REGIONAL ASSESSMENTS OF THE HYDROCARBON GENERATION POTENTIAL OF
SELECTED NORTH AMERICAN PROTEROZOIC ROCK SEQUENCES

Progress Report

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M.H. Engel and R.D. Elmore

School of Geology and Geophysics

The University of Oklahoma

Norman, Oklahoma 73019

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PROJECT SUMMARY

Our primary research objectives for the first year of this grant are nearing completion. This includes comprehensive sedimentologic/organic geochemical studies of two positionally distinct, unmetamorphosed units, the Nonesuch Formation (~1.1 Ga lacustrine rift deposit) and the Dripping Spring Quartzite (~1.3 Ga marine shelf deposit). As discussed in this progress report, an attempt has been made to 1) identify source rocks by quantification and characterization of constituent organic matter, 2) recognize depositional/diagenetic/catagenetic factors that may have influenced source rock quality and 3) evaluate the possibility of previous or current hydrocarbon generation and migration.

Organic petrology and geochemical analyses suggest important differences between kerogens in the Michigan (MI) and Wisconsin (WI) Nonesuch Formation study areas. When considered within a geographic/stratigraphic framework, the Nonesuch Formation in the MI study area exhibits superior source rock potential. Additional analytical information ($\delta^{13}\text{C}$ values for kerogen and carbonate, $\delta^{15}\text{N}$ values for kerogen, pyrolysis/GC/MS), when considered collectively, suggest a fundamental difference in the depositional/diagenetic chemical regime between the two study areas. It is suggested that sedimentary organic matter in the WI area was subject to more extensive microbial alteration during early diagenesis. It is also possible that thermal maturity levels were slightly to moderately higher in WI than MI. Petrologic evidence for migrated bitumens and the stable isotope composition of late vein carbonates suggest, furthermore, that oil generation and migration may have actually been more extensive in the WI study area.

Sedimentologic analysis of the Dripping Spring Quartzite suggests overall deposition as a prograding tidal flat. Two organic-rich units within the

formation, the gray and black facies (representing sheet flow deposition on the mixed flat and mud flat portions of the tidal flats, respectively) were described in detail (cores) and sampled for petrologic and geochemical analysis. Gray facies total organic carbon (TOC) levels rarely exceed 1% and $\delta^{13}\text{C}$ kerogen values vary considerably ($\Delta^{13}\text{C} = 2.9 \text{ ‰}$). In contrast, black facies TOC levels are consistently high (typically >1%) and $\delta^{13}\text{C}$ kerogen variability is limited ($\Delta^{13}\text{C} = 0.7 \text{ ‰}$). Whereas few consistent variations in kerogen $\delta^{13}\text{C}$ values are noted with lithology or vein frequency, isotope enrichment trends are apparent up section in both units, particularly in the gray facies. Pyrolysis-FID, petrologic, paleontologic and XRF analysis reveals that isotopic variation between and among these two units resulted both from distinct organic source materials and the selective destruction and possible mineral replacement of organic constituents. Our studies on these organic-rich facies suggest that limited petroleum potential exists as a result of such mineralization processes. In turn, it is speculated that organic matter was responsible for the enhanced concentration of a variety of trace elements.

As indicated in our proposal, the second year of this project will concentrate on the collection of unmetamorphosed, organic-rich samples from the Lower and Upper Tindir Group in east-central Alaska. As in the previous case studies, our intent is to develop an understanding of the nature of the organic matter associated with these Proterozoic age samples within the context of the regional depositional environments and to begin to assess the economic potential of the region with respect to possible future frontier exploration efforts. Our strategy for sample collection in Alaska this summer has benefited greatly from cooperation with Professor G.M. Young (University of Western Ontario), who has provided us with detailed field notes and columns on the Upper and Lower Tindir Group in Alaska and Yukon Territory. We are also

recieving assistance from Dr. J.D. Aitken (Institute of Sedimentary Geology, Geological Survey of Canada), who has provided us with detailed sections of the Little Dal Group. The previous field experience of these scientists will enable us to focus our sample collection efforts this summer on the most promising, organic-rich units.

I. INTRODUCTION

Whereas commercial production of Proterozoic-sourced oil and gas has been achieved in only a few provinces (basins in the USSR, China and Oman), numerous such occurrences are indicated or speculated in various basins in Asia, Africa, Australia and North America. The role of organic matter in the concentration of economic metals in sedimentary settings unique to or common in the Precambrian is also an active area of investigation. These studies, when considered in conjunction with data derived from geochemical analyses of Precambrian kerogens, extracts and oils, contribute to our understanding of the history of the Earth's hydrosphere-atmosphere-lithosphere-biosphere system.

We have conducted a geochemical survey study (TOC and $\delta^{13}\text{C}_{\text{KER}}$) of more than one dozen U.S. Middle and Upper Proterozoic sedimentary formations (~450 samples representing the Lower Belt Group, MT; Big Cottonwood, Mineral Fork, Red Pine Shale formations, UT; Dripping Spring Quartzite, AZ; Nonesuch Formation, MI/WI). Comprehensive sedimentologic/geochemical studies on two positionally distinct, unmetamorphosed units, the Nonesuch Formation (~1.1 Ga lacustrine rift deposit) and the Dripping Spring Quartzite (~1.3 Ga marine shelf deposit) are nearing completion. Using a variety of descriptive and analytical techniques, we have made an effort to: 1) identify source rocks by quantification and characterization of constituent organic matter, 2) understand what depositional/diagenetic/catagenetic factors may have influenced source rock quality, 3) to evaluate the possibility of previous hydrocarbon generation and migration using general petrologic, geochemical and geologic information, and 4) to suggest what factors should be considered in efforts to refine established stable isotope secular trends and apply isotope stratigraphy techniques.

II. THE NONESUCH FORMATION

Our earlier studies on the 1.1 Ga Nonesuch Formation, Mid-Continent rift (Milavec, 1986; Imbus et al., 1988; Elmore et al., 1989) established a regional stratigraphic/ sedimentologic framework and suggested, in relative terms, kerogen type and maturity. Observed differences in kerogen character may have had an important impact on the amount and quality of hydrocarbon product generated and expelled in different portions of the basin. Having the advantage of a geographic and stratigraphic framework, additional data generated may be compiled and interpreted in a manner conducive to developing a geochemical depositional/ diagenetic model for the Nonesuch Formation sediments.

Table 1 outlines the results of previous and recent work on the Nonesuch Formation. In the ensuing discussion, this data will be summarized with respect to the following geographic/stratigraphic-sedimentologic framework: east (Michigan) and west (Wisconsin) lower, middle and upper stratigraphic divisions (Marginal Lacustrine Assemblage and the shallow-water portion of its transition with the Lacustrine Assemblage, the shale facies of the Lacustrine Assemblage and underlying Marginal Lacustrine Assemblage and the remaining overlying portions of the Lacustrine Assemblage extending into the Fluvial-Lacustrine Assemblage, respectively). Interpretations bearing on different levels of organic matter accumulation and preservation, and hence source rock quality, will be included where appropriate.

A. Total Organic Carbon (TOC)

Two separate surveys (see Table 1) seeking to quantify the distribution of organic carbon with respect of geographic/stratigraphic location and facies interpretation produced similar results. Higher TOC values (>0.5%) are typical of the Lacustrine Assemblage shale facies (particularly in the east) and of

Table 1. Summary of results of analyses applied to the Nonesuch Formation.

TOC: Two surveys conductedI (n=183), Range = 0-3.0%^{1,2}

II (n=218), Range = 0-1.9%

ORGANIC PETROLOGY (n=55): Two "assemblages" are recognized¹

OP-1 - filamentous (algal?) materials brightly fluoresce yellow-green.

Incident white light shows well-defined boundaries and filament translucence.

OP-2 - filamentous materials poorly or non-fluorescence.

Incident white light shows poorly defined boundaries and occasional filaments are opaque.

ROCK EVAL PYROLYSIS (n=41)

HI - 18 to 454 (mg HC/g Org C)

OI - 0 to 46 (mg CO₂/g Org C)T_{max} - 433 to 452°C

PY-GC-MS: Two surveys

Kerogens (n=9)¹ - aliphatic- and aromatic-dominated kerogens correspond to OP-1 and 2 and east and west (respectively).Whole rock (n=20) - transition character to the above aliphatic/aromatic distinction above made.
- geographic distinction is somewhat blurred, however. $\delta^{13}\text{C}_{\text{KER}}$

Range: -27.57 to -34.72 ‰, significant enrichment in samples with less than 0.15% TOC.

 $\delta^{13}\text{C}_{\text{CARB}}$ and $\delta^{18}\text{O}_{\text{CARB}}$ $\delta^{13}\text{C}_{\text{CARB}}$: Range -1.7 to -20.4 ‰ $\delta^{18}\text{O}_{\text{CARB}}$: Range -2.3 to -18.0 ‰

SULFUR

% S_{TOT} Range: 0.17 to 3.47% $\delta^{34}\text{S}_{\text{SULFIDE}}$ Range: (currently under investigation)

NITROGEN

% N_{ORG} Range: $\delta^{15}\text{N}_{\text{ORG}}$ Range: +2.72 to +8.48

¹Imbus et al. (1988)²Imbus et al. (1990)

dark, well-laminated fine-grained sediments in general. The distribution of TOC suggests possible variations in 1) primary productivity and/or sedimentologic regimes, 2) quality of organic preservation during diagenesis or 3) carbon loss during hydrocarbon generation and expulsion. The interpretation by Milavec (1986) that sedimentologic details in the east and west are largely similar and the results of additional analysis (discussed below) serve to constrain the possible interpretations.

B. Organic Petrology

Imbus et al. (1988) recognized the prevalence of filamentous (algal?) organic materials in organic-rich Nonesuch Formation samples. Based on distinct features observed in reflected white light and blue light fluorescence, two organic "assemblages" were recognized (see Table 1 for definitions). Although the occurrence of OP-1 and OP-2 is basin wide, a clear preference for the east and west, respectively, is evident. The darker colors of filamentous materials (incident white light) in the west would appear to suggest a more severe thermal history. The close association of these organoclasts with a dark granular material resembling bituminite (cf. Teichmüller, 1982), however, suggests poor preservation of organoclasts or protokerogens (i.e., a secondary source) relative to those in the east. Furthermore, as OP-1 and OP-2 are occasionally observed in the same section, significant differences in thermal maturity are difficult to support. There remains, in addition, the possibility that the material resembling bituminite consists of unexpelled oil.

C. Rock Eval Pyrolysis

Kerogen type classification for the 41 Nonesuch Formation samples analyzed by Rock Eval (see Table 1) is difficult in many cases due to low pyrolytic yields. Of those samples with hydrogen indices exceeding 200, a range in

chemical type from "purely" type I (i.e. oxygen index = 0) to intermediate type II/III was observed. Organic-rich rocks with high hydrogen and low oxygen indices are common in lacustrine settings (e.g., Jones, 1987). The relatively high oxygen indices observed in a few samples may indicate kerogen oxidation or the diagenetic production of humic substances. These processes have previously been described for Precambrian kerogens (e.g., Imbus and McKirdy, 1990 and references therein). Most of these samples are from the east study area with apparently no stratigraphic preference.

Rock Eval $T_{\max}$ temperatures, although available for only 17 samples (again, due to low pyrolytic yields), are somewhat higher in the west. The differences observed ($\sim 7^{\circ}\text{C}$, approximately equivalent to an $R_o = 0.3\%$ difference; cf. Tissot and Welte, 1984, p. 522) are insufficient, however, to suggest significant thermal evolution for these organic-rich specimens with HI values less than 200. As most of the samples in question are from the western study area, it is suggested that these values may reflect early diagenetic alteration of the sedimentary organic matter in this region.

D. Pyrolysis-Gas Chromatography-Mass Spectrometry (PY-GC-MS)

A distinctive molecular signature for OP-1 and OP-2 kerogens (i.e., aliphatic and aromatic character, respectively; see Table 1) was established by Imbus et al. (1988) using PY-GC-MS. To a large extent, the geographic distinction between these kerogens made in the same study was confirmed in recent PY-GC-MS work. In addition, kerogens exhibiting molecular signatures intermediate to the aliphatic and aromatic end members were observed. Aliphatic kerogens are prevalent in the lower and middle stratigraphic portions of the east. Aromatic and aliphatic/aromatic transitional kerogens represent mostly middle and upper portions of both study areas. Carbonate laminites from both study areas are more likely to host kerogens that are aliphatic in

composition.

As with the previously discussed organic petrologic and Rock Eval pyrolysis data, the geographic/stratigraphic distribution of kerogens bearing different molecular signatures strongly suggests local depositional/diagenetic influence rather than a regional thermal maturity trend. Complicating matters, however, are the results of stepwise pyrolysis studies on selected aliphatic- and aromatic-dominated kerogens. Considering normalized values of the compounds *n*-octene, *m*+*p* xylenes and phenol (cf. kerogen typing scheme of Larter, 1984), the evolution of possibly representative aliphatic, aromatic and oxygen-containing compounds may be monitored at two consecutive temperature stages. It is interesting that higher proportions of *n*-octene are evolved in the lower temperature stage (450°C maximum) in the aromatic kerogen than in the aliphatic kerogen. The evolution of *n*-octene in the aliphatic kerogen, however, exceeds that of the aromatic kerogen in the higher temperature stage. The evolution of *m*+*p* xylenes is proportional in both stages for both kerogens. Phenol is uniformly low (~2-4%) in all stages except the low temperature stage for the aliphatic kerogen (17.4%). Finally, the aromatic kerogen appears to be somewhat more refractory, as higher levels of pyrolysates are generated in the high temperature stage.

The stepwise pyrolysis study reveals some information about the structure of typical kerogens from the east and west (i.e., OP-1/aliphatic versus OP-2/aromatic, respectively), despite the distinct possibility that the compounds considered may not be representative of pyrolysates in general. Of particular interest is the relatively refractory nature of aliphatic components of kerogen relative to aromatic components. In a sense, this infers that the aromatic kerogens consist of "loose thermally-degradable kerogens" (c.f., Philp and van de Meent, 1983) whereas aliphatic kerogens may consist of thermally-resistant

sporopollenin-type polymers (e.g., Combaz, 1971; Dungworth et al., 1971; Bestougeff et al., 1985). The high phenol content of the aliphatic (eastern) kerogens suggests either the incorporation of oxygen into a specific organoclast component (e.g., an algal sheath) or the possible enhanced preservation of carbohydrate derivatives.

A direct correlation between kerogen pyrolysates and extracts or oils is not usually possible on the basis of molecular ratios. General characteristics, however, such as relative aliphatic content are useful. It was concluded by Imbus et al. (1988) that the White Pine Mine bitumen-impregnated sandstone (associated with an indigenous oil seep in Ontonagon County, MI), comprised almost exclusively of *n*-alkanes, was likely derived from the typically aliphatic-dominated eastern kerogens. A similar conclusion may be made from our recent studies. The distribution of *n*-alkanes in the extract of a western sample, however, showed greater similarity to the oil than did that of an eastern sample. As the diagenetic/catagenetic history of organic-rich sediments was indeed complex (e.g., Kelly and Nishioka, 1985), however, the significance of such a comparison is in doubt.

Finally, a search for biological marker compounds in kerogen pyrolysates, rock extracts and the White Pine Mine oil was conducted. Hopane compounds were detected only in aliphatic kerogen pyrolysates (C₂₇₋₃₁ pseudohomologous series). As the filamentous materials readily evident in the aliphatic kerogens appear to have algal (perhaps eukaryotic) affinities, sterane compounds were expected but were not detected. The indigeneity of the hopane compounds detected was confirmed by stepwise pyrolysis. Furthermore, the proportions of the two major hopane peaks reversed in low versus high stage levels (i.e., low: 17 (H)-trisnorhopane (Tm) < 30-norhopane and vice versa in the high temperature stage). Although hopanes and steranes have been detected

in a number of Proterozoic extracts and oils (Imbus and McKirdy, 1990) and indeed in the Nonesuch Formation extracts (Summons et al., 1988), ours may be the first such report of an occurrence in the anhydrous pyrolysates of a Precambrian kerogen.

E. Kerogen Stable Carbon Isotope Study

The observed range in $\delta^{13}\text{C}_{\text{KER}}$ values for 218 Nonesuch Formation kerogens is reduced considerably when only sediments with $\geq 0.15\%$ TOC are considered (see Table 1). On this basis, ^{13}C enriched kerogens may be described as representing principally lower to middle portions of the formation, particularly in the east, that are fine-grained, poorly laminated and carbonate-lean ($\% \text{CaCO}_3 < 20\%$). Kerogens that are depleted in ^{13}C typically occur in the western study area, especially in lower and lower-middle sections. Many of these samples may have been deposited in relatively shallow water (e.g., mudflat) and/or exhibit carbonate laminite lithology.

An average $\delta^{13}\text{C}_{\text{KER}}$ depletion of 0.30 ‰ was observed for the western samples relative to the eastern samples. Potentially, this observation may result from 1) the possibly isotopically-depleted nature of "bituminite" (prevalent in the west), 2) isotopically-depleted CO_2 (aq) or $\text{CO}_3^{2-}/\text{HCO}_3^-$ in the western lake waters. An extensive set of experiments designed to address the former possibility were conducted. Stable isotope analysis of extracts (using solvents of increasing polarity) and their respective kerogen residues gives no evidence for a depleted soluble or partially soluble organic material. As both unexpelled oil and bituminite would be expected to be at least partially soluble, it is likely that ^{13}C depleted organic matter in the western samples resides in the remnants of filamentous organic materials (i.e., likely similar or identical to those in the east). Thus, the latter possibility involving lake water chemistry becomes an attractive alternative (see ensuing

discussion).

F. Carbonate Carbon and Oxygen Stable Isotope Study

Nonesuch Formation samples analysed for carbonate stable isotope composition may be placed in three major groups (see Table 1 for total range of values). Group 1 consists of $\delta^{13}\text{C}_{\text{CARB}}$ -enriched and $\delta^{18}\text{O}_{\text{CARB}}$ -enriched samples. All of these samples are carbonate-rich ($\geq 20\%$), represent carbonate laminite lithologies and are from the lower and middle portions of the formation (east and west). These samples are similar in isotopic composition to stromatolites and pure carbonate cements in the underlying Copper Harbor Formation. Samples in the second group ($\delta^{13}\text{C}_{\text{CARB}}$ -depleted, $\delta^{18}\text{O}_{\text{CARB}}$ -enriched) are well mixed with respect to carbonate content and geographic/stratigraphic location. Similar isotope compositions were observed for carbonate-lean cements from the Copper Harbor Formation and for a calcitized evaporite bed from the upper portion of a western core. The final group is depleted to very depleted in $\delta^{13}\text{C}_{\text{CARB}}$ and depleted in $\delta^{18}\text{O}_{\text{CARB}}$. Constituent samples are mostly carbonate-lean and are from middle and upper portions of the eastern study area. Late vein carbonates and calcite present in fractures have a similar isotope composition.

The three groups may be interpreted as follows:

- 1) A primary depositional signal is preserved. As the $\delta^{13}\text{C}_{\text{CARB}}$ values are slightly depleted relative to typical marine carbonates (cf. Keith and Weber, 1964; Anderson and Arthur, 1983) a lacustrine interpretation is attractive.
- 2) As these samples are primarily carbonate lean, primary depositional signals may be partially obscured by diagenetic processes.
- 3) These samples are typically very lean in CaCO_3 and thus may represent diagenetic carbonate precipitation. The influence of meteoric water is evident from the depleted $\delta^{18}\text{O}_{\text{CARB}}$ values.

There is some geochemical evidence to suggest that organic primary production and calcite precipitation were coupled in the east (c.f. a planktonic bloom/carbonate precipitation model, e.g. Kelts and Hsü, 1978). The lack of such geochemical signals in the west, despite similar lithologies, suggest that other processes, perhaps recycling of degrading organic matter, may have obscured telling signals. The detection of this east-west distinction may provide an explanation for isotopically-depleted kerogens present in the west.

G. Other Studies

An effort to cross-correlate numerous geochemical parameters (TOC, $\delta^{13}\text{C}_{\text{KER}}$, $\% \text{CaCO}_3$, $\delta^{13}\text{C}_{\text{CARB}}$, molecular parameters from PY-GC-MS analysis, $\% \text{N}_{\text{KER}}$, $\delta^{15}\text{N}_{\text{KER}}$, $\% \text{S}_{\text{TOTAL}}$, ELEMENTAL, SULFIDE and $\delta^{34}\text{S}_{\text{SULFIDE}}$) is currently in progress. Preliminary results confirm many of the interpretations discussed above. Once the choice of specimens and geochemical parameters (especially molecular parameters) is optimized, we should be able to formulate a comprehensive geochemical depositional/diagenetic model for the Nonesuch Formation.

H. Summary and Conclusions

The results of TOC and Rock Eval analyses demonstrate a superior source rock potential for the eastern study area (Michigan) relative to that of the west (Wisconsin). Based on commonly applied criteria (e.g., Tissot and Welte, 1984), it may be concluded that source rock potential ranks as moderate to good for several intervals in Michigan.

The majority of our recent efforts have focused on proposing an explanation for differences in petroleum potential between the two study areas. Sedimentologic analyses suggest that the depositional settings in Michigan and Wisconsin were essentially equivalent. Our previous petrologic and geochemical work makes a strong case for differential preservation of organic matter

(probably during diagenesis) as the principal influence on kerogen quality rather than a regional thermal maturity trend. The present study largely confirms this conclusion and provides evidence for differing details in the overall carbon budget in east and west portions of the Nonesuch Lake. Statistical analysis of elemental, stable isotope and molecular data now in progress may provide details on what processes were involved in influencing kerogen composition.

III. THE DRIPPING SPRING QUARTZITE

The Dripping Spring Quartzite (~1.3 Ga Apache Group, southeastern Arizona) was chosen for a comprehensive sedimentologic/geochemical study on the basis of 1) the high level of organic carbon in two intervals, 2) good outcrop exposures and the availability of core sections, 3) its ability to represent depositional settings common in the Proterozoic and 4) the opportunity to investigate the association between organic-rich sediments and anomalous concentrations of trace elements. In this report, we present the results of a sedimentologic study for the Dripping Spring Quartzite and a combined sedimentologic/geochemical study of two organic-rich units, the gray and black facies, within the upper member of the formation.

A. Sedimentology

Previous workers (e.g., Wrucke, 1990) have suggested that the Dripping Spring was deposited in a shallow marine or shelf setting. A facies study of the Dripping Spring was undertaken to develop a more detailed depositional model and to better understand the context in which the gray and black facies were deposited. Seven sections and one core were described. The Dripping Spring can generally be subdivided into three members within the outcrop belt: a lower conglomerate that is not always present, a middle sandstone unit, and an upper siltstone (gray and black facies).

Seven facies are recognized in the Dripping Spring Quartzite. Table 2 summarizes descriptive data derived from the core and outcrop sections examined as well as likely depositional interpretations.

The overall depositional environment for the Dripping Spring (with the possible exception of the lower conglomerate member, facies I) is shallow marine. Although the nature of the rocks and the inferred depositional processes suggest that several specific depositional settings are permissible (e.g., restricted bay, shallow shelf), the nature of the overall sequence suggests a prograding tidal flat. The evidence for reversing flow (e.g., herringbone cross stratification) strongly suggests the action of tidal currents. The nature of the deposits in the gray and black facies are consistent with deposition on a tidal flat (e.g., Elliot, 1986). The overall vertical trend (fining upward, declining bed thickness, change in stratification types) of the deposit suggests a transition from tidal sand sheet (Facies II, III, IV), to sandflat (Facies V), mixed flat (Facies VI), and mud flat (Facies VII). This sequence is similar to other sequences interpreted to record progradation of a tidal flat (Elliot, 1986).

B. Geochemical and Petrologic Studies

A TOC and $\delta^{13}\text{C}_{\text{KER}}$ survey was conducted for numerous gray and black facies samples in an attempt to document variations in these parameters with lithology and position in the sections. Additional analyses, including pyrolysis-flame ionization detection (PY-FID, a partial analog of Rock Eval pyrolysis), X-ray fluorescence (XRF) and reflected and incident white light microscopy (thin sections), were performed in an attempt to suggest what factors may be involved in stable isotope depletion and enrichment. Most of the samples analyzed were taken from cores drilled at the Theodore Roosevelt Dam site (Gila County, AZ) although selected outcrop specimens were also included in the study. Control

Table 2. Results of Dripping Spring Quartzite Sedimentologic Study

<u>Facies</u>	<u>Description</u>	<u>Interpretation</u>
I	-Conglomerate with SS lenses dispersed throughout	-braided stream
II	-Medium grained feldspathic SS; large scale trough cross-bedding interbedded with plane bedding	-dune migration in a sandbar setting
III	-Coarse grained feldspathic SS; small scale trough cross-bedding and abundant ripples	-sand sheet deposit by tidal currents
IV	-Coarse to very coarse grained feldspathic SS; herringbone cross-stratification is characteristic; associated with basal alluvial deposit	-reworking of alluvial material by tidal processes, transgressive event during active fan deposition
V	-Fine grained, slightly feldspathic to quartzite sandstone; common dark gray siltstone laminae; sediment sorting include abundant ripple cross-stratification, plane, undulatory and flaser bedding	-sandflat
VI (GF)	-Interbedded dark gray siltstone and light to medium gray very fine SS; scattered occurrences of carbonaceous material	-sheetflow on the mixed flat portion of the tidal flat
VII (BF)	-Interbedded shales with subordinate siltstone beds and very fine grained sandstone laminae, all extensively rippled; shale and siltstone units are carbonaceous	-sheetflow on the mud portion of the tidal flat

samples, particularly from the black facies, were useful in assessing the influence of veins (e.g., pyrite, hematite and silica-filled) on $\delta^{13}\text{C}_{\text{KER}}$ values.

1. Total Organic Carbon and $\delta^{13}\text{C}_{\text{KER}}$ Study

A total of 57 samples over the approximately 60-foot gray facies core section were analyzed for TOC and $\delta^{13}\text{C}_{\text{KER}}$. Total organic carbon values typically range from 0.2 to 0.6%, but one specimen with 1.8% TOC was encountered. A $\delta^{13}\text{C}_{\text{KER}}$ range of -29.74 to -32.59 ‰ was observed. An isotope enrichment trend is apparent with decreasing TOC levels. In general, substantial ^{13}C enrichment occurs only in samples that have very low TOC values or those which appear to be extensively oxidized or vein-penetrated. Although few differences in $\delta^{13}\text{C}_{\text{KER}}$ values are evident among defined lithologies (except a somewhat variable signal in coarser-grained sediments), a distinct ^{13}C enrichment trend occurs up section. TOC and $\delta^{13}\text{C}_{\text{KER}}$ values in outcrop compare well to the core specimens in the case of the Bull Canyon section (type section described by Shride, 1967) despite the higher levels of mineralization evident at this site. In contrast, TOC values were low and $\delta^{13}\text{C}_{\text{KER}}$ values enriched at an extensively mineralized gray facies section along U.S. Highway 177 (see Pierce, 1967).

A total of 78 samples from the 75-foot black facies were selected for TOC and $\delta^{13}\text{C}_{\text{KER}}$ analysis. The range of $\delta^{13}\text{C}_{\text{KER}}$ values (-31.28 to -32.01 ‰) is considerably smaller than that observed for the gray facies. Also in contrast to the gray facies are the consistently high levels of TOC in the black facies (mostly 1-3%, with a range up to 3.6%). No difference was noted among the various defined lithologic categories but a subtle isotope enrichment trend was observed upsection. Large veins, particularly those filled with pyrite, are present in abundance in the black facies. TOC and stable isotope analyses

adjacent to and at increasing distances away from these veins reveal, for the most part, little change. Likewise, little difference in these parameters was detected between the black facies core samples and specimens from the more mineralized outcrop sections.

2. Pyrolysis-FID, Organic Petrology and Trace Element Study

A subset of the gray and black facies samples (n=6 and 8, respectively) included in the TOC/ $\delta^{13}\text{C}_{\text{KER}}$ survey study were selected for further analysis to detect the possible influence of organoclast input, diagenetic preservation, post-diagenetic thermal alteration and mineralization. Pairs of isotopically-enriched and depleted samples representing similar lithologies were selected for the analyses.

PY-FID analysis showed, in general, an increase in " T_{max} " of 3-19°C in the enriched sample of each pair (except in the case of one enriched gray facies specimen). Although the increase in T_{max} values between depleted and enriched samples in the pairs considered are significant, they do not appear to increase proportionally with $\delta^{13}\text{C}_{\text{KER}}$ enrichment. This suggests that possible thermal influences (e.g., from hydrothermal veins) only partially influence stable isotope values.

XRF analysis of these specimens showed unexpectedly low levels of Th and U (i.e., compared to Granger and Raup, 1969; Nutt, 1984). Among the trace elements sought (Ni, Ca, Zn, Cu, Ga, Nb, Zr, Rb, Sr, Th, U, Pb, Y), Zr and Rb appeared to be in the highest concentration in both facies (100-400 ppm range). Percent values of iron, as Fe_2O_3 , and ppm values of the trace elements listed above, do not change in a regular fashion between depleted and enriched samples in the gray and black facies. When the same values are normalized with respect to TOC, however, there is a marked increase in values with isotope enrichment in virtually every case. This observation would appear to suggest an organic

control on the concentration of these elements. It is possible, for example, that a mineralization mechanism involving the destruction of organic matter and its subsequent replacement by inorganic phases may have occurred. The distinct possibility that the contrasts observed in the ratios between enriched and depleted samples may reflect a mathematical artifact must, however, be borne in mind. In an effort to suggest the nature of observed variations, a general organic petrologic study was undertaken.

Organic matter in the gray facies consists principally of brown to dark brown/black organoclasts (50 x 200-300 μm) and minor matrix. Black facies organic matter consists almost exclusively of a black matrix. No fluorescence completely attributable to organic matter was observed. The presence of hematite appears to be important in many of the gray and black facies samples, particularly in the $\delta^{13}\text{C}_{\text{KER}}$ -enriched specimens. Hematite apparently replaces organoclasts in the gray facies and has a patchy distribution in the black facies matrix. In highly mineralized specimens of the gray facies (from the U.S. Highway 177 outcrop site) organic-rich lamellar complexes clearly appear to be partially replaced by hematite. Paleontologic studies, conducted in conjunction with the present study show, in some cases, a clear replacement of certain microfossils with mineral matter. It is not clear, however, whether this replacement occurred during early diagenesis (e.g., pyrite replacement of organic material) or is indicative of post-diagenetic mineralization (hematite after pyrite or direct organic destruction and mineral replacement).

3. Discussion

Isotopic variations between and within the gray and black facies reflects a combination of depositional/diagenetic and post-diagenetic influences. TOC, $\delta^{13}\text{C}_{\text{KER}}$ and organic petrographic distinctions between the gray and black facies clearly indicate different organic inputs. There is also evidence for a change

in the nature of organic matter going upsection in each case based on the $\delta^{13}\text{C}$ enrichment trend. Overall, gray facies sediments appear to have been more susceptible to organic alteration by vein intrusion than the black facies sediments. As selective replacement among organoclasts in this facies appear to have taken place and initial organic carbon levels were likely low, it is not difficult to understand this phenomenon.

A number of studies have attempted to describe the timing and mechanism of mineralization, particularly for uranium, in the organic-rich Dripping Spring Quartzite intervals (e.g., Granger and Raup, 1969; Nutt, 1984). Possible mechanisms range from depositional concentration of trace elements to post-diagenetic emplacement via the influence of diabase dikes and sills. Hot artesian water ($>70^\circ\text{C}$) is even presently associated with the Dripping Spring sediments at the Roosevelt Dam site (L. Crutchfield, U.S. Bureau of Reclamation, pers. comm., 1988). Although this study does not provide definitive evidence for any of the mechanisms proposed, we have established a framework for further investigation into the role of organic matter in mineralization. Future studies will include XRD and more detailed petrologic and trace element studies to document the extent of carbon loss associated with mineralization and specifically how mineralization has influenced the source rock potential and $\delta^{13}\text{C}_{\text{KER}}$ composition of this unit. Such an approach is receiving increasing acceptance as a means of documenting the mutual influences of organic matter and minerals in the Proterozoic.

IV. SURVEY STUDY

The TOC and $\delta^{13}\text{C}_{\text{KER}}$ data generated for the Nonesuch Formation and the Dripping Spring Quartzite were included in an overall survey study including other units. Table 3 lists the formations studied, their depositional

TABLE 3. PROTEROZOIC ROCK UNITS ANALYSED FOR TOC AND $\delta^{13}\text{C}_{\text{ker}}$ *

FORMATION (ABBREV.)	DEPO. SETTING	META. LEVEL	TOC (w)
Mineral Fork (MF)	Glacio-Mar.	subGS?	0.31
Red Pine Shale (RPS)	Sh. Mar.?	None	0.19
Big Cottonwood (BC)	Sh. Mar.	subGS?	0.23
▶ Nonesuch Shale (NS)	Lacustrine	None	0.34
Mescal Ls (MLS)	Sh. Mar. Tidal	<subGS	<0.10
▶ Dripping Spr. Qtz.	Shelf		
Black Facies (BF)	Restr. Bay	<subGS	1.54
Gray Facies (GF)	Mudflat	<subGS	0.39
Chamberlain Shale/ Newland Ls (MT-I)	Various Mar.	<subGS?	0.13
Greyson Shale (MT-II)	Sh.-Deep Mar.	subGS-GS	0.22

*Other spls (>n=35): include Cambrian (BC); Misc. Spls. from MI/WI, MT, ON; TN, UT.

settings, approximate metamorphic levels and TOC means. Figure 1 summarizes the results of the $\delta^{13}\text{C}_{\text{KER}}$ determinations for each of these units with respect to their respective geologic ages. A considerable $\delta^{13}\text{C}_{\text{KER}}$ range was observed for the units considered (~ -16.5 ‰ for the Red Pine Shale to ~ -32.5 ‰ for the Nonesuch Formation). Of the formations considered, only the Big Cottonwood Formation (UT) plots close to the approximate secular trend line established for this time interval (Schidlowski, 1987). This is not at all surprising given that for both the present study and those from which the secular trend was established these data represent organic matter accumulated in distinct depositional environments which were ultimately subject to different diagenetic processes and thermal alteration phenomena. The present study has documented possible influences of many of these factors. It is anticipated that stable isotope studies modelled on our approach and combined with paleontologic information will serve to refine secular trends as well as enable the successful application of isotope stratigraphy.

FIGURE 1

V. REFERENCES

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VI. STUDENT PARTICIPATION

As indicated in our initial proposal, a significant portion of the funds that have been provided by DOE for this project are being used to support the research efforts of two graduate students. Mr. Scott Imbus is currently completing a Ph.D. thesis in Organic Geochemistry under the direction of Michael Engel. As evidenced by the publications and talks listed below, Scott has been actively involved in our investigation of the chemistry and hydrocarbon generation potential of organic matter in Proterozoic sedimentary rocks. Scott will continue working with us this summer and fall on the second phase of this project which will focus on potential Proterozoic source rocks in Alaska. Mr. Kelvin Cates is working on a M.S. degree under the direction of Douglas Elmore. Kelvin's thesis will involve a detailed sedimentologic study of the lower and upper Tindir Groups in Alaska.

VII. PRESENTATIONS AND PUBLICATIONS

As evidenced by references cited in the above progress report and the citations that follow, we have accomplished our primary objectives for the first year of this project and are continuing to report the results of this work in a timely fashion. The following is a list of presentations and publications that have resulted in part from DOE support effective September 1, 1989. Additional reprints and preprints of papers published in 1988-1990 are provided in Appendix I.

Recent Presentations and Publications Related to this Grant

Imbus, S.W., McCollum, R.A., Maynard, R.J., Elmore, R.D. and Engel, M.H. (1989) Integration of sedimentologic and geochemical data for the Middle Proterozoic Dripping Spring Quartzite Formation, southeastern Arizona, 14th International Meeting on Organic Geochemistry, Paris, France, 65 (Abstract).

Imbus, S.W., Engel, M.H., Elmore, R.D. and Maynard, R.J. (1989) Organic geochemical, petrographic and sedimentologic analysis of selected North American Proterozoic clastic rock units. Geol. Soc. Am. An. Mtg., Abstracts with Programs 21, A10 (Abstract).

Horodyski, R.J., Imbus, S.W. and Engel, M.H. (1989) Acritarchs and other microfossils from the Middle Proterozoic Dripping Spring Quartzite, Apache Group, Arizona. Geol. Soc. Am. An. Mtg., Abstracts with Programs 21, A114 (Abstract).

Imbus, S.W., Engel, M.H. and Elmore, R.D. (1990) Sedimentology and organic geochemistry of the Middle Proterozoic Nonesuch Formation: Hydrocarbon source rock assessment of a lacustrine rift deposit. Bull. Am. Assoc. Pet. Geol. (Special Volume), Manuscript Accepted.

VIII. BUDGET FOR SECOND YEAR OF THIS GRANT

In our original proposal, we requested a total of \$115,467 for the second year of this grant. Whereas moderate increases have occurred since the time that this proposal was submitted (e.g. salaries, university indirect costs, travel, etc), we feel that, with careful reorganization of our initial budget request, we can accomplish our goals at this original level of funding. What follows on the next page is a slightly modified budget that reflects current university overhead adjustments, but stays within the total budget initially requested from DOE at the time this proposal was submitted.

BUDGET FOR YEAR 2 (SEPT. 1, 1990 - AUG. 31, 1991)

PERSONNEL

Principal Investigator (MHE, 1.9 summer mos.)	9,516
Co-Principal Investigator (RDE, 1.9 summer mos.)	9,266
Postdoctoral Associate (SWI, 12 mos.)	20,000
Equipment Technician (3 mos.)	5,750
Graduate Research Assistant (1, 12 mos.)	<u>10,200</u>

Total Personnel	54,732
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FRINGE BENEFITS

26% on Professionals	11,578
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TRAVEL*

Domestic Professional Meetings (GSA, AAPG)	2,000
Field Work**	<u>3,600</u>

Total Travel	5,600
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MATERIALS AND SUPPLIES

GC columns, reagents, solvents, glassware, etc.	3,175
Expendable supplies for Finnigan Delta E isotope ratio mass spectrometer and Pyran Pyrolysis System	<u>4,000</u>

Total Materials and Supplies	7,175
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TOTAL DIRECT COSTS	79,085
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INDIRECT COSTS

(46% MTDC as set by DHHS)	36,380
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TOTAL BUDGET FOR YEAR 2	\$115,465
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*Travel expenses will be reimbursed at actual, reasonable and necessary costs.

**Field Work (Year 2)

Funds are requested to conduct field work in Alaska to collect Proterozoic rock samples for organic geochemical and sedimentologic studies.

1. Travel

A. Airfare for 2 scientists (OKC-Fairbanks)	1,600
B. Rental car	500

2. Living expenses (room and board) for two weeks of field work	<u>1,500</u>
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Total	\$3,600
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*preprint
revised.
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END

**DATE
FILMED**

9/3/93