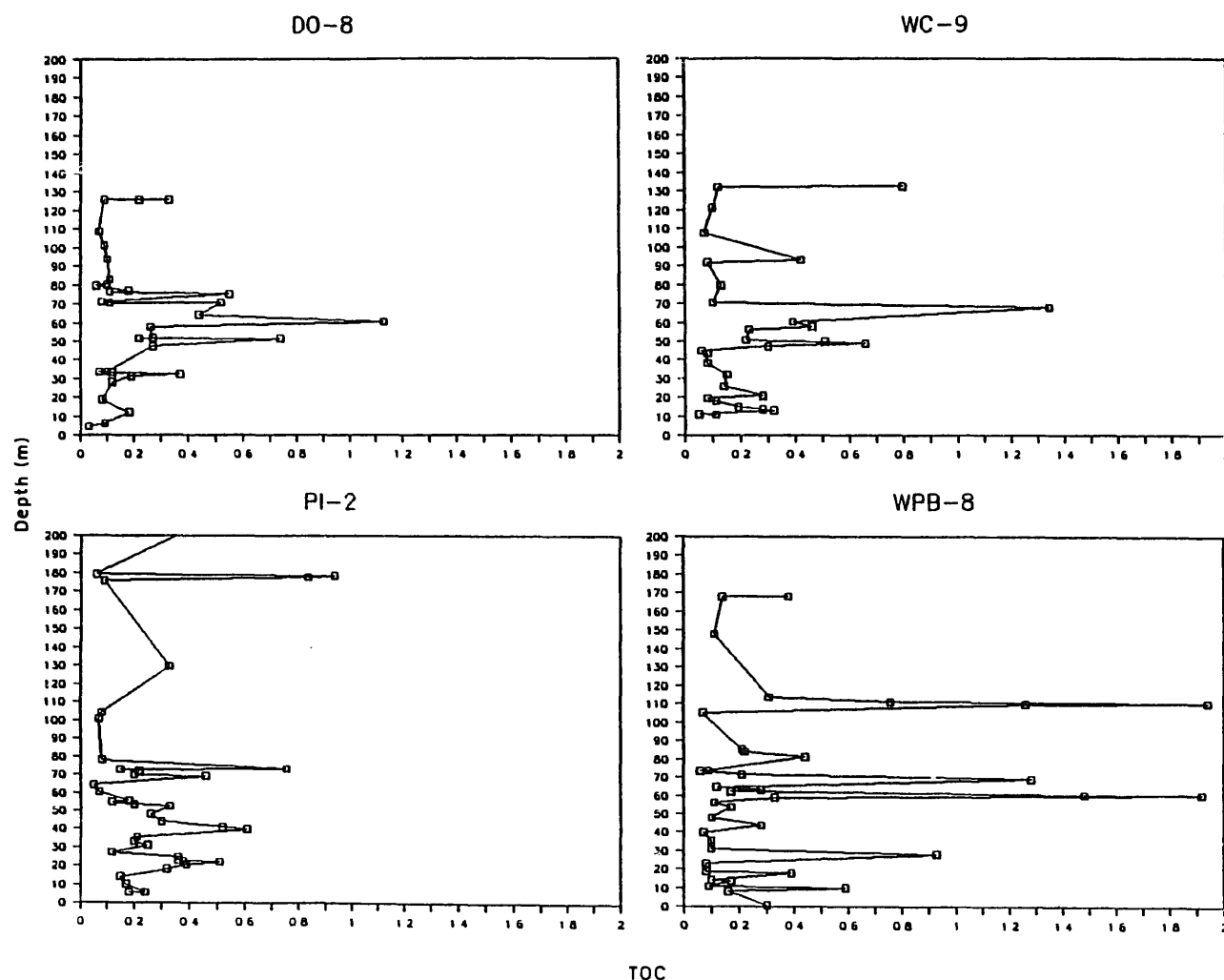


Fig. 3. Distribution of organic carbon in the Nonesuch Formation based on four selected, regularly sampled core sections (west: DO-8, WC-9; east PI-2, WPB-8).

ern relative to the western sections indicates more rapid sedimentation in the east. Generally, higher organic carbon levels in the east may have resulted from enhanced preservation of organic detritus afforded by rapid burial without a net dilution effect (cf. Bralower and Thierstein, 1984).

3.3. Kerogen type and maturity

The results of Rock Eval[®] pyrolysis on 41 Nonesuch Formation samples are shown in Table 1. The data plotted on a modified van Krevelen diagram (Fig. 4) show considerable variability for a single formation, particularly one of pre-Devonian age. A traditional interpretation of these data would invoke a large range in thermal maturity to explain apparent disproportionation of hydrogen (decrease of HI down the Type-I or -II coalification tracks). The observed T_{\max} range, for which no east-west segregation is apparent, corresponds to the "oil generation window" thermal regime for Type-II kerogens (cf. Espitalié and Joubert, 1987). Lack of evidence for TOC level and lithology as primary influences on HI composition and essential thermal maturity equivalence throughout the basin enables inferences concerning kerogen type to be made (cf. Tissot and Welte, 1984).

Type-I kerogens (HI > 300, OI < 10; eastern only) are likely indicative of algal input typical of lacustrine environments. Type-II kerogens (HI < 300, OI < 25; two eastern and one western), possibly represent degraded algal material or the input of other organic material (including bacterial biomass). Contribution of terrestrially derived higher-plant materials to produce Type-II-III kerogens (OI > 25; eastern lower and upper divisions) is obviously precluded in a Precambrian sediment. Given the geographic/stratigraphic distribution of these samples, it is proposed that oxidation of organic matter via exposure to hydrothermal fluids took place for the two eastern lower di-

vision samples (cf. Ho et al., 1990) and oxidation via exposure to the atmosphere in shallow ponded environments occurred in the upper eastern division (cf. Milavec, 1986). Kerogens whose HI and OI values preclude typing, may be attributed to extensive degradation via oxidation or microbial activity or low initial organic carbon contents.

A combined organic petrographic and PY-GC-MS study of the Nonesuch Formation was previously presented by Imbus et al. (1988). In that study, the presence of a brightly fluorescing, "filamentous organic material" (hereafter referred to as FOM), of apparent algal origin, was found to prevail in the eastern study area. Pyrolysates of kerogens isolated from rocks bearing this material consist dominantly of aliphatic moieties (especially normal alkanes). Conversely, western samples, with one notable exception, were found to be essentially devoid of brightly fluorescing FOM but to contain substantial quantities of a poorly fluorescing, dark-gray reflecting material. This material, resembling the coal maceral "bituminite", an algal and bacterial degradation product (cf. Teichmüller, 1982), consists of much higher proportions of aromatic pyrolysates. The exception to this east-west rule, a carbonate laminite sample from the lower west division, was sufficient to eliminate geographic distinctions in thermal maturity as an explanation for relative fluorescent qualities of FOM and the presence of "bituminite". It was proposed that generally superior conditions for organic preservation ensured the conservation of brightly fluorescing FOM in the east. The prevalence of bituminite in the west was attributed to the degradation of algal material. Subsequent analyses, conducted on whole-rock samples with a more representative geographic/stratigraphic distribution (Imbus, 1990), although confirming this east-west distinction, show that relative aliphatic/aromatic composition may be described as a continuum (discussed in Section 3.5).

TABLE 1

Results of Rock Eval[®] pyrolysis for 41 selected Nonesuch Formation samples

Sample I.D.	Geogr./strat.* ¹	TOC* ²	% CaCO ₃	HI* ³	OI* ³	KTR* ³	GP* ³	T _{max} * ⁴ (°C)
DO-8 K	W-M	0.3	51.0	107	3	0.22	0.46	U
DO-8 L	W-M	0.4	59.6	183	3	0.31	1.02	U
DO-8 N	W-M	1.2	14.8	136	3	0.09	1.72	452
DO-8 S6	W-U	0.6	17.1	45	0	0.10	0.29	U
DO-8 R	W-U	0.5	15.0	36	0	0.05	0.19	U
WC-25 S2	W-L	1.5	13.9	78	20	0.03	1.21	452
WC-25 B	W-M	0.7	48.3	251	9	0.01	1.88	450
WC-25 F	W-L	0.4	33.5	179	15	0.11	0.79	U
WC-25 M	W-U	1.4	9.1	123	9	0.03	1.75	449
WC-9 I	W-M	0.5	48.1	147	6	0.22	0.91	U
WC-9 00	W-M	0.6	50.0	133	7	0.17	0.90	I
WC-9 L	W-M	0.4	16.3	159	0	0.20	0.82	U
WC-9 97	W-M	1.2	10.9	162	4	0.12	2.28	449
WC-3 J	W-M	0.6	13.8	75	0	0.07	0.47	U
WC-3 K	W-M	0.6	22.6	115	15	0.08	0.76	U
WC-3 L	W-M	0.6	12.9	70	0	0.06	0.47	U
2 J	B	0.2	24.0	58	16	0.18	0.17	U
2 K	B	0.2	21.2	17	13	0.33	0.06	U
6b F	E-L	0.5	30.4	110	20	0.38	0.56	U
6b O	E-M	0.8	11.3	415	11	0.06	3.50	433
6b P	E-M	0.6	11.3	313	0	0.05	1.82	447
PI-2 R	E-U	0.2	12.3	190	0	0.08	3.49	U
PI-2 Z	E-U	0.8	10.6	224	5	0.03	1.97	445
PI-2 AA	E-U	0.8	11.6	38	0	0.03	0.30	U
PI-2 CC	E-U	0.5	8.9	105	0	0.09	0.54	U
8 F	E-L	0.9	26.9	18	7	0.59	0.39	U
8 G	E-M	0.7	35.8	31	20	0.52	0.42	U
WPB-8 G	E-L	0.5	27.3	89	21	0.10	0.48	U
WPB-8 I	E-L	0.8	38.2	314	6	0.02	2.66	445
WPB-8 M	E-M	1.7	11.4	454	15	0.02	7.82	445
WPB-8 47	E-M	1.5	11.3	432	2	0.02	6.79	443
WPB-8 45	E-M	1.7	12.3	450	3	0.02	7.70	445
WPB-8 W	E-U	1.9	12.9	445	0	0.02	8.23	443
WPB-1 G	E-L	0.8	36.4	275	46	0.03	1.92	444
WPB-1 J	E-L	0.5	13.6	70	8	0.06	0.36	U
WPB-4 B	E-L	0.7	40.0	238	30	0.02	1.62	444
WPB-4 I	E-M	0.4	13.6	295	0	0.07	1.38	440
WPB-4 Q	E-U	0.5	12.3	188	24	0.03	0.99	U
WPB-4 R	E-U	0.6	15.5	91	20	0.05	0.62	U
11 F	E-L	0.5	33.1	88	8	0.24	0.65	U
11 H	E-M	0.8	20.2	161	2	0.14	1.59	442

*¹Geographic/stratigraphic subdivisions: E, W= east and west study areas, respectively; L, M, U= lower, middle and upper stratigraphic divisions, respectively; B= outcrop section 2 (see Fig. 1).

*²TOC analyzed by Texaco, Inc., Houston, Texas; % CaCO₃ data from present study.

*³HI= hydrogen index (mg HC/g C_{org}); OI= oxygen index (mg CO₂/g C_{org}); KTR= kerogen transformation ratio [S₁/(S₁+S₂)]; GP= genetic potential (S₁+S₂).

*⁴T_{max}= temperature at which maximum pyrolytic destruction of kerogen occurs. Values were not determined for many samples for the following reasons: U= T_{max}-values < 400°C are not representative of kerogen transformation; I= hydrocarbon yields are too low to derive reliable interpretations (Texaco, Inc. criteria).

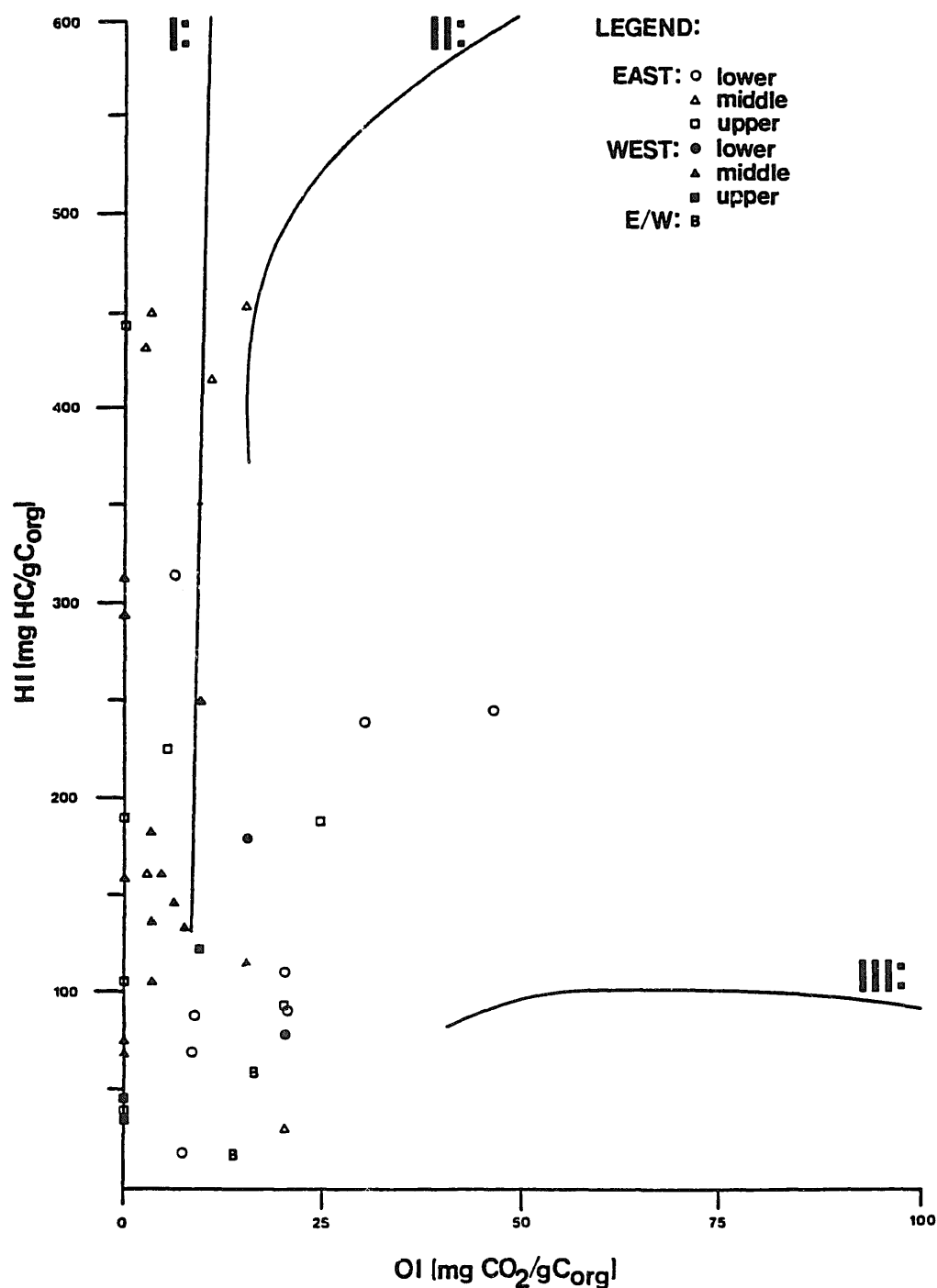
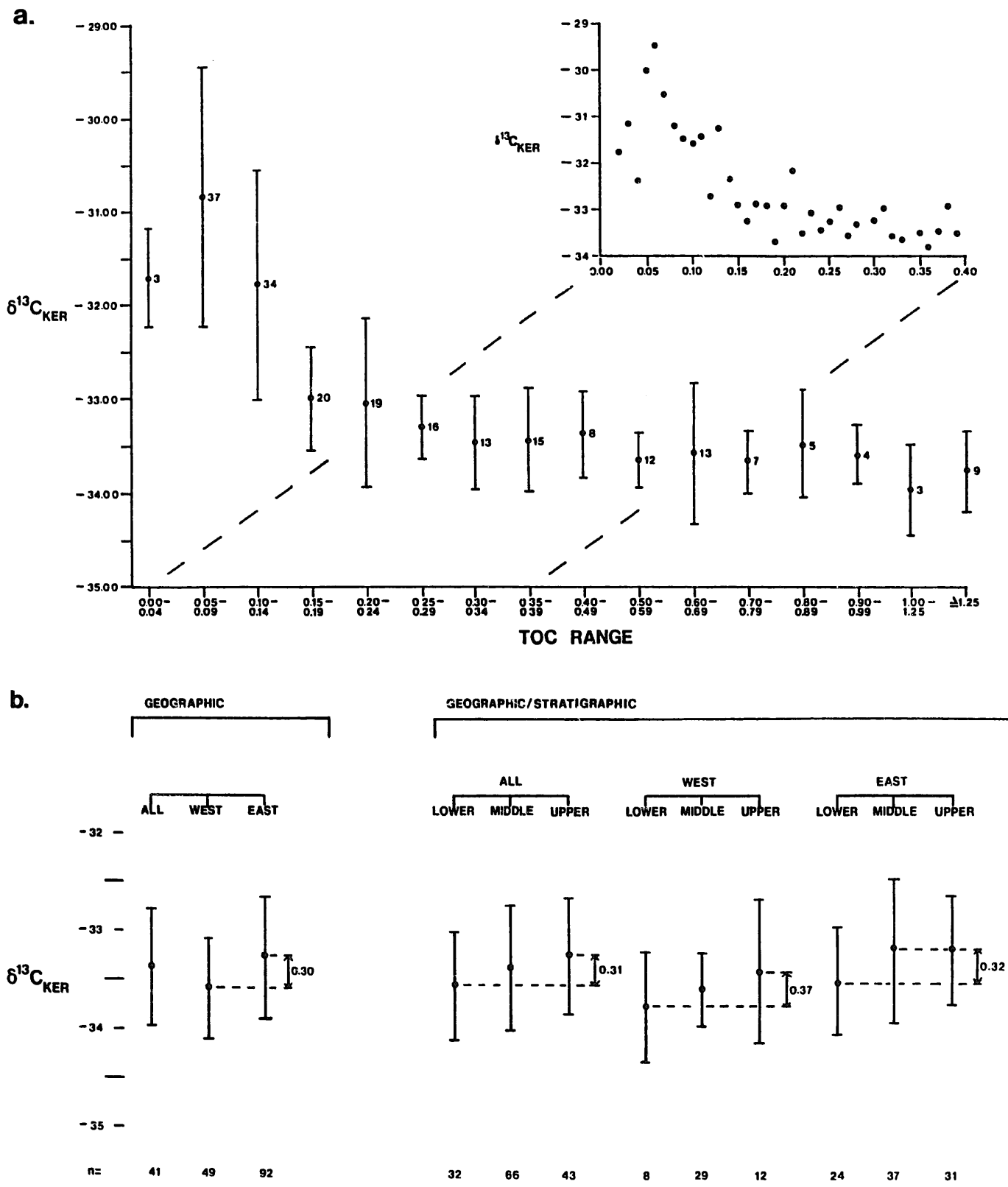


Fig. 4. Modified van Krevelen diagram depicting a cross-plot of hydrogen and oxygen indices (*HI* and *OI*, respectively).

3.4. Kerogen stable carbon isotopes ($\delta^{13}C_{KER}$)

A host of diagenetic and post-diagenetic processes may produce kerogen stable isotope values that do not strictly reflect the isotopic

composition of the source biota. The influence of chemical and/or bacterial degradation of organic matter during its passage through the water column or its residence in early sediments may involve enrichment or depletion



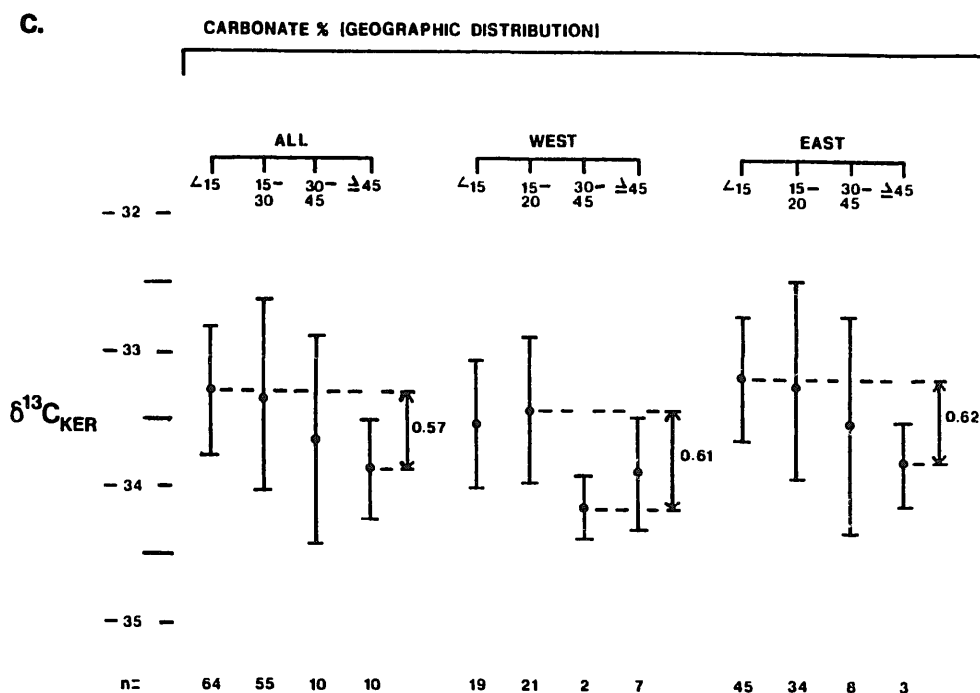


Fig. 5. Compiled results of $\delta^{13}C_{KER}$ analyses: (a) influence of TOC; (b) with respect to geographic and stratigraphic/sedimentologic subdivision; and (c) with respect to % carbonate.

(or no change) in the $\delta^{13}C$ composition of kerogen (e.g., Hayes et al., 1983). Alteration of source isotopic signature, which may be documented using carbonate $\delta^{13}C$ - or sulfide $\delta^{34}S$ -values (e.g., Hatcher et al., 1983; Gautier, 1985; Curtis, 1987; Pierre, 1989), depend on the magnitude of each degradative process involved (i.e. aerobic oxidation vs. anaerobic sulfate reduction, methanogenesis, etc.), on specific sedimentary conditions (i.e. "open" vs. "closed" sedimentary regimes) and the degree to which bacterial biomass contributed carbon to the kerogen. Finally, post-diagenetic overprinting of source and diagenetic isotopic signals become increasingly important as kerogen-containing sediments evolve from catagenetic, metagenetic and metamorphic thermal regimes (McKirdy, 1974; Hayes et al., 1983).

The present kerogen stable carbon isotope study of the Nonesuch Formation seeks to identify isotopic variability on the basis of geographic/stratigraphic and lithologic attributes. Once the relative importance of geographic and

stratigraphic position and lithologic character on kerogen $\delta^{13}C$ composition has been established, additional pyrolysis data and new elemental and stable isotopic data for carbonate carbon, sulfide sulfur and organic nitrogen will be presented (Sections 3.5 and 3.6) to help establish the relative importance of source biota vs. secondary biological and diagenetic influence on the nature of the Nonesuch Formation kerogens.

The mean $\delta^{13}C_{KER}$ -value for 218 Nonesuch Formation kerogens analysed in the present study is -32.68‰ ($\pm 1.36\text{‰}$). The total range observed (-34.72 to -27.57‰) is considerable for a single formation. The values determined are, in general, depleted relative to those commonly observed in Phanerozoic-Precambrian kerogens over the age range: 0–3.8 Ga ($-26 \pm 7\text{‰}$); cf. Schidlowski, 1987).

Kerogens that comprise $<0.15\%$ of their host rocks tend to be strongly enriched in ^{13}C (Fig. 5a). A number of possibilities, including destruction of isotopically light organic constituents via oxidation or microbial activity,

alteration by mineralizing fluids or difficulties inherent to analysing small organically derived CO₂ volumes, may account for this observation. To avoid complications from such factors, the compilation of kerogen stable carbon isotopic data with respect to geologic and geochemical parameters will be made using only whole-rock samples with $\geq 0.15\%$ TOC.

Two approaches to documenting the distribution of $\delta^{13}\text{C}_{\text{KER}}$ -values with respect to geographic/stratigraphic, paleoenvironmental and lithologic parameters were undertaken. First, generalizations were made from samples with statistically enriched and depleted $\delta^{13}\text{C}_{\text{KER}}$ -values (i.e. above and below, respectively, the standard deviation range for samples with $\% \text{TOC} \geq 0.15$: $-33.39 \pm 0.60\text{‰}$). This assessment revealed that the isotopically enriched samples are primarily from the eastern lower and middle stratigraphic levels.

The second assessment involved compiling $\delta^{13}\text{C}_{\text{KER}}$ data with respect to the following categories: "geographic" (east vs. west), "stratigraphic" (lower, middle and upper), "unit lithology" (roughly equivalent to the facies of Milavec, 1986), average "grain size" of individual samples, "paleo-water depth" (speculative assignments based on depositional interpretations of Milavec, 1986) and $\% \text{CaCO}_3$. Eastern kerogens are enriched relative to western kerogens by 0.30‰ (Fig. 5b). An enrichment trend up section is apparent in the west and for the formation overall. Of the parameters "unit lithology", grain size and "paleo-water depth", geographic/stratigraphic variability in $\delta^{13}\text{C}_{\text{KER}}$ is evident only for "unit lithology", i.e. kerogen ^{13}C enrichment is associated with finer grain sizes. A strong trend of kerogen ^{13}C depletion is apparent with increasing $\% \text{CaCO}_3$ in the east and overall (Fig. 5c).

Whereas it is tempting to ascribe the consistent ^{13}C depletion of western kerogens (particularly lower and middle intervals) to differential source input between the east and west, the apparent inverse relationship between $\delta^{13}\text{C}_{\text{KER}}$

and fine-grained sedimentary packages ("unit lithologies") points to diagenetic origins of variability. Alternatively, the strong association of isotopically light kerogens and high carbonate contents is suggestive of contrasting carbon cycles in the ancient Nonesuch water body (east vs. west). The distribution of kerogen carbon isotope values with geographic/stratigraphic situation may have originated from one or any combination of these factors.

3.5. Specialized molecular and carbon isotope studies

The east and west Nonesuch Formation study areas and, in some cases stratigraphic divisions of the formation, are distinguishable on the basis of organic geochemical (TOC, Rock Eval[®] pyrolysis, PY-GC-MS and $\delta^{13}\text{C}_{\text{KER}}$) and organic petrologic parameters. The establishment of positive, negative or non-correlations between $\delta^{13}\text{C}_{\text{KER}}$ and kerogen molecular pyrolysate composition (and by extension, among Rock Eval[®]: HI and organic petrology) might have considerable bearing on which of the following, theoretical end-member scenarios might account for the observed geographic/stratigraphic distinctions: (1) origin of the kerogens from single vs. multiple primary producers, (2) pre-eminence of a single primary producer (e.g., FOM) that suffered variable bacterial degradation (and/or bacterial contribution) and subsequent differential recombination of isotopically distinct moieties, or (3) a pre-eminent primary producer (which suffered variable bacterial degradation/contribution little influencing stable isotope values) that utilized isotopically distinct carbonate feedstock resulting from variable carbon cycling [i.e. distinct hydrologic cycles allowing, for example, incorporation of CO₂ in exchange with the atmosphere vs. incorporation of isotopically depleted CO₂ derived from degraded organic matter (recycling)].

Ultimately, the ability to distinguish which of these processes was most influential depends on an understanding of kerogen hetero-

geneity. The initial approach to this problem entails an expanded PY-GC-MS study (relative to that of Imbus et al., 1988) on a suite of samples from each study area that have contrasting $\delta^{13}\text{C}_{\text{KER}}$ and % CaCO_3 contents. One sample each from the east and west that have contrasting kerogen pyrolysate and carbon isotope characteristics were selected for a set of specialized extraction, pyrolysis and isotope analyses.

In contrast to the PY-GC-MS study presented by Imbus et al. (1988), less geographic segregation is noted in the present pyrolysis study (Table 2; Fig. 6) between aliphatic and aromatic kerogens [i.e. east (A) and west (B)]; and brightly fluorescing vs. non-fluorescing FOM, respectively). A continuum between end-member pyrolysate composition is illustrated by the correlation between the "aliphaticity" parameter $\Sigma n\text{-C}_{8-22}/(\text{xylene} + \text{toluene})$ and HI (@ 99.8% C.I.). The only aliphatic kerogens (pyrolysate group A) present in the west are associated with carbonate-rich samples (~50% CaCO_3). This observation strongly suggests a preservation mechanism afforded by environmental conditions associated with carbonate precipitation or perhaps entombment via rapid carbonate sedimentation and early cementation. Eastern samples comprised of aromatic pyrolysates (pyrolysate group B) occur either in the upper portion of the formation which witnessed the gradual demise of deep water conditions (cf. Milavec, 1986) or in the lower portion of the formation in the east, which was locally subject to hydrothermal alteration (cf. Ho et al., 1990). Although the limited organic petrologic data available for this data set show a strong relationship between fluorescing FOM relative abundance and HI, there is no correlation between $\delta^{13}\text{C}_{\text{KER}}$ and the "aliphaticity"-related Rock Eval® and selected molecular pyrolysate parameters (Table 2).

A few additional conclusions concerning the nature of "aliphatic" vs. "aromatic" or gener-

ally east vs. west kerogens, respectively, may be drawn from the data (Table 2). Molecular parameters, which, by analogy to extracts, are maturity-related (e.g., octene/*m*- + *p*-xylenes, % $n\text{-C}_8/n\text{-C}_{8-22}$, R_c), show no consistent geographic trends. Indeed, the mean values for the T_{max} parameter (a measure of kerogen refractivity) are essentially equal. This observation and the occurrence of fluorescing FOM in most eastern samples and in carbonate-rich western samples is conclusive in establishing equivalent thermal maturity regimes in the east and west. The b/e (see Table 2 for definition), a measure of the abundance of branched-cyclic alkanes relative to that of *n*-alkanes, suggests a greater bacterial biomass contribution to the "aromatic" (generally western) kerogens.

Specialized extract and pyrolysate molecular studies performed on selected eastern (WPB-8 47; b/e=0.16) and western (WC-3 J; b/e=0.90) kerogens are revealing (Imbus, 1990). Extract from the western sample is highly ^{13}C -enriched relative to its extracted residue ($\Delta_{\text{extract-kerogen residue}}$: 1st extraction=2.3‰; 2nd extraction=0.9‰) vs. no to moderate ^{13}C enrichment of the eastern sample ($\Delta_{\text{extract-kerogen residue}}$: 1st extraction=0‰; 2nd extraction=1.0‰). A similar kerogen-bitumen ^{13}C relationship was reported by Hieshima et al. (1990).

Thermal slicing of these samples via stepwise PY-GC-MS demonstrated that, whereas pyrolysate yields were comparable for the east and west samples at each of the stages [i.e. ~30 and ~70% of the total yield for the low- (330–450°C) and high-temperature (450–615°C) stages, respectively], the b/e ratio was higher in the low-temperature stage than in the high-temperature stage (factor of 2–3), and far greater in each stage of the western kerogen than in corresponding stages for the eastern kerogen (factor of 4–7). Each sample showed an increase of aliphatic content from the low- to high-temperature stages. A sequence of pentacyclic triterpanes (C_{27-31}) was detected in

TABLE 2

Pyrolysis classification and selected geochemical parameters and molecular ratios (see text for explanation)

Pyrolysis sample I.D.	Geogr./ strat. ⁴²	TOC	$\delta^{13}\text{C}_{\text{ker}}$ (‰ vs. PDB)	% CaCO_3	HI/OI	T_{max}^{43}	% $n\text{-C}_9$ (N) ⁴⁴	octene ⁴⁵ m + p-xylyl	creosols ⁴⁵ octene	creosols ⁴⁵ m + p-xylyl	$\Sigma n\text{-C}_{16-22}$ tol + xyl	naphth- ⁴⁷ tol	$\Sigma n\text{-C}_{16-18}$ ene/ane	R_z^{49}	$\text{C}_{17}^{10}/\text{C}_{18}$	b/e ¹¹ (45-20)
A:																
WC-25 B	W-M	0.69	-34.72	48.3	251/9	18.0	17.5	0.67	0.42	0.28	2.45	0.24	0.86	0.74	0.98	0.15
WC-9 00	W-M	0.51	-34.02	50.0	133/7	18.2	15.8	0.34	0.07	0.03	2.01	0.51	0.57	0.76	1.00	0.40
WPB-8 D	E-L	0.59	-33.81	27.1	n.d./	17.6	14.0	0.34	0.78	0.27	2.24	0.77	0.56	0.68	1.00	0.25
n.d. ¹²																
WPB-8 I	E-L	0.93	-34.05	38.2	314/6	17.7	14.9	0.65	0.57	0.37	2.75	0.19	0.77	0.76	1.01	0.15
WPB-8 M	E-M	1.92	-33.63	11.4	454/15	17.5	19.6	0.66	0.40	0.26	2.49	0.19	0.67	0.76	0.95	0.20
WPB-8 47	E-M	1.48	-33.42	11.3	432/2	17.6	15.9	0.60	0.76	0.46	2.95	0.31	0.76	0.76	1.00	0.16
WPB-8 45	E-M	1.28	-33.33	12.3	450/3	18.2	14.3	0.60	0.84	0.51	3.68	0.43	0.75	0.77	1.00	0.18
A/B:																
DO-8 N	W-M	1.13	-33.50	14.8	136/3	n.d.	29.1	0.44	0.04	0.02	0.71	0.15	0.45	0.69	1.04	0.61
WPB-1 J	E-L	0.54	-33.75	13.6	70/8	17.5	17.4	0.36	0.08	0.03	0.66	0.22	0.35	0.61	0.97	0.94
B:																
DO-8 S6	W-U	0.52	-34.08	17.1	45/0	18.2	44.9	0.44	0.03	0.01	0.51	0.18	0.37	0.52	1.03	1.00
WC-25 S6	W-L	1.46	-34.63	13.9	78/20	17.6	34.9	0.16	1.11	0.18	0.23	0.27	0.56	0.69	0.96	1.01
WC-M M	W-U	1.27	-33.49	9.1	123/9	n.d.	22.0	0.13	1.16	0.15	1.69	0.76	0.59	0.65	1.02	0.33
WC-3 J	W-M	0.65	-33.99	13.8	75/0	18.3	32.7	0.32	0.04	0.01	0.74	0.16	0.28	0.64	0.96	0.90
6b F	E-L	0.56	-33.63	30.4	110/20	n.d.	33.2	0.43	0.05	0.02	0.77	0.13	0.45	0.57	0.98	0.42
PI-2 AA	E-U	0.94	-33.43	11.6	38/0	17.6	47.0	0.24	0.04	0.01	0.96	0.22	0.31	0.53	1.01	0.86
WPB-4 R	E-U	0.72	-33.05	35.5	91/20	17.2	38.3	0.29	0.20	0.06	0.79	0.20	0.36	0.67	1.03	0.93
11 H	E-M	1.05	-33.90	20.2	161/2	18.1	27.6	0.41	0.03	0.01	1.14	0.23	0.46	0.84	1.01	0.61
C:																
PI-2 Z	E-U	0.84	-33.94	13.6	224/5	17.7	24.5	0.70	0.36	0.25	1.76	0.12	0.70	0.73	0.88	0.17
WPB-4 Q	E-U	0.58	-33.01	13.3	188/24	17.4	21.5	0.32	0.91	0.29	1.12	0.34	0.55	0.73	0.94	0.36
Indet. 2 K B																
		0.37	-33.34	34.2	17/13	18.6	21.3	-	-	-	-	-	-	-	-	-
Bitumen WPM E-L																
		6.75	-33.30	23.2	n.d./	n.d.	14.3	0.10	-	-	1.38	1.09	0.06	0.52	0.99	1.52
n.d.																

¹See text; Indet. = indeterminate due to low pyrolysis yield.²Geographic/stratigraphic subdivisions: E, W = east and west study areas, respectively; L, M, U = lower, middle and upper stratigraphic divisions, respectively; B = outcrop section 2 (see Fig. 4).³ T_{max} refers to retention times for maximum pyrolysis evolution (i.e. proportional to Rock Eval[®] pyrolysis T_{max}).⁴Normalized abundance of $n\text{-C}_9$ (alkene + alkane) over the $n\text{-C}_{16-22}$ range.⁵After the kerogen pyrolysis typing scheme of Larter (1984) except creosols (two, methyl phenol isomers) are used rather than phenol.⁶Sum of alkenes + alkanes ($n\text{-C}_{16-22}$) over toluene + xylenes ($m\text{-}$ + $p\text{-}$ + $o\text{-}$ xylenes and ethyl benzene).⁷Naphthalene/toluene.⁸Ratio of sum of alkenes over that of alkanes ($n\text{-C}_{16-18}$ range).⁹Calculated vitrinite reflectance using the MPI- T relationship (cf. Radke and Welte, 1983).¹⁰Carbon preference index using $n\text{-alkenes}$ + $n\text{-alkanes}$.¹¹Ratio of presumed branched alkenes/alkanes over $n\text{-alkenes}$ ($n\text{-C}_{15-20}$ range).¹²Not determined.¹³Ratio could not be determined due to lack of well-defined peaks.

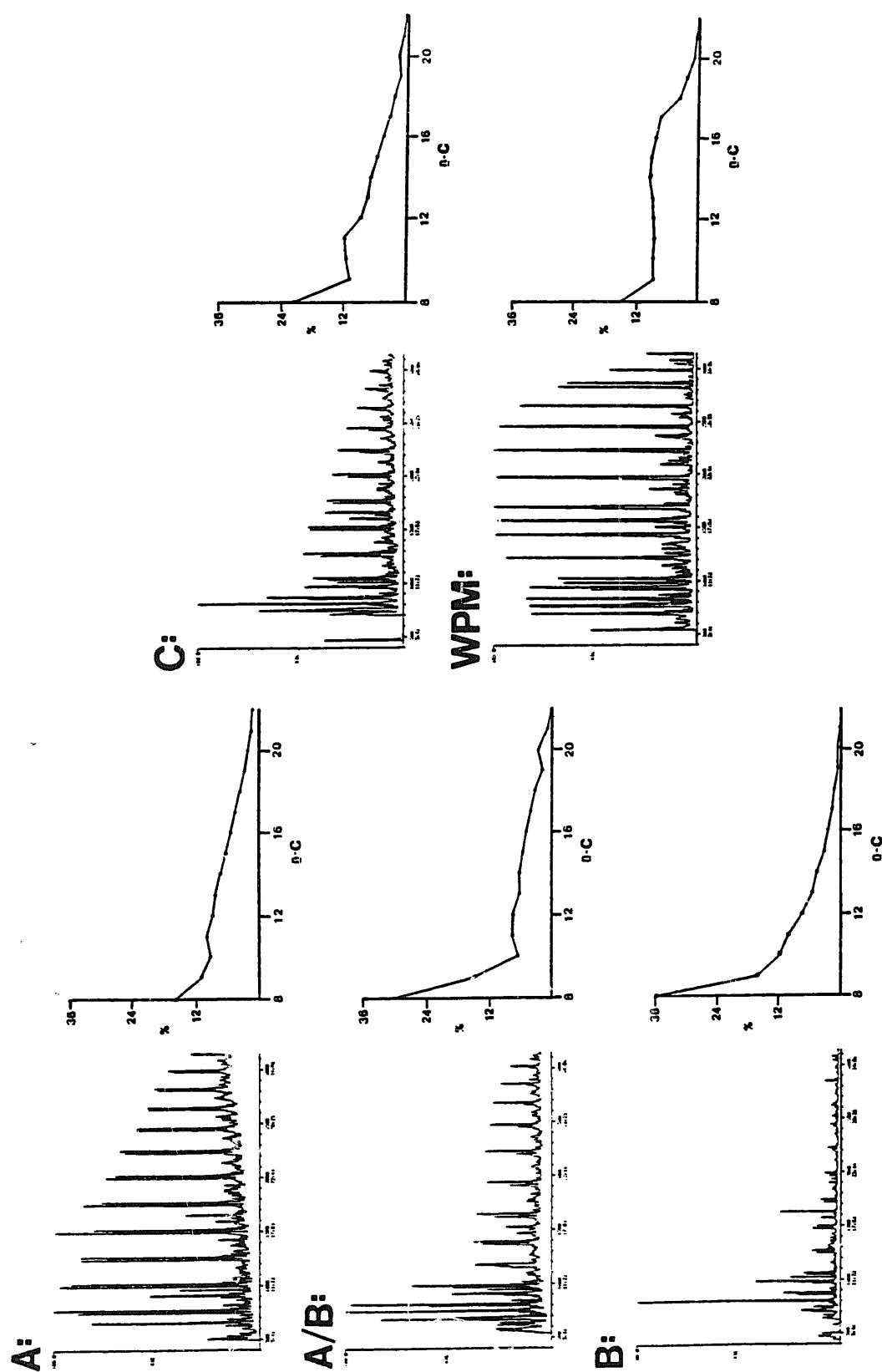


Fig. 6. PY-GC-MS RIC (reconstructed ion chromatogram) traces and normalized n -alkane plus n -alkane distribution (n -C₈₋₂₂) for samples representing Nonesuch Formation kerogen pyrolysate groups. Pyrolysate group A/B represents a continuum between the A and B end-members whereas C appears to have a unique molecular distribution. WPM, representing a bitumen impregnated sandstone from the White Pine Mine, appears, by its high aliphatic content, to be related to group A kerogens.

both thermal slices in the eastern kerogen but they were absent in the western kerogen (Imbus, 1990). Sterane compounds were not detected in the pyrolysates. Recently, Pratt et al. (1991) reported suites of pentacyclic triterpanes (C_{27-35}) and steranes (C_{26-30}) from Nonesuch Formation solvent extracts and the White Pine Mine seep. The unusual abundance of a C_{30} sterane compound (24-*n*-propyl cholestane) was proposed to indicate a marine depositional environment. Inference of a marine vs. lacustrine origin for the Nonesuch Formation on the basis of biological marker parameters lacks foundation at present due to the unusual biomarker distributions noted in some Proterozoic sediments (e.g., Grantham and Wakefield, 1988; Summons et al., 1988a) and the absence of data from firmly established Precambrian analogs.

The heterogeneity of pyrolysate group-B kerogens and the contrast in overall molecular composition of pyrolysate group-A and -B kerogens, does not account for the mean 0.3‰ $\delta^{13}C_{KER}$ depletion of the western relative to the eastern kerogens. With the exception of the "b/e" ratio, no relationship is apparent between pyrolysate molecular ratios and $\delta^{13}C_{KER}$. Sequential solvent extraction of the western sample produced an isotopically enriched extract (in contrast to the typical relationship; cf. Stahl, 1977) with no corresponding depletion in the extracted kerogen. Evidently, this highly enriched extractable material (which probably has a counterpart in the subordinate, labile fraction of the western kerogen) represents the contribution of a non-FOM, perhaps bacterial-derived, organic material (see also Hieshima et al., 1989). Whereas bacterial activity apparently influenced the molecular composition of pyrolysate group-B kerogens, it did so without altering its overall isotopic composition. These considerations compel us to look towards influences unrelated to molecular composition to explain kerogen stable carbon isotopic variability in the Nonesuch Formation.

3.6. Additional elemental and stable isotope studies (C_{CARB} , S , N)

3.6.1. Carbonate carbon and oxygen stable isotopes ($\delta^{13}C_{CARB}$, $\delta^{18}O_{CARB}$). Carbonate carbon and oxygen stable isotope analyses ($\delta^{13}C_{CARB}$, $\delta^{18}O_{CARB}$, respectively) were performed on 69 "regular" Nonesuch Formation samples representing the full range of % $CaCO_3$ values. Additional samples analysed included calcite-filled veins and fractures (some hosting oil-filled vugs) and a calcitized evaporite bed (upper west "carbonate facies"; cf. Elmore et al., 1989) from the Nonesuch Formation and Copper Harbor Formation stromatolites, oncolites and calcite cements associated with arkoses and conglomerates (Table 3).

The regular Nonesuch Formation samples show a considerable $\delta^{13}C_{CARB}$ and $\delta^{18}O_{CARB}$ range (−20.5 to −1.7‰ and −17.9 to −2.3‰, respectively). This range spans the "marine limestones", "lacustrine limestones" and "common diagenetic cements" fields (see Fig. 7a). A basis for distinguishing "sedimentary" vs. "diagenetic" carbonates is proposed (Fig. 7b). Carbonate-rich samples (> ~20% $CaCO_3$), mostly representing carbonate laminitic lithologies (see Fig. 7c for distribution of carbonate-rich samples), are usually isotopically enriched relative to carbonate lean, or "diagenetic" carbonates. The diagenetic carbonates likely represent early cements where ^{18}O -depleted and late cements where ^{18}O -enriched. The boundary of $\delta^{18}O_{CARB} = -12‰$ was selected based on isotopic trends known to result from meteoric water influence (cf. Kharaka et al., 1985) and the presence of minute calcite veins and fractures associated with samples bearing these $\delta^{18}O_{CARB}$ -values.

Some observations and tentative interpretations are made by examining isotopic data obtained from samples other than the "regular" Nonesuch Formation samples. Several distinct portions of two mineralized (Fe-oxides and Cu) Copper Harbor Formation stromatolite samples (eastern outcrops) produced

a narrow range of $\delta^{13}\text{C}_{\text{CARB}}$ - and $\delta^{18}\text{O}_{\text{CARB}}$ -values (-2.3 to -1.2‰ and -7.7 to -6.8‰ , respectively). As these values overlap those of the Nonesuch Formation carbonate laminites, it is tempting to invoke a common dissolved carbonate feedstock that reflects the ancient water body chemistry (lacustrine or marine) and/or hydrothermal influence. Close similarities in $\delta^{13}\text{C}_{\text{CARB}}$ -values among the aforementioned samples and hydrothermal calcites from the Portage Lake Lava Series underlying the Copper Harbor Conglomerate (Livnat, 1983) appear to favor the latter interpretation. The $\delta^{18}\text{O}_{\text{CARB}}$ -values vary widely, however, and, at any rate, isotopic signals are seldom distinct enough to factor out simple coincidence. Cements associated with arkosic sandstones in the Copper Harbor Formation are depleted in both ^{13}C and ^{18}O , suggesting organic and meteoric influence. Finally, calcite-filled veins and fractures (sometimes associated with oil), commonly found in the upper east and upper west (respectively), often have extremely depleted $\delta^{13}\text{C}_{\text{CARB}}$ - and $\delta^{18}\text{O}_{\text{CARB}}$ -values (to $\sim -22\text{‰}$ and $\sim -15\text{‰}$, respectively). These calcites probably precipitated from meteoric water-bearing oil oxidation products (late cements).

The possible role of the "planktonic bloom" model for calcite precipitation in lacustrine settings was invoked by Elmore et al. (1989) to explain the origin of carbonate laminites in the Nonesuch Formation. The similar carbon and oxygen isotopic values for the carbonate laminites of the Nonesuch Formation (present study) and the Middle Devonian Orcadian Basin lacustrine (calc-micritic) carbonate laminites (Janaway and Parnell, 1989) may represent signals typical of lacustrine carbonate laminites or, simply coincidence. In contrast, the $\delta^{13}\text{C}_{\text{CARB}}$ -depleted values associated with carbonate lean samples originates from well-understood processes involving the incorporation of organic degradation by-products of bacterial oxidation or sulfate reduction as opposed to bacterial fermentation or abiotic re-

actions (cf. Irwin et al., 1977; Pierre, 1989) into early cements.

Cross-correlation (linear regression) of the parameters TOC, % CaCO_3 , $\delta^{13}\text{C}_{\text{KER}}$, $\delta^{13}\text{C}_{\text{CARB}}$ and HI may enable a better understanding of the ancient Nonesuch carbon cycle. The distribution of $\delta^{18}\text{O}_{\text{CARB}}$ -values may be useful in detecting overprinting by early or later diagenetic processes (e.g., recrystallization by connate, hydrothermal or meteoric waters).

Positive correlations between % CaCO_3 and $\delta^{13}\text{C}_{\text{CARB}}$ are noted for both the east and west lower + middle carbonate laminites. A similar relationship, observed in modern Lake Greifen (Switzerland) calcite laminites by McKenzie (1982, 1985), was interpreted as an indicator of calcite precipitation in response to late spring-early summer mass planktonic blooms (cf. Kelts and Hsü, 1978). Dissolved carbonate ions available for calcite precipitation become increasingly enriched in ^{13}C as photosynthetic organisms preferentially abstract isotopically depleted inorganic carbon. That only a marginally positive correlation between these parameters is noted for the east may indicate calcite precipitation at a greater water depth or that other processes interfered with the signal.

An apparent (but not statistically significant) positive correlation between TOC and % CaCO_3 in the east may lend further support to a link between planktonic blooms and calcite precipitation. The inverse correlation between TOC and $\delta^{13}\text{C}_{\text{KER}}$ noted for the west is an indication of recycling of degradation products. Strong negative correlations between $\delta^{13}\text{C}_{\text{KER}}$ and HI (east and west) suggest that lower HI values resulting from degradation are achieved by the preferential loss of isotopically depleted aliphatic moieties. This relationship was not observed for the general population of Nonesuch Formation samples.

The $\delta^{18}\text{O}_{\text{CARB}}$ -values observed for the carbonate-rich samples are suggestive of limited meteoric influence. The relationship between $\delta^{13}\text{C}_{\text{CARB}}$ and $\delta^{18}\text{O}_{\text{CARB}}$ has been used by Tal-

TABLE 3

Results of carbonate stable isotope analyses for "regular" Nonesuch Formation samples, Copper Harbor Formation stromatolites and cements and other, miscellaneous samples

Sample I.D.	Geogr./ strat.* ¹	Carb./ lith.* ^{2,3}	TOC	$\delta^{13}\text{C}_{\text{KER}}$ (‰ vs. PDB)	% CaCO_3	$\delta^{13}\text{C}_{\text{CARB}}$ (‰ vs. PDB)	$\delta^{18}\text{O}_{\text{CARB}}$ (‰ vs. PDB)
DO-8 F	W-L	—	0.37	−33.63	16.3	−7.28	−7.58
DO-8 G	W-L	+	0.10	−33.18	31.9	−6.18	−9.31
DO-8 K	W-M	+	0.27	−33.45	57.0	−2.82	−8.53
DO-8 M	W-M	+	0.74	−33.99	34.6	−2.03	−9.11
DO-8 29	W-M	+	0.22	−33.68	53.1	−2.32	−7.90
DO-8 L	W-M	+	0.27	−33.80	59.6	−2.37	−8.37
DO-8 27	W-U	—	0.44	−33.67	14.4	−5.77	−6.37
DO-8 56	W-U	—	0.52	−34.08	17.1	−9.65	−5.26
DO-8 R	W-U	—	0.55	−33.79	15.0	−8.31	−2.83
DO-8 58	W-U	—	0.33	−33.90	14.4	−11.44	−5.14
WC-25 A	W-L	0	0.24	−34.04	22.4	−10.76	−9.11
WC-25 S2	W-L	—	1.46	−34.63	13.9	−8.36	−4.46
WC-25 B	W-L	+	0.69	−34.72	48.3	−2.79	−7.90
WC-25 F	W-M	+	0.39	−34.32	33.5	−1.90	−8.07
WC-25 I	W-M	—	0.28	−33.41	14.3	−7.88	−6.35
WC-25 L	W-U	—	0.25	−33.51	15.7	−9.88	−8.74
WC-9 D	W-M	—	0.32	−33.38	16.0	−9.08	−13.01
WC-9 E	W-M	0	0.19	−33.92	28.1	−7.40	−10.69
WC-9 I	W-M	+	0.30	−33.70	48.1	−3.07	−9.72
WC-9 K	W-M	—	0.66	−33.96	19.5	−1.85	−9.17
WC-9 00	W-M	0	0.51	−34.02	50.0	−2.29	−9.05
WC-9 L	W-M	—	0.46	−33.46	16.3	−5.96	−5.41
WC-9 97	W-M	— (I)	1.34	−34.18	10.9	−5.51	−5.49
WC-3 B	W-L	— (I)	0.07	−31.62	50.0	−4.10	−10.04
WC-3 H	W-M	0 (I)	0.35	−33.96	55.7	−1.93	−8.62
WC-3 J	W-M	— (I)	0.65	−33.99	13.8	−7.72	−3.03
WC-3 K	W-M	0	0.65	−33.90	22.6	−5.27	−11.50
2 K	B	0	0.37	−33.34	21.2	−10.48	−16.00
6b F	E-L	0	0.56	−33.63	30.4	−2.46	−8.18
PI-2 A	E-L	0	0.24	−33.61	22.4	−7.57	−6.75
PI-2 C	E-M	+	0.39	−33.68	44.2	−2.59	−8.47
PI-2 805	E-M	+	0.41	−33.78	53.8	−2.49	−8.17
PI-2 D	E-M	0	0.38	−33.69	42.2	−2.09	−6.95
PI-2 J	E-M	—	0.52	−33.48	12.5	−10.54	−8.05
PI-2 19	E-M	—	0.70	−33.64	13.4	−10.08	−12.35
PI-2 S	E-U	—	0.46	−32.63	17.4	−9.54	−7.59
PI-2 Y	E-U	0	0.33	−34.07	22.8	−5.95	−5.35
PI-2 BB	E-U	+	0.09	−31.92	31.8	−12.06	−12.21
PI-2 Z	E-U	—	0.84	−33.94	10.6	−7.27	−8.01
PI-2 AA	E-U	—	0.94	−33.4?	11.6	−10.14	−2.29
PI-2 CC	E-U	—	0.39	−32.63	8.9	−8.32	−2.76
8 G	E-L	0	0.80	−33.05	35.8	−1.78	−8.41
8 H	E-M	—	0.80	−32.71	10.3	−8.30	−12.30
8 Y	E-U	—	0.61	−33.03	12.0	−20.43	−14.65
WPB-8 D	E-L	0	0.59	−33.81	27.1	−2.43	−9.13
WPB-8 I	E-L	0	0.93	−34.05	38.2	−2.20	−8.75
WPB-8 M	E-M	—	1.93	−33.63	11.4	−6.57	−5.62
WPB-8 45	E-M	—	1.28	−33.33	12.3	−10.50	−12.95
WPB-8 V	E-U	0	0.22	−33.26	24.9	−9.17	−9.39
WPB-8 W	E-U	—	1.94	−33.53	12.9	−10.21	−4.70

TABLE 3 (continued)

Sample I.D.	Geogr./ strat.* ¹	Carb./ lith.* ^{2,3}	TOC	$\delta^{13}\text{C}_{\text{KER}}$ (‰ vs. PDB)	% CaCO_3	$\delta^{13}\text{C}_{\text{CARB}}$ (‰ vs. PDB)	$\delta^{18}\text{O}_{\text{CARB}}$ (‰ vs. PDB)
WPB-8 X	E-U	—	0.76	−33.87	14.7	−12.43	−12.62
WPB-8 21	E-U	— (2)	0.38	−32.14	12.6	−20.46	−16.80
WPB-1 G	E-L	+ (3)	0.69	−33.82	36.4	−1.68	−7.47
WPB-1 54	E-L	+ (1,2)	0.42	−34.14	49.4	−3.42	−10.20
WPB-1 I	E-L	+ (3)	0.67	−33.96	31.8	−2.16	−8.69
WPB-1 J	E-L	— (1)	0.54	−33.75	13.6	−8.70	−13.76
WPB-1 O	E-M	—	0.66	−33.16	12.9	−15.06	−14.66
WPB-1 S	E-M	—	0.04	−32.19	17.9	−15.55	−16.35
WPB-1 V	E-M	—	0.91	−33.48	12.8	−6.22	−6.83
WPB-4 A	E-L	— (2)	0.64	−31.58	39.9	−12.19	−17.90
WPB-4 B	E-L	0	0.64	−33.93	40.0	−2.43	−8.95
WPB-4 G	E-M	—	0.54	−33.55	15.0	−14.08	−14.73
WPB-4 H	E-M	—	0.37	−33.27	12.6	−12.52	−8.48
WPB-4 N	E-U	+	0.10	−29.97	20.3	−12.08	−8.42
WPB-4 Q	E-U	—	0.58	−33.01	12.3	−12.34	−14.67
WPB-4 R	E-U	—	0.72	−33.05	15.5	−8.18	−8.35
WPB-4 V	E-U	—	1.11	−34.46	16.9	−10.22	−8.96
11 F	E-L	+	0.65	−33.74	33.1	−2.00	−9.18
11 H	E-M	0	1.05	−33.90	20.2	−3.66	−9.59
S1* ³ a	E-CuH	ah	n.d.	n.d.	90+	−1.21	−6.82
S1 b	E-CuH	ah	n.d.	n.d.	90+	−1.23	−6.81
S1 c	E-CuH	om	n.d.	n.d.	90+	−1.36	−7.37
S2* ³ a (1)	E-CuH	m	n.d.	n.d.	90+	−2.26	−8.30
S2 a (2)	E-CuH	m	n.d.	n.d.	90+	−1.90	−7.11
S2 b	E-CuH	ah	n.d.	n.d.	90+	−1.33	−7.28
S2 c (1)	E-CuH	gdm	n.d.	n.d.	90+	−1.26	−7.55
S2 c (2)	E-CuH	cdm	n.d.	n.d.	90+	−1.28	−7.69
S2 e	E-CuH	onc	n.d.	n.d.	90+	−1.25	−7.60
S2 f	E-CuH	oxz	n.d.	n.d.	90+	−1.40	−7.56
E* ³	W-U	~0	n.d.	n.d.	~100	−6.10	−8.69
V* ³ 1	E-CuH	lv (S2)	n.d.	n.d.	~100	−2.46	−7.22
V 2	W-U	lv	n.d.	n.d.	~75	−22.57	−9.72
V 3	W-U	lv	n.d.	n.d.	~75	−22.72	−15.58
C* ³ 1	E-CuH	cgic	n.d.	n.d.	~100	−1.86	−6.29
C 2	W-CuH	cgic	n.d.	n.d.	~100	−2.68	−7.20
C 3	E-CuH	arkc	n.d.	n.d.	~25	−8.19	−10.90
C 4	W-CuH	arkc	n.d.	n.d.	~25	−10.77	−13.81
F* ³ 1	E-U	lf (333)	n.d.	n.d.	~50	−18.46	−12.59
F 2	E-U	lf(o)	n.d.	n.d.	~50	−5.89	−8.32
F 3	E-U	lf(o)	n.d.	n.d.	~50	−15.44	−13.35

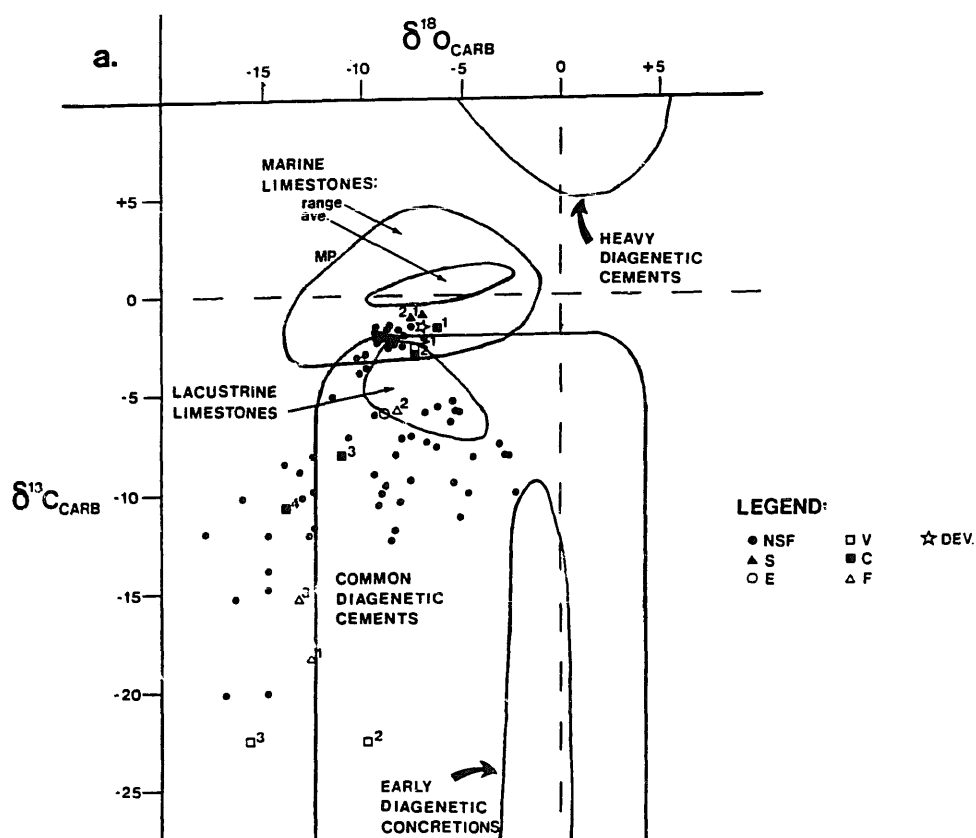
*¹Geographic/stratigraphic subdivisions: E, W= east and west study areas, respectively; L, M, U= lower, middle and upper stratigraphic divisions, respectively; B= outcrop section 2 (see Fig. 1).

*²Carbonate lithology: —, 0, + = non-, possible and definite carbonate laminite character; number in parentheses refers to other carbonate features: 1 = calcite-filled late veins; 2 = recrystallized zones; 3 = other features (e.g., calcite-rich fluid escape structures).

*³Samples other than "regular" Nonesuch Formation samples (CuH = Copper Harbor Fm.): S = stromatolites (ah = algal head, om = oolitic matrix, m = mat, gdm = grain-dominated matrix, cdm = cement-dominated matrix, onc = oncolite, oxz = oxidized zone); E = calcitized evaporite bed (cf. carbonate facies; Elmore et al., 1989); V = veins (lv = late vein); C = cements (cgic = associated with conglomerate facies, arkc = associated with arkosic facies); F = fractures (lf = late fractures, (o) = associated with oil).

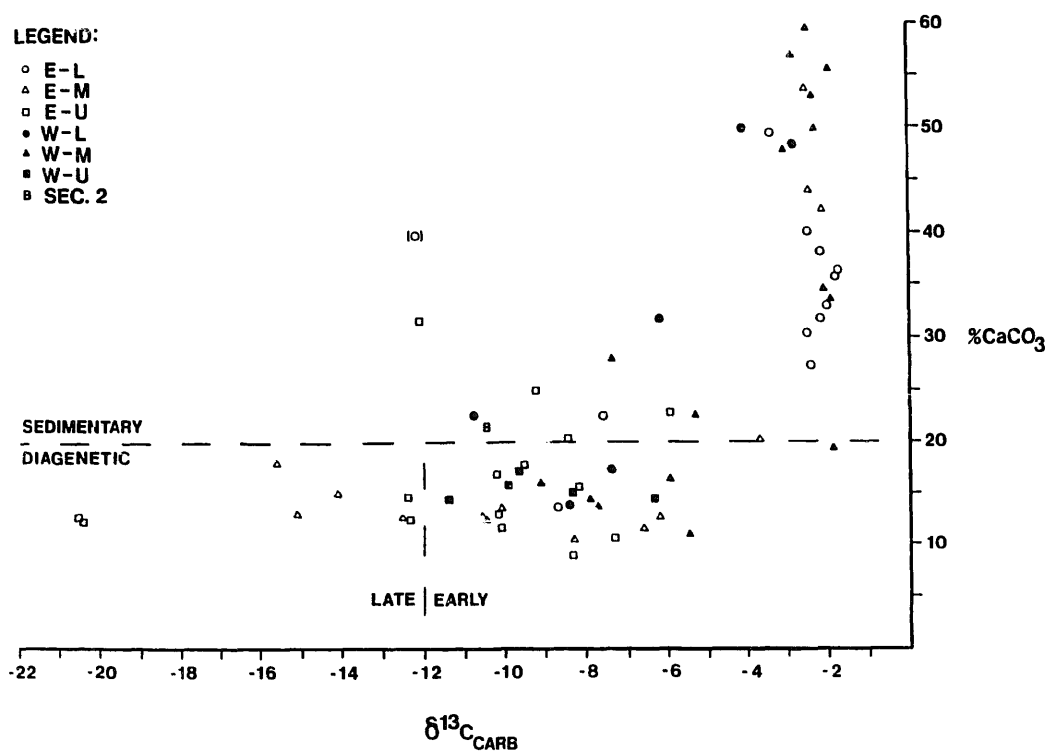
bot (1990) to infer modern lacustrine hydrologic cycles. Accordingly, the positive correlation between these parameters in the west sug-

gests a closed hydrologic cycle whereas the lack of such a correlation in the east suggests an open hydrologic cycle.



b. LEGEND:

- E-L
- △ E-M
- E-U
- W-L
- ▲ W-M
- W-U
- 8 SEC. 2



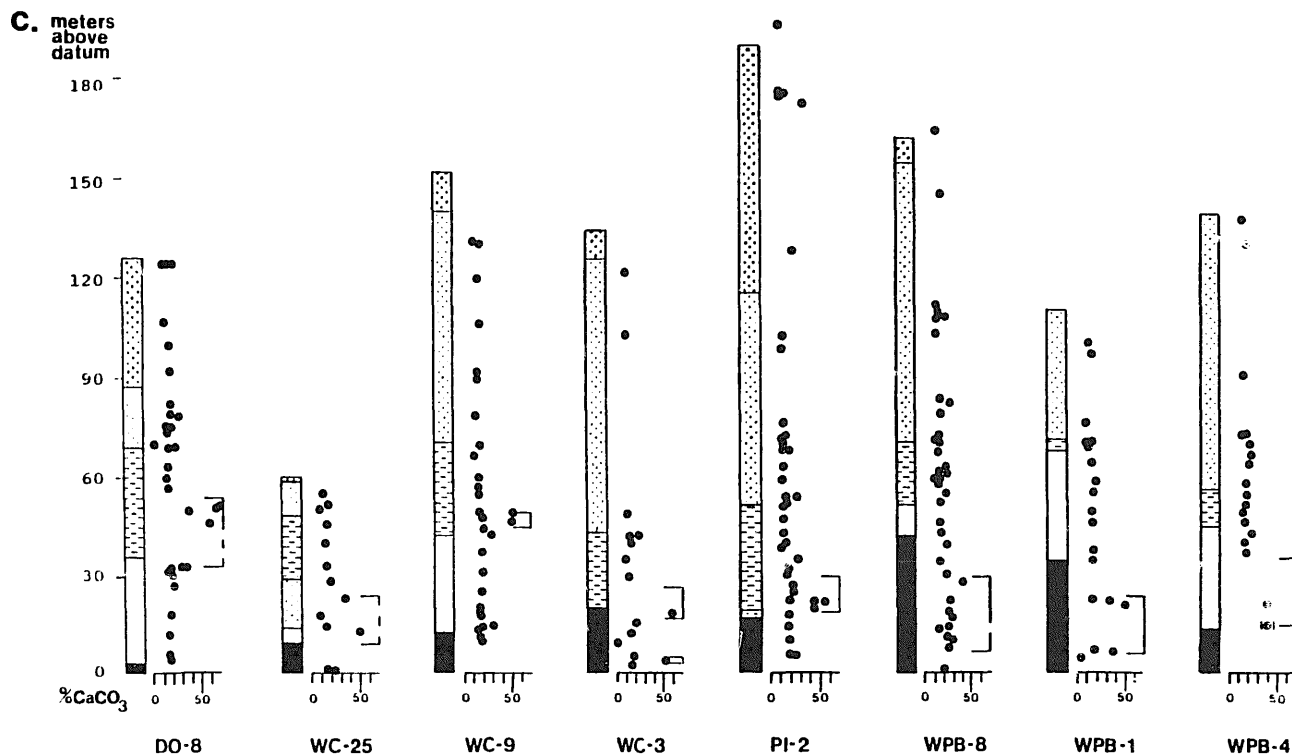


Fig. 7. Nonesuch Formation carbonate stable isotope study. a. A cross-plot of $\delta^{13}\text{C}_{\text{CARB}}$ and $\delta^{18}\text{O}_{\text{CARB}}$ for Nonesuch and Copper Harbor Formation samples (see Table 3 for legend) analysed in the present study superimposed over common depositional and diagenetic fields and Orcadian Basin carbonate laminites (*star* = after Janaway and Parnell, 1989) (after Anderson and Arthur, 1983; Dimitrakopoulos and Muehlenbachs, 1987; Janaway and Parnell, 1989). b. Proposed classification of sedimentary and early/late diagenetic carbonates from the Nonesuch Formation. c. Approximate distribution of carbonate laminates (enclosed in *brackets*).

3.6.2. Total sulfur and sulfide sulfur stable isotopes (S , $\delta^{34}S$). Total sulfur (% S) values typically reflect the quantity of reduced sulfur in rocks (i.e. sedimentary sulfide, principally pyrite). In the present study, % S (Table 4) was found to range from 0.2% to 3.5% (mean = $1.92 \pm 0.76\%$). Burnie et al. (1972), in their analysis of the lower Nonesuch Formation sedimentary sulfides at the White Pine Mine, obtained somewhat lower values (maximum = 2.0%; mean = $1.04 \pm 0.62\%$).

The Nonesuch Formation % S and TOC data (and resultant regression lines) are plotted in Fig. 8. Despite the considerable scatter, an

overall positive trend between TOC and % S is noted both visually and statistically (significant at 99.0% C.I.; see ALL in Fig. 8). If only samples from the lower+middle portions of the formation (east and west; designated as L+M) are considered, a positive correlation significant at 95% C.I. is obtained. Whereas a significant correlation (98% C.I.) is obtained when only the eastern lower+middle samples are considered [E(L+M)], the corresponding correlation for the western samples is not significant [W(L+M)].

The Nonesuch Formation regression lines (Fig. 8) fall between established "euxinic" and

TABLE 4

Results of total sulfur and sulfide $\delta^{34}\text{S}_{\text{PY}}$ analyses of selected Nonesuch Formation samples

Sample I.D.	Geogr./strat.* ¹	TOC* ²	$\delta^{13}\text{C}_{\text{KER}}$ (‰ vs. PDB)	% CaCO_3 * ²	HI* ³	% S* ⁴	S/C* ⁵	$\delta^{34}\text{S}_{\text{FY}}$ * ⁶ (‰ vs. CDT)	$\frac{\text{sel}}{\text{oct+tol}}$ * ⁷
DO-8 K	W-M	0.3	-33.45	57.0	107	1.4	4.7	n.d.* ⁸	n.d.
DO-8 L	W-M	0.4	-33.80	59.6	183	1.2	3.0	n.d.	n.d.
DO-8 W	W-M	1.2	-33.50	14.8	136	2.4	2.0	n.d.	1.1
DO-8 56	W-U	0.6	-34.08	17.1	45	1.1	1.8	5.5	0.4
DO-8 R	W-U	0.5	-33.79	15.0	36	1.1	2.2	n.d.	n.d.
WC-25 52	W-L	1.5	-34.63	13.9	78	0.2	0.1	—* ⁹	0.0
WC-25 B	W-M	0.7	-34.72	48.3	251	1.1	1.6	-0.9	2.0
WC-25 F	W-L	0.4	-34.32	33.5	179	1.2	3.0	n.d.	n.d.
WC-25 M	W-U	1.4	-33.49	9.1	123	3.3	2.4	4.5	6.0
WC-9 I	W-M	0.5	-33.70	48.1	147	1.6	3.2	n.d.	n.d.
WC-9 00	W-M	0.6	-34.02	50.0	133	1.0	1.7	13.1	1.2
WC-9 L	W-M	0.4	-33.46	16.3	159	2.5	6.2	n.d.	n.d.
WC-9 97	W-M	1.2	-34.18	10.9	162	2.4	2.0	n.d.	n.d.
WC-3 J	W-M	0.6	-33.99	13.8	75	2.1	3.5	7.6	1.4
WC-3 K	W-M	0.6	-33.90	22.6	115	2.4	4.0	n.d.	n.d.
WC-3 L	W-M	0.6	-33.46	12.9	70	2.0	3.3	n.d.	n.d.
2 J	B	0.2	-33.98	24.0	58	1.1	5.5	n.d.	n.d.
2 K	B	0.2	-33.34	21.2	17	1.1	5.5	n.d.	1.0
6b F	E-L	0.5	-33.63	30.4	110	0.9	1.8	n.d.	0.1
6b O	E-M	0.8	-33.46	11.3	415	1.6	2.0	n.d.	n.d.
6b P	E-M	0.6	-33.50	11.3	313	1.6	2.7	n.d.	n.d.
PI-2 R	E-U	0.2	-32.79	12.3	190	3.0	15.0	n.d.	n.d.
PI-2 Z	E-Ut	0.8	-33.94	10.6	224	2.0	2.5	3.9	2.2
PI-2 AA	E-U	0.8	-33.43	11.6	38	2.4	3.0	7.8	2.2
PI-2 CC	E-U	0.5	-32.63	8.9	105	2.6	5.2	n.d.	n.d.
8 F	E-L	0.9	-33.67	26.9	18	2.7	3.0	n.d.	n.d.
8 G	E-M	0.7	-33.05	35.8	31	1.2	1.7	n.d.	n.d.
WPB-8 G	E-L	0.5	-33.62	27.3	89	1.8	3.6	n.d.	n.d.
WPB-8 I	E-L	0.8	-34.05	38.2	314	1.3	1.6	-2.5	0.4
WPB-8 M	E-M	1.7	-33.63	11.4	454	3.5	2.1	8.7	2.0
WPB-8 47	E-M	1.5	-33.42	11.3	432	2.3	1.5	7.1	2.2
WPB-8 45	E-M	1.7	-33.33	12.3	450	3.0	1.8	5.7	2.3
WPB-8 W	E-U	1.9	-33.53	12.9	443	3.0	1.6	n.d.	n.d.
WPB-1 G	E-L	0.8	-33.82	36.4	275	2.3	2.9	n.d.	n.d.
WPB-1 J	E-L	0.5	-33.75	13.6	70	1.8	3.6	-2.5	1.1
WPB-4 B	E-L	0.7	-33.93	40.0	238	2.8	4.0	n.d.	n.d.
WPB-4 I	E-M	0.4	-33.77	13.6	295	2.1	5.2	n.d.	n.d.
WPB-4 Q	E-U	0.5	-33.01	12.3	188	2.6	5.2	9.6	6.5
WPB-4 R	E-U	0.6	-33.05	15.5	91	1.8	3.0	6.6	1.2
11 F	E-L	0.5	-33.74	33.1	88	1.4	2.8	n.d.	n.d.
11 H	E-M	0.8	-33.90	20.2	161	2.0	2.5	T.S.	4.6

*¹Geographic/stratigraphic subdivisions: E, W= east and west study areas, respectively; L, M, U= lower, middle and upper stratigraphic divisions, respectively; B= outcrop section 2 (see Fig. 1).

*²TOC analyzed by Texaco, Inc., Houston, Texas; % CaCO_3 data from present study.

*³Rock Eval® hydrogen index.

*⁴%S-total sulfur analyzed by Texaco, Inc., Houston, Texas.

*⁵S/C= total sulfur/TOC.

*⁶Sulfide stable sulfur isotopes analyzed by Coastal Laboratories, Inc., Austin, Texas.

*⁷Ratio of elemental sulfur and *n*-octene toluene as determined by PY-GC-MS analysis.

*⁸Not determined.

*⁹Insufficient yield for analysis.

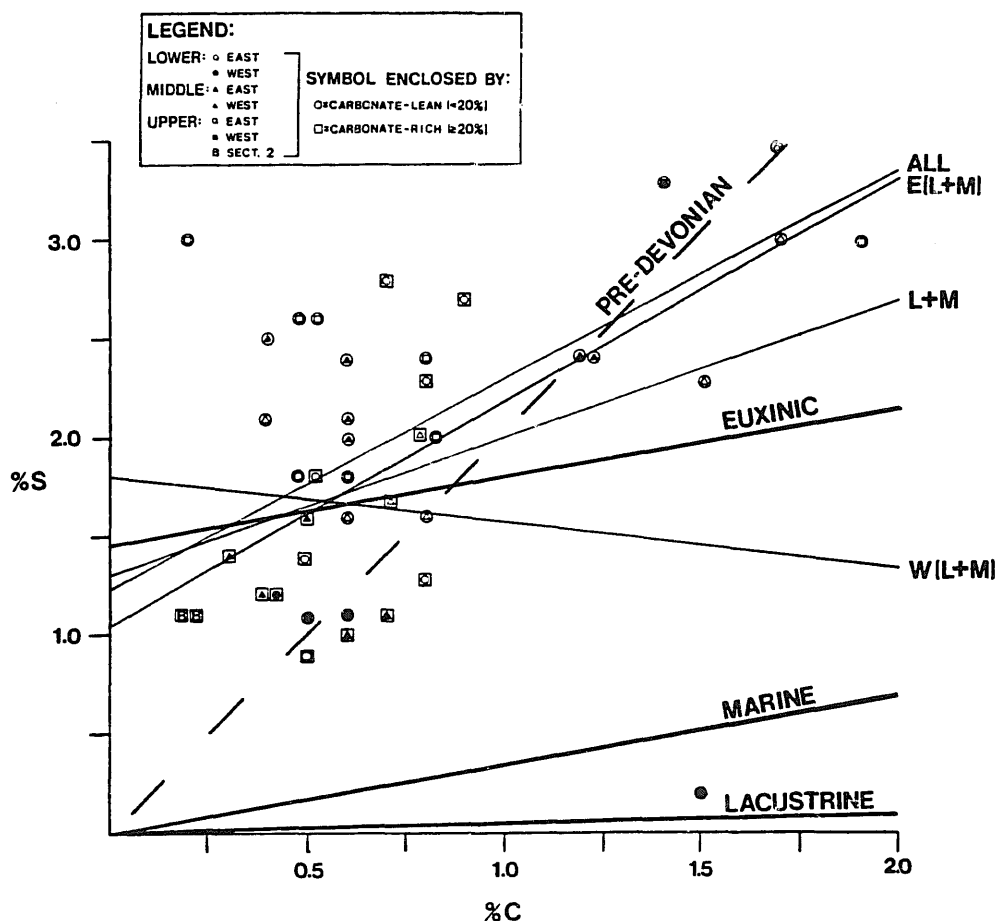


Fig. 8. Cross-plot of Nonesuch Formation carbon and sulfur elemental data. Regression lines are shown both for the predicted S and C relationships established in the literature (after Berner and Raiswell, 1983; Berner, 1984; Holser et al., 1988) and for selected geographic/stratigraphic divisions of the Nonesuch Formation.

“pre-Devonian” lines (in the high-TOC portion) and have positive S intercepts. Therefore, pyrite deposition in the Nonesuch waters may reflect the “euxinic” situation whereby pyrite is formed both in the water column and at the sediment–water interface (cf. Leventhal, 1983; Berner, 1984). Superimposed upon this process, perhaps, is one or more of the three possible secular influences postulated for pre-Devonian sediments by Berner and Raiswell (1983), particularly the presence of higher proportions of more metabolizable organic matter. However, the fact remains that pyrite formation is typically low in lacustrine systems relative to those of normal marine salinity (barring of course highly saline lakes, for which at present no evidence exists for the Nonesuch Formation). Pyrite, as documented by % S determinations and petrographic observation, is undeniably present in substantial quantities in the Nonesuch Formation and

shows an overall positive relationship to TOC. Therefore, we are faced with evidence possibly refuting a lacustrine interpretation for the Nonesuch Formation or the need to examine alternative mechanisms for the presence of high levels of sulfur in the formation.

Three general mechanisms accounting for the magnitude of pyrite formation in the quantities observed, consistent with a lacustrine depositional model, may be proposed for the Nonesuch Formation.

(1) On the basis of the pyrite formation reactions outlined by Davison (1988), substantial levels of pyrite may have been formed from the accumulation of sulfide ions (derived from biologic processes and subsequently oxidized to sulfate) in the lake.

(2) A variety of external sulfate sources may have been introduced to the lake waters (e.g., erosion of sulfate-bearing terranes, marine incursions).

(3) Injection of sulfur-rich hydrothermal fluids, either into the water body or early sediments, is clearly possible.

A possible, analogous situation was reported by Donnelly and Jackson (1988). The Woollogorang Formation (Middle Proterozoic lacustrine sediments, northern Australia) has % S levels up to 4%. Sulfur appears to be positively correlated to TOC only among samples with <0.3% S. Anomalously high S/C ratios exhibited by many samples were attributed to the introduction of hydrothermal sulfide.

Two general situations are frequently cited in the literature as influencing the magnitude of isotopic fractionation between marine sulfate (secular ranges between $\delta^{34}\text{S} = \sim +10$ to $+30\text{‰}$ throughout the Phanerozoic; cf. Holsen et al., 1988) and sedimentary sulfide. In "open" systems, which are typical of normal marine environments, continual diffusion of seawater into pore waters (upper few cm of sediment) enables large fractionation (typically, $\delta^{34}\text{S}_{\text{SULFIDE}}$ -depletion between -30 and -10‰ from sedimentary sulfate are expected; cf. Hoefs, 1980). "Closed" systems may form in sediments below the top few cm of sediment where the supply of fresh SO_4^{2-} is limited. Applying a Rayleigh distillation model, Schidlowski et al. (1983) proposed a range of sulfide values between -5 and $+5\text{‰}$ (assuming contemporary seawater sulfate $\delta^{34}\text{S} = +20\text{‰}$) for a closed system. They furthermore suggest that euxinic settings, low in sulfate, may approximate a "closed" system.

The Nonesuch Formation $\delta^{34}\text{S}_{\text{SULFIDE}}$ -values obtained in the present study (Table 4) range from -2.5 to $+13.1\text{‰}$ ($n=14$; $\mu = +5.30 \pm 4.56\text{‰}$). No distinction is evident between the east and west study areas. Significant correlations were not obtained between $\delta^{34}\text{S}_{\text{SULFIDE}}$ and % S or TOC. An extensive $\delta^{34}\text{S}_{\text{SULFIDE}}$ study of the lower Nonesuch Formation at the White Pine Mine locality by Burnie et al. (1972) resulted in a mean value similar to that determined in the present study ($+4.48\text{‰}$), but a much larger range (-15.83

to $+31.26\text{‰}$). In general, Burnie et al. (1972) appear to favor a bacterial system, well-nourished with respect to organic matter (but periodically SO_4^{2-} -starved due to brackish conditions), as responsible for the values observed. They further noted an up-section depletion in $\delta^{34}\text{S}_{\text{SULFIDE}}$ -values. This was attributed to the gradual transition to more typically euxinic conditions.

The $\delta^{34}\text{S}_{\text{SULFIDE}}$ range determined for the Nonesuch Formation in the present study and the principal range of -10 to $+18\text{‰}$ determined by Burnie et al. (1972) are relatively enriched compared to normal marine sediments where sulfate concentrations are not limiting (i.e. "open" conditions). However, isotopically enriched $\delta^{34}\text{S}$ -values of Middle Proterozoic sulfides appear to be typical, according to a compilation by Strauss and Schieber (1990). They contend that the distinction between isotopically light (e.g., "early" pyrites of the Newland Formation, Lower Belt Group, Montana) and heavy (the "late" pyrites of the Newland Formation and the bulk of other Middle and Upper Proterozoic units) is one of open vs. restricted conditions with respect to sulfate availability. However, it was acknowledged that biased sampling of deposits associated with sulfide mineralization may too have been influential (i.e. hydrothermally derived sulfides typically have $\delta^{34}\text{S}$ -values of $\sim 0\text{‰}$; cf. Kaplan, 1983). Similarities in $\delta^{34}\text{S}_{\text{SULFIDE}}$ -values between the Nonesuch Formation samples examined and sulfide-bearing veins in the region (cf. Livnat, 1983) are suggestive of hydrothermal influence. Anomalously high S/C ratios in the Nonesuch Formation are apparently corroborative, but linear relationships between % S and TOC argue for pyrite formation via bacterial sulfate reduction in a euxinic setting.

3.6.3. Nitrogen elemental and stable isotopic analysis (% N and $\delta^{15}\text{N}$). Analysis of 25 Nonesuch Formation samples for organically bound nitrogen elemental abundances (% N, C/N)

and stable isotope composition ($\delta^{15}\text{N}$) was conducted in an attempt to infer ancient nitrogen flux and biochemical incorporation mechanisms (Table 5). The samples selected for analysis represent the east and west study areas and contrasting $\delta^{13}\text{C}_{\text{KER}}$ composition. Average nitrogen abundances (% N) appear to be essentially equivalent between the east and west study areas, although C/N are, on average, greater in the east. This suggests a disproportionate concentration of N in the west. Isotopically enriched $\delta^{15}\text{N}$ -values are associated with low C/N values and depleted $\delta^{13}\text{C}_{\text{KER}}$ -values.

TABLE 5

Results of kerogen $\delta^{15}\text{N}$ analysis for selected Nonesuch Formation samples

Sample I.D.	Geogr./ strat.* ¹	TOC	$\delta^{13}\text{C}_{\text{KER}}$ (‰ vs. PDB)	% N	C/N	$\delta^{15}\text{N}_{\text{KER}}$ (‰ vs. atm. N_2)
DO-8 S6	W-U	0.52	-34.08	0.048	12.6	+3.45
WC-25 S2	W-L	1.46	-34.63	0.124	13.8	+8.48
WC-25 B	W-M	0.69	-34.72	0.044	18.3	+5.44
WC-9 00	W-M	0.52	-34.02	0.042	14.5	+4.43
WC-3 J	W-M	0.38	-33.99	0.040	18.9	+3.45
2 K	B	0.37	-33.26	0.026	16.5	+4.21
PI-2 19	E-M	0.70	-33.64	0.046	17.6	+4.35
PI-2 Z	E-U	0.84	-33.94	0.044	22.1	+3.21
PI-2 AA	E-U	0.94	-33.43	0.052	21.0	+4.96
8 H	E-M	0.80	-32.71	0.048	19.3	+3.10
WPB-8 D	E-L	0.59	-33.81	0.028	22.6	+3.16
WPB-8 I	E-L	0.93	-34.05	0.054	20.0	+3.78
WPB-8 M	E-M	1.92	-33.63	0.100	22.3	+3.89
WPB-8 47	E-M	1.48	-33.42	0.091	18.9	+4.82
WPB-8 45	E-M	1.28	-33.33	0.042	21.0	+2.94
WPB-8 X	E-U	0.76	-33.87	-	-	+3.41
WPB-1 J	E-L	0.54	-33.75	0.032	19.6	+3.32
WPB-1 O	E-M	0.66	-33.16	0.038	20.1	+2.72
WPB-1 V	E-M	0.91	-33.48	0.044	23.9	+3.23
WPB-4 B	E-L	0.64	-33.93	0.034	21.8	+3.81
WPB-4 G	E-L	0.54	-33.55	0.036	17.4	+3.17
WPB-4 Q	E-U	0.58	-33.01	0.034	19.8	+3.33
WPB-4 R	E-U	0.72	-33.05	0.040	20.9	+3.68
WPB-4 V	E-U	1.11	-34.07	0.054	23.8	+3.30
11 F	E-L	0.65	-33.74	0.044	17.1	+3.78
11 H	E-M	1.05	-33.90	0.052	23.4	+3.05

*¹Geographic/stratigraphic subdivisions: E, W=east and west study areas, respectively; L, M, U=lower, middle and upper stratigraphic divisions, respectively; B=outcrop section 2 (see Fig. 1).

The total $\delta^{15}\text{N}$ range observed for the Nonesuch Formation (+2.7 to +8.5‰) is largely coincident with the depleted end of the range observed for marine sediments (cf. Schidlowski et al., 1983). Isotopically depleted $\delta^{15}\text{N}$ -values are suggestive of the incorporation of molecular nitrogen ($\delta^{15}\text{N}_{\text{AIR}}=0\text{‰}$) via the activity of symbiotic nitrogen-fixing bacteria associated with higher plants and/or the ability of some free-living prokaryotes (e.g., some cyanobacteria) to fix atmospheric nitrogen. Such incorporation processes typically involve little, if any isotopic fractionation. Isotopically enriched values approaching $\delta^{15}\text{N}=+10\text{‰}$, in contrast, suggest planktonic growth in marine regimes where nitrogen metabolism is effectively limited to the assimilation of nitrate. Intermediate values suggest the mixed contribution of isotopically depleted terrestrial and isotopically enriched marine biomass. The situation in the Precambrian may be simpler as only aquatic algae and microbial organisms were extant. Conceptually, therefore, $\delta^{15}\text{N}$ -values approaching 0‰ would suggest contribution principally of nitrogen fixers (e.g., cyanobacteria) whereas more enriched values indicate additional fractionation (e.g., bacterial degradation).

The nitrogen cycling scenario outlined above, might account for the more enriched $\delta^{15}\text{N}$ -values in the west. That depleted $\delta^{13}\text{C}_{\text{KER}}$ -values (which were previously suggested to originate via recycling of CO_2 from degrading organic matter) are associated with enriched $\delta^{15}\text{N}$ -values, implies the occurrence of greater microbial degradation and subsequent re-incorporation of the products into the biomass of primary producers in the west.

4. Summary and conclusions

The present study, using diverse lines of geochemical data, seeks to account for biotic, sedimentologic, diagenetic and catagenetic factors influencing the nature of sedimentary organic matter in the Middle Proterozoic No-

nesuch Formation. Principal findings and their possible implications for Precambrian organic geochemical studies are outlined below.

Several geochemical parameters distinguish the east (Michigan) and west (Wisconsin) Nonesuch Formation study areas. Secondary distinctions are noted with stratigraphy and lithology. Diminished total organic carbon levels in the west are associated with a dark-gray-black reflective material resembling the algal degradation product bituminite. In contrast, a fluorescing filamentous organic material (FOM), possibly algal in origin, is prevalent in the east. The relative abundance (or absence) of fluorescing-FOM is reflected by the quantity and character of bulk and molecular pyrolysates. Notable exceptions to the aforementioned organic petrologic distinction is conclusive in attributing east/west distinctions to influences other than thermal maturity.

Variability in $\delta^{13}\text{C}_{\text{KER}}$ -values were noted with geographic/stratigraphic position in the basin (the west was depleted in ^{13}C by 0.30‰ relative to the east and a general ^{13}C enrichment was noted up section), with grain size (a moderate depletion in ^{13}C with increasing grain size) and % CaCO_3 (a strong ^{13}C depletion with increasing % CaCO_3). Based on these observations, three influences on $\delta^{13}\text{C}_{\text{KER}}$ variability are possible: (1) diverse primary producers; (2) differential degradation of similar primary producers and subsequent incorporation of resultant components into kerogens; and (3) the origin of inorganic carbon substrates available during photosynthesis. Specialized molecular and stable carbon isotope studies on east and west (aliphatic and aromatic, respectively) kerogens are consistent with differential degradation of the same kerogen precursors.

Cross-correlations among organic (kerogen) and inorganic (carbonate) elemental and carbon stable isotope data from carbonate laminites ($\geq 20\%$ CaCO_3) provide evidence for carbonate precipitation via a "planktonic bloom" mechanism. A negative correlation

between TOC and $\delta^{13}\text{C}_{\text{KER}}$ in the west may indicate enhanced availability of isotopically light CO_2 derived from organic degradation. Lower HI values associated with enriched $\delta^{13}\text{C}_{\text{KER}}$ -values in the west (not observed with the general population of Nonesuch Formation samples) suggest that degradation may involve the loss of ^{13}C -depleted, aliphatic moieties. Carbonate carbon vs. oxygen stable isotope relationships are suggestive of a closed hydrologic system in the west and an open hydrologic system in the east.

Despite the large scatter of data on a total sulfur (% S) and TOC plot, an overall positive correlation is made between these parameters. That this positive correlation persists among eastern samples but is not apparent in the west suggests that the sulfur and carbon cycle is disrupted in the west, possibly due to recycling of degradation products. Isotopically enriched nitrogen stable isotope values in the west are also indicative of degradation (nitrate metabolism or concentration).

The geochemical distinctions noted above are attributed to differential preservation of similar primary producers in the east and west study areas. If not the result of segregation of the Nonesuch water body by a structural boundary, distinct rates of sedimentation or oxic-anoxic boundary depths due to variable tectonic and hydrologic conditions may be involved. Consistencies among parameters related to the ancient carbon system may ultimately be used to infer rates of primary productivity and degradation.

Remarkable isotopic similarities exist among Nonesuch Formation, Copper Harbor Conglomerate and Portage Lake Lava Series hydrothermal carbonates and sulfides. In addition to explaining elevated sulfur values in a presumed lacustrine setting, confirmation of a hydrothermal fluid contribution to the water body or early sediment pore-water chemistry would have important implications for the timing of Cu mineralization in the basal Nonesuch Formation (cf. Kelly and Nishioka,

1985). A hydrothermal source for carbonate ions incorporated into the carbonate laminites (early to middle stage of Nonesuch deposition), for example, would argue for the emplacement of Cu and Cu-sulfides in early sediments (e.g., Vogel et al., 1976) as opposed to lithified(?) sediments at a post-Nonesuch time (e.g., Livnat, 1983).

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References

- Anderson, T.F. and Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and paleoenvironmental problems. In: M.A. Arthur (Organizer), *Stable Isotopes in Sedimentary Geology*. Soc. Econ. Paleontol. Mineral., Short Course, 10: 1-1-1-151.
- Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochim. Cosmochim. Acta*, 48: 605-615.
- Berner, R.A. and Raiswell, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: A new theory. *Geochim. Cosmochim. Acta*, 47: 855-862.
- Bralower, T.J. and Thierstein, H.R., 1984. Low productivity and slow deep-water circulation in mid-Cretaceous oceans. *Geology*, 12: 614-618.
- Burnie, S.W., Schwarcz, H.P. and Crockett, J.H., 1972. A sulfur isotopic study of the White Pine Mine, Michigan. *Econ. Geol.*, 67: 895-914.
- Curtis, C.D., 1987. Inorganic geochemistry and petroleum exploration. *Adv. Pet. Geochem.*, 2: 91-140.
- Davison, W., 1988. Interactions of iron, carbon and sulphur in marine and lacustrine sediments. In: A.J. Fleet, K. Kelts and M.R. Talbot (Editors), *Lacustrine Petroleum Source Rocks*. Blackwell, Oxford, pp. 131-137.
- Dickas, A.B., 1986. Comparative Precambrian stratigraphy and structure along the Mid-Continent rift. *Am. Assoc. Pet. Geol. Bull.*, 70: 225-238.
- Dimitrakopoulos, R. and Muehlenbachs, K., 1987. Biodegradation of petroleum as a source of ^{13}C -enriched carbon dioxide in the formation of carbonate cement. In: N. Clauer and S. Chaudhuri (Editors), *Isotopes in the Sedimentary Cycle*. Chem. Geol. (Isot. Geosci. Sect.), 65: 283-291 (special issue).
- Donnelly, T.H. and Jackson, M.J., 1988. Sedimentology and geochemistry of a mid-Proterozoic lacustrine unit from northern Australia. *Sediment. Geol.*, 58: 145-169.
- Elmore, R.D., 1981. The Copper Harbor Conglomerate and Nonesuch Shale: Sedimentation in a Precambrian intracontinental rift, upper Michigan. Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 200 pp.
- Elmore, R.D., Milavec, G.J., Imbus, S.W. and Engel, M.H., 1989. The Precambrian Nonesuch Formation of the North American Mid-Continent Rift, sedimentology and organic geochemical aspects of lacustrine deposition. *Precambrian Res.*, 43: 191-213.
- Espitalié, J. and Joubert, L., 1987. Use of T_{max} as a maturation index in petroleum exploration. In: R.K. Kumar, P. Dwivedi, V. Bonerjé and V. Gupta (Editors), *Petroleum Geochemistry and Exploration in the Afro-Asian Region*. Balkema, Rotterdam, pp. 67-73.
- Gautier, D.L., 1985. Interpretation of early diagenesis in ancient marine sediments. In: D.C. Gautier, Y.K. Kharaka and R.C. Surdam (Editors), *Relationship of Organic Matter and Mineral Diagenesis*. Soc. Econ. Paleontol. Mineral., Short Course, 17: 6-78.
- Grantham, P.J. and Wakefield, L.L., 1988. Variations in the sterane carbon number distributions of marine source rock derived crude oils through geologic time. *Org. Geochem.*, 12: 61-73.
- Hatcher, P.G., Spiker, E.C., Szeverenyi, N.M. and Maciel, G.E., 1983. Selective preservation and origin of petroleum-forming aquatic kerogen. *Nature (London)*, 305: 498-501.
- Hayes, J.M., Kaplan, I.R. and Wedeking, K.M., 1983. Precambrian organic geochemistry, preservation of the record. In: J.W. Schopf (Editor), *Earth's Earliest Biosphere*. Princeton University Press, Princeton, N.J., pp. 93-134.
- Hieshima, G.B., Zoback, D.A. and Pratt, L.M., 1989. Petroleum potential of Precambrian Nonesuch Formation, Mid-Continent Rift System. *Am. Assoc. Pet. Geol. Bull.*, 73: 363 (abstract).
- Hieshima, G.B., Pratt, L.M. and Hayes, J.M., 1990. Novel isotopic compositions of total organic carbon and bitumen in the Nonesuch Formation, North American Mid-Continent Rift. *Am. Assoc. Pet. Geol. Bull.*, 74: 674 (abstract).
- Ho, E.S., Meyers, P.A. and Mauk, J.L., 1990. Organic geochemical study of mineralization in the Keweenaw Nonesuch Formation at White Pine, Michigan. *Org. Geochem.*, 16: 229-234.

- Hoefs, J., 1980. *Stable Isotope Geochemistry*. Springer, Berlin, 208 pp.
- Holser, W.T., Schidlowski, M., Mackenzie, F.T. and Maynard, J.B., 1988. Geochemical cycles of carbon and sulfur. In: C.B. Gregor, R.M. Garrells, F.T. Mackenzie and J.B. Maynard (Editors), *Chemical Cycles in the Evolution of the Earth*. Wiley, New York, N.Y., pp. 105–173.
- Imbus, S.W., 1990. Organic Petrologic and Geochemical Studies on the Oronto Group Nonesuch Formation (Middle Proterozoic) of the Midcontinent Rift System, Northern Wisconsin and Upper Peninsula Michigan. Ph.D. Thesis, University of Oklahoma, Norman, Okla., 393 pp.
- Imbus, S.W., Engel, M.H., Elmore, R.D. and Zumberge, J.E., 1988. The origin, distribution and hydrocarbon generation potential of the organic-rich facies in the Nonesuch Formation, Central North American Rift system: A regional study. *Org. Geochem.*, 13: 207–219.
- Imbus, S.W., Engel, M.H. and Elmore, R.D., 1990. Organic geochemistry and sedimentology of the Middle Proterozoic Nonesuch formation: Hydrocarbon source rock assessment of a lacustrine rift deposit. In: B.J. Katz (Editor), *Lacustrine Exploration: Case Studies and Modern Analogs*. Am. Assoc. Pet. Geol. Mem., 50: 197–208.
- Irwin, H., Curtis, C.D. and Coleman, M., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature (London)*, 269: 209–213.
- Janaway, T.M. and Parnell, J., 1989. Carbonate production within the Orcadian Basin, northern Scotland: A petrographic and geochemical study. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 70: 89–105.
- Kaplan, I.R., 1983. Stable isotopes of sulfur, nitrogen and deuterium in Recent marine environments. In: M.A. Arthur (Organizer), *Stable Isotopes in Sedimentary Geology*. Soc. Econ. Paleontol. Mineral., Short Course, 10: 2-1 to 2-108.
- Kelly, W.C. and Nishioka, G.K., 1985. Precambrian oil inclusions in late veins and the role of hydrocarbons in copper mineralization at White Pine, Michigan. *Geology*, 13: 334–337.
- Kelts, K. and Hsü, K.J., 1978. Freshwater carbonate sedimentation. In: A. Lerman (Editor), *Lakes: Chemistry, Geology, Physics*. Springer, New York, N.Y., pp. 295–323.
- Kharaka, Y.K., Hull, R.W. and Carothers, W.W., 1985. Water-rock interactions in sedimentary basins. In: D.C. Gautier, Y.K. Kharaka and R.C. Surdam (Editors), *Relations of Organic Matter and Mineral Diagenesis*. Soc. Econ. Paleontol. Mineral., Short Course, 17: 79–176.
- Larter, S.R., 1984. Application of analytical pyrolysis techniques to kerogen characterizations and fossil fuel exploration/exploitation. In: K.J. Voorhees (Editor), *Analytical Pyrolysis*. Butterworths, London, pp. 212–275.
- Leventhal, J.S., 1983. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. *Geochim. Cosmochim. Acta*, 47: 133–137.
- Livnat, A., 1983. Metamorphism and copper mineralization of the Portage Lake Series, northern Michigan. Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 292 pp.
- Macko, S.A., Lee, W.Y. and Parker, P.L., 1982. Nitrogen and carbon isotope fractionation by two species of marine amphipods: Laboratory and field studies. *J. Exp. Mar. Biol. Ecol.*, 63: 45–49.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.*, 18: 849–857.
- McKenzie, J.A., 1982. Carbon-13 cycle in Lake Greifen: a model for restricted ocean basins. In: S.O. Schlanger and M.B. Cita (Editors), *Nature and Origin of Cretaceous Carbon-Rich Facies*. Academic Press, London, pp. 197–207.
- McKenzie, J.A., 1985. Carbon isotopes and productivity in the lacustrine and marine environment. In: W. Summ (Editor), *Chemical Processes in Lakes*. Wiley, New York, N.Y., pp. 99–118.
- McKirdy, D.M., 1974. Organic geochemistry in Precambrian research. *Precambrian Res.*, 1: 75–137.
- Milavec, G.J., 1986. The Nonesuch Formation: Precambrian sedimentation in an intracratonic rift. Masters Thesis, University of Oklahoma, Norman, Okla., 142 pp.
- Pierre, C., 1989. Sedimentation and diagenesis in restricted marine basins. In: P. Fritz and J.Ch. Fontes (Editors), *Handbook of Environmental Isotope Geochemistry*, Vol. 3. The Marine Environment, A. Elsevier, Amsterdam, pp. 257–315.
- Pratt, L.M., Summons, R.E. and Hieshima, G.B., 1991. Sterane and triterpane biomarkers in the Precambrian Nonesuch Formation, North American Midcontinent Rift. *Geochim. Cosmochim. Acta*, 55: 911–916.
- Radke, M. and Welte, D.H., 1983. The Methylphenanthrene Index (MPI): A maturity parameter based on aromatic hydrocarbons. In: M. Bjørøy, P. Albrecht, C. Cornford, et al. (Editors), *Advances in Organic Geochemistry 1981*. Wiley, New York, N.Y., pp. 504–512.
- Schidlowski, M., 1987. Application of stable carbon isotopes to early biochemical evolution of Earth. *Annu. Rev. Earth Planet. Sci.*, 15: 47–72.
- Schidlowski, M., Hayes, J.M. and Kaplan, I.R., 1983. Isotopic inferences of ancient biochemistries: Carbon, Sulfur, Hydrogen, and Nitrogen. In: J.W. Schopf (Editor), *Earth's Earliest Biosphere*. Princeton University Press, Princeton, N.J., pp. 149–186.
- Schopf, J.W., Hayes, J.M. and Walter, M.R., 1983. Evolution of Earth's earliest ecosystems: Recent progress

- and unsolved problems. In: J.W. Schopf (Editor), *Earth's Earliest Biosphere*. Princeton University Press, Princeton, N.J., pp. 361–384.
- Stahl, W.J., 1977. Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chem. Geol.*, 20: 121–149.
- Strauss, H. and Schieber, J., 1990. A sulfur isotope study of pyrite genesis: The Mid-Proterozoic Newland Formation, Belt Supergroup, Montana. *Geochim. Cosmochim. Acta*, 54: 197–204.
- Summons, R.E., Powell, T.G. and Boreham, C.J., 1988a. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, northern Australia, III. *Geochim. Cosmochim. Acta*, 52: 1747–1763.
- Summons, R.E., Brassell, S.C., Eglinton, G., Evans, E., Horodyski, R.J., Robinson, N. and Ward, D.M., 1988b. Distinctive hydrocarbon biomarkers from fossiliferous sediment of the Late Proterozoic Walcott Member, Chuar Group, Grand Canyon, Arizona. *Geochim. Cosmochim. Acta*, 52: 2625–2637.
- Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol. (Isot. Geosci. Sect.)*, 80: 261–279.
- Teichmüller, M., 1982. Origin of the petrographic constituents of coal. In: E. Stach, M.Th. Mackowski, M. Teichmüller, G.H. Taylor, D. Chandra and R. Teichmüller (Editors), *Stach's Textbook of Coal Petrology*. Bornträger, Berlin, pp. 219–294.
- Tissot, B.P. and Welte, D.H., 1984. *Petroleum Formation and Occurrence*. Springer, Berlin, 2nd ed., 699 pp.
- Veizer, J., 1988. The evolving exogenic cycle. In: C.B. Gregor, R.M. Garrells, F.T. MacKenzie and J.B. Maynard (Editors), *Chemical Cycles in the Evolution of the Earth*. Wiley, New York, N.Y., pp. 175–220.
- Vogel, T.A., McBride, M.B. and Ehrlich, R., 1976. Syn-genetic model for the origin of the White Pine copper deposit. *Annu. Inst. Lake Superior Geol.*, 22: 65–66 (abstract).
- Walter, M.R., 1987. The timing of major evolutionary innovations from the origins of life to the Metaphyta and Metazoa: The geological evidence. In: K.W.S. Campbell and M.F. Day (Editors), *Rates of Evolution*. Allan & Unwin, London, pp. 15–33.
- Windley, B.F., 1984. *The Evolving Continents*. Wiley, New York, N.Y., 2nd ed., 399 pp.