Origin and Maturation of the Organic Matter in the Middle Ordovician Guttenberg Member of the Decorah Formation of Southwestern Wisconsin

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ABSTRACT

Samples from an unmineralized exposure of the Guttenberg Member of the Decorah Formation were characterized by hydrocarbon source rock parameters; organic carbon (22.16 percent), sulfur (0.13 percent), hydrogen index (989.2), oxygen index (17.0), asphaltenes (47.28 percent), resins (22.45 percent), and hydrocarbons (30.27 percent), a carbon preference index of 1.113, a pristane to phytane ratio of 0.93, and a pristane to C17 ratio of 0.08. The bitumen extract contained 20.75 percent paraffins and napthenes and 9.52 percent aromatics. Alkanes ranged from C15 to C36, with C15 to C19 predominating. The carbon preference ratio and the presence of C30 favor marine algae as the parent material for the organic matter. The transformation ratio (0.02), derived from the hydrogen and oxygen indices, reveals thermal immaturity and a history of shallow burial (less than 700 meters) within the basin. Temperatures of 50 °C to 90 °C are indicated by conodont color and kerogen color from the same sample. A geothermal gradient, in the neighborhood of 3.2 °C to 9.0 °C per 100 m, was calculated. All of these indicators of maturation are irreversible and thus represent average basinal temperatures experienced since Middle Ordovician deposition.

INTRODUCTION

Maturation of organic matter provides an indicator of the thermal history of sedimentary basins (Dow, 1977). Organic geochemistry is being used increasingly to provide insight into the origin of organic matter, its depositional environment and the diagenetic history of the enclosing formation. In this paper the characterization of organic matter in the Middle Ordovician Guttenberg Member of the Decorah Formation is used to estimate average basinal temperatures in southwestern Wisconsin. No direct estimates of basinal temperatures have been made previously. The results of the organic characterization are supplemented by kerogen and conodont thermal maturation color analysis (Peters and others, 1977, Epstein and others, 1977 and Rejebian and others, 1987) which serves as an independent indicator of maximum temperatures experienced by the samples.

Descriptions of the general geology and stratigraphy of the study area in addition to study of another organic-rich member (Quimbys Mill; fig. 1) below the Guttenberg can be found in work by Heyl and others (1959), and Hatch, Heyl and King (1985).

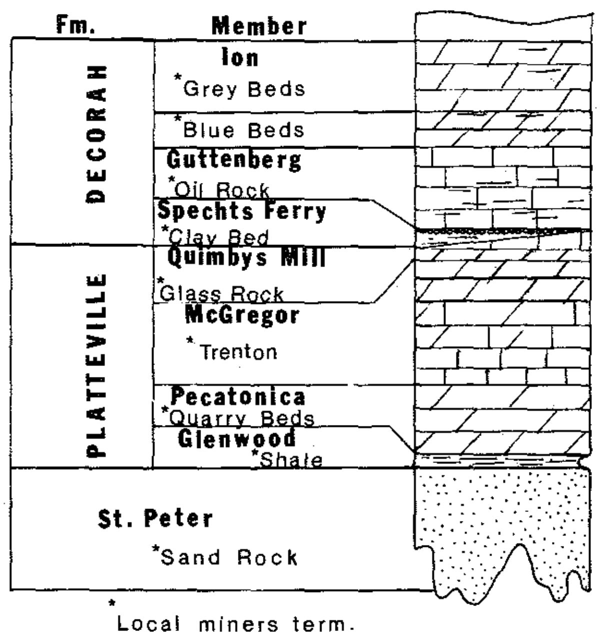

Figure 1. Stratigraphic section of southwestern Wisconsin showing both the organic-rich Quimbys Mill Member and the Guttenberg Member.

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Two previous studies have been conducted on the geochemical nature of the Guttenberg organic matter and its relationship to the zinc-lead deposits in southwest Wisconsin. Gize and Hoering (1980) and Fowler and Douglas (1984) both used samples taken from mineralized areas. The sample taken for Rock-Eval analysis (see Tissot and Welte, 1984) in this study was taken from an unmineralized zone so that the basinal status of maturation might be determined.

PROCEDURES

This study utilized organic geochemistry, kerogen and conodont thermal maturation color to evaluate the degree of organic maturation in the study area. Samples for this study were taken from three locations shown in figure 2. The unmineralized road cut from Highway 61 southwest of Platteville, Wisconsin was sampled for the Rock-Eval analysis. (The Rock-Eval process was developed by Espitalie' and others, 1977 and is amply described by Tissot and Welte, 1984.) Two other samples came from known mineralized zones (fig. 2) and were used for microscopic comparison with the sample from the unmineralized site. All samples were examined by transmitted and reflected light microscopy.

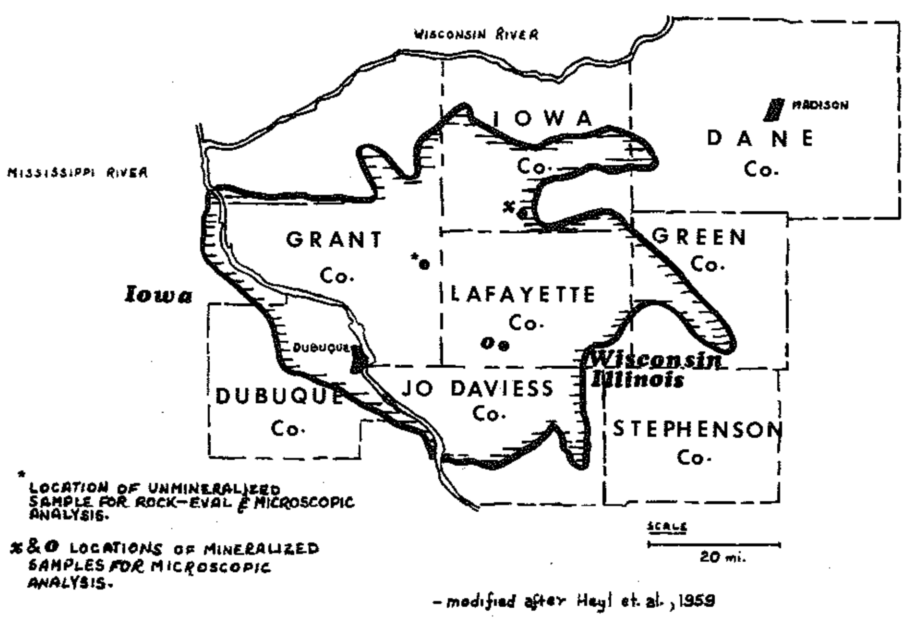

Figure 2. Location map of the study area (modified from Heyl and others, 1959). The sample for the Rock-Eval analysis was taken near Platteville, Wisconsin. The mineralized samples for microscopic comparison were from Mineral Point and the Shullsburg area.

RESULTS

The kerogen from the unmineralized site is high in organic carbon (22.16 percent) and low in total sulfur (0.13 percent). Of the bitumen extracted, there was a larger fraction of the paraffin-napthene groups (20.75 percent) compared to the aromatics (9.52 percent). The resins made up 22.45 percent and the asphaltenes 47.28 percent of the bitumen.

The C15 Saturate Hydrocarbon Analysis (table 1) gave a range of C15 to C36 with the range weighted towards the lighter alkane compounds between C15 and C20. The major components are C15 at 26.10 percent and C17 at 28.74 percent, along with C16 at 17.82 percent, C19 at 11.67 percent, C18 at 4.34 percent, phytane at 2.57 percent and pristane at 2.39 percent. The pristane-to-phytane ratio of 0.93 shows phytane as slightly dominant. The carbon preference index (CPI) of 1.113 shows little odd-carbon chain bias.

The hydrogen index (HI) and the oxygen index (OI) reflect the nature of organisms that were the source of the organic matter and the degree of maturity that organic matter has reached. The HI and OI for the Guttenberg were found to be 989.2 and 17.0 respectively. When compared with other oils (fig. 3), the Guttenberg indeed appears to be a Type-I algaly derived kerogen that is very immature and has high genetic potential due to a very high hydrogen to carbon ratio. The Guttenberg transformation ratio (table 1), when plotted on the Depth versus Transformation Ratio Plot (Espitalie' and others, 1977, fig. 4) shows the Guttenberg basin has experienced a depth of no more than 700 m.

Deposition of the region's zinc-lead deposits was a hydrothermal event with temperatures of the ore-forming solutions reaching temperatures near 200 °C (Giordano and Barnes, 1981).

Differences between mineralized and unmineralized samples occur both in kerogen color and degree of carbonate dissolution. The southern-most sample, from a mineralized zone, displays only moderate carbonate dissolution with much of the carbonate intact and a red-brown kerogen color which corresponds to maturation temperatures between 100 °C and 200 °C (see Peters and others, 1977). The two northern samples, one mineralized and the other unmineralized (used for the Rock-Eval tests) show nearly complete carbonate dissolution with the kerogen occurring as grain coatings around insoluble quartz-silt and clay particles. Both of these samples also display the same light yellow kerogen colors (Peters and others, 1977) that indicate maturation temperatures below 100 °C. Conodonts were discovered in the unmineralized sample and their translucent light red-brown color (Epstein and others, 1977) indicates temperature (50 °C to 90 °C) in accordance to that shown by the surrounding kerogen.

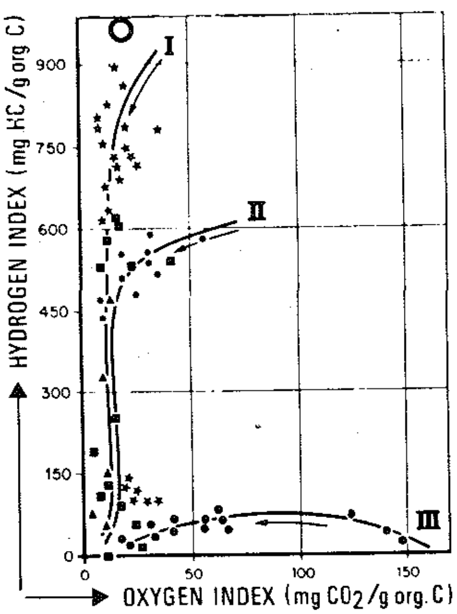

Figure 3. Plot of HI and OI of Guttenberg compares the Guttenberg to other oil. It shows the Guttenberg is a Type-I immature alginite. Guttenberg is shown as an open circle (modified from Espitalie' and others, 1977).

These permanent, cumulative and irreversible thermo-color maturation temperatures can be used in conjunction with the maximum depth of burial (which was derived from the transformation ratio, see fig. 4) to estimate the maximum range of thermal gradients for the Guttenberg basin since the Middle Ordovician. This can be done by using the standard linear gradient model of $y = mx + c$ (Asquith and others, 1982) where y is the temperature indicated by the unmineralized Guttenberg sample (which ranges between 50 °C and 90 °C; x is the maximum depth of burial of the Guttenberg samples (700 m); and c is the mean surface temperature which is assumed to be near 27 °C (80 °F) for a shallow platformal carbonate environment from the Middle Ordovician to the present. The variable m then corresponds to the geothermal gradient for the Guttenberg which ranges between 3.2 °C per 100 m and 9.0 °C per 100 m. Schlumberger (1986) suggests a modern global range between 1.09 °C per 100 m and 2.92 °C per 100 m.

DISCUSSION

The geochemical fossil indicators present in the unmineralized sample are characteristic of a relatively pure marine oil with no terrestrial plant contamination. The proof lies in the alkane range of C15 to C36 with a distinct weighting of occurrence between C15 and C20. In particular, the dominance of C15 and C17 definitely points to marine algae as the pre-cursor of the present kerogen (Tissot and Welte, 1984).

Algal origins are also indicated by the pristane and phytane proportions and ratio. Pristane tends to occur in low concentrations in marine benthonic algae (Laminarioles) and generally occur in planktonic algae and in assemblage with phytane in zooplankton. Therefore, when phytane predominates over pristane, a reducing type of environment is indicated, such as might be expected for marine benthonic algae (Tissot and Welte, 1984). Moldowan (1985) also has shown that presence of C30 steranes (found in this study) indicate organic matter from a marine environment. Likely contributing organisms during the Ordovician were Acritarchs, Chlorophyceae (green algae) and Cyanophyceae (blue-green algae). The environment at this time is typically ascribed to a shallow platformal carbonate-type of marine environment.

The hydrogen (HI) and oxygen (OI) indices are both related to the contributing organisms and do indicate that the Guttenberg kerogen is algally derived organic matter with excellent hydrogen saturation. This is evidenced by the hydrogen index of 989.2 and oxygen index of 17.0.

Table 1. Summary of the Rock-Eval analysis performed by Getty Research on the Guttenberg sample.

C-15+ Saturate Hydrocarbon Analysis

n-Alkane	%
C15	26.10
C16	17.82
C17	28.74
Pristane	2.39
C18	4.34
Phytane	2.57
C19	11.67
C20	1.39
C21	0.80
C22	0.76
C23	0.83
C24	0.37
C25	0.33
C26	0.24
C27	0.27
C28	0.20
C29	0.16
C30	0.12
C31	0.11
C32	0.12
C33	0.08
C34	0.15
C35	0.34
C36	0.11

CPI for C25 to C32 is 1.113
Pristane/Phytane is 0.93
Pristane/C17 is 0.08

Group Type Analysis of Bitumen Extract

rock weight	10.4009 grams
Hydrocarbons (%)	30.27
Paraffin-Naphthene (%)	20.75
Aromatics (%)	9.52
Resins (%)	22.45
Asphaltenes (%)	47.28

Rock-Eval pyrolysis

% organic carbon	22.16
HI (hydrogen index)	989.20
% sulfur	0.13
OI (oxygen index)	17.00
TR (transformation ratio)	0.02
TMAX (maximum temperature)	440°C

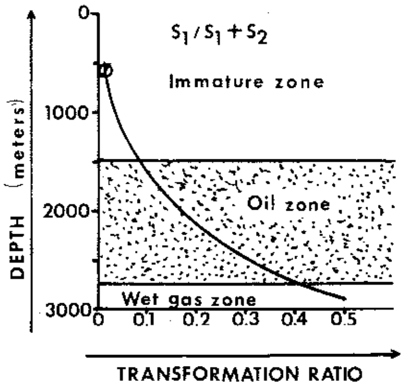

Figure 4. Plot of the transformation ratio vs. depth shows the Guttenberg to be at the top of the curve and at the corresponding depth of 700 m. Guttenberg is shown as an open circle (modified from Espitalie' and others, 1977).

The transformation ratio, when plotted on Espitalie's (1977) plot (fig. 4), seems to indicate a maximum burial depth for the Guttenberg of 700 m. When this information is linked to the indicated maturation temperatures of the organic matter, the resulting maximum thermal gradient range for the Guttenberg basin (3.2 °C and 9.0 °C per 100 m, fig. 5) is obviously high in comparison to the accepted modern range (1.09 °c to 2.92 °C per 100 m) for geothermal gradients.

The present geothermal gradient for an adjacent basin (Illinois Basin) ranges between 2.19 °C and 3.65 °C per 100 m (Barrows and Cluff, 1984). The Michigan Basin (Cercone, 1984) has a present gradient of 2.5 °C per 100 m. Barrows and others observed that Damberger (1971, 1974) found Pennsylvanian coal ranks in Illinois could not be accounted for by present burial depths and temperatures and suggests either deeper burial or that the geothermal gradient increased at some time in the past. Cercone also was troubled with unusually high paleogeothermal gradients (3.5 °C to 4.5 °C per 100 m) in the Michigan Basin.

It is premature to assert that these three basins experienced hydrothermal solutions from the same source responsible for the southwest Wisconsin zinc-lead district. A new theory by George deV. Klein and Albert T. Hsui concerning the origin of cratonic basins (1987) does indeed link the thermal subsidence histories of the Illinois, Michigan and Williston basins with other intercratonic basins throughout the world. They date the formation of these basins as around 550 to 500 Ma and suggest they formed concurrently with the rifting and breakup of a late Precambrian supercontinent (Klein and Hsui, 1987). Evidence from the Guttenberg samples, however, does indicate that hydrothermal solutions affected organic matter in and adjacent to mineralized zones as well as areas without even microscopic evidence

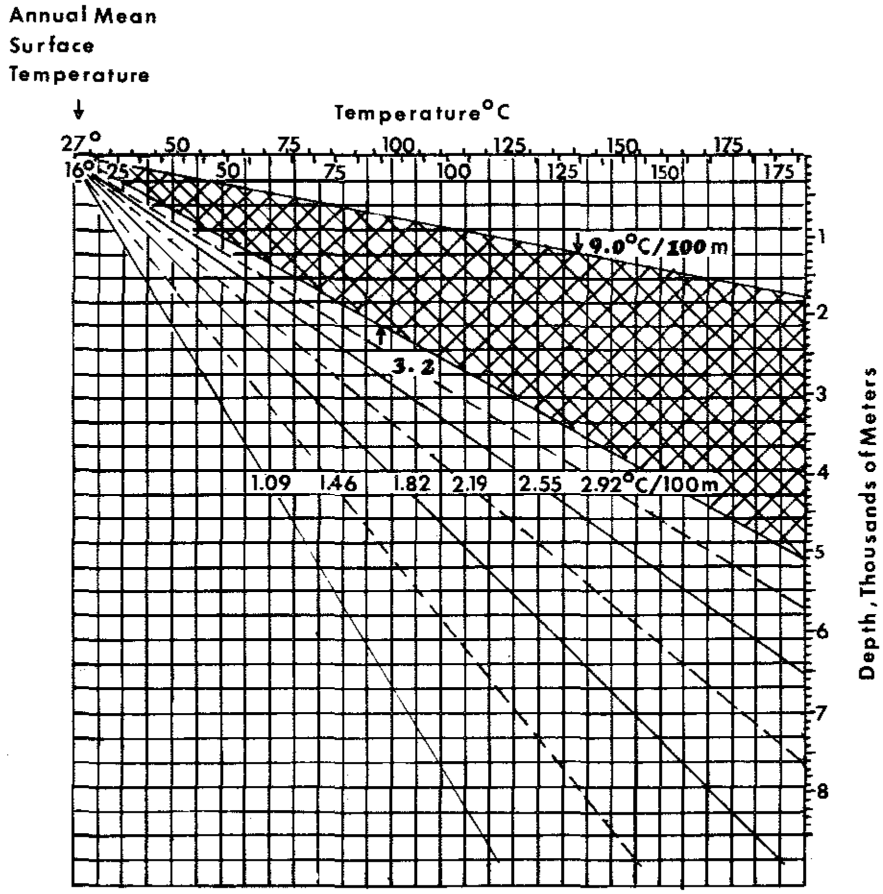

Figure 5. Standard Schlumberger, Inc. geothermal gradient plot showing the normal range of geothermal gradients currently found worldwide. The Guttenberg paleo-geothermal gradient in the cross-hatchered area shows a higher than normal range. Workers in both the Illinois and Michigan basins report paleo-geothermal gradients within this range for some time since the Middle Ordovician (modified from Schlumberger, Inc., 1986).

of mineralization. This global event may be the cause for the curious Guttenberg paleo-geothermal gradient and perhaps the actual mineralization of the region as well.

CONCLUSIONS

1. The Guttenberg oil rock is a Type-I immature kerogen.

2. The Guttenberg Member experienced average regional temperatures of no more than 100 °C as confirmed by conodont and kerogen thermo-color development.

3. Probable burial depths are estimated at about 700 m from the transformation ratio.

4. Maturation of the hydrocarbon is locally affected by varying temperatures of the mineralizing solutions as evidenced by the 200 ° C maturation temperature in the southernmost mineralized sample land the 50 °C to 90 °C maturation temperatures in the samples to the north.

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