From: Froelich, A.J. and Robinson, G. R. (eds.), Studies of the Early Mesozoic Basins of the Eastern United States U.S. Geological Survey Bulletin, 1776, p. 63-68.

SOURCE OF KEROGEN IN BLACK SHALES FROM THE HARTFORD AND NEWARK BASINS, EASTERN UNITED STATES

E.C. Spiker, R.K. Kotra, P.G. Hatcher, R.M. Gottfried, M.F. Horan, and Paul E. Olsen[1]

Abstract

To determine the source of kerogen in Mesozoic black shales, a comparison was made between the stable carbon isotopic compositions and the degree of aromaticity of kerogen and of associated coalified wood fragments (phytoclasts) from the Hartford and Newark basins. A correlation between the aromaticity and $^{13}C/^{12}C$ ratio in samples of relatively low maturity, equivalent to subbituminous to high volatile bituminous rank, indicates that the kerogens were derived from a mixture of autochthonous lacustrine algae and allocthonous woody plant detritus, including soil organic matter. Mass balance calculations indicate that the woody plant contribution can be quite high, ranging between approximately 30 and 70 percent of the total kerogen. The abundance of terrestrial-derived organic matter in the kerogen may have favored the generation of natural gas more than oil in these basins.

INTRODUCTION

Lacustrine units of the Hartford and Newark basins in the Eastern United States consist of mudstones and black laminated shales. The black shales examined contain about 0.5 to 3.5 weight percent organic matter, the bulk of which is insoluble kerogen. This kerogen may be derived from both autochthonous lacustrine algae (termed Type I kerogen) and allochthonous terrestrial plant detritus (termed Type III kerogen). Such a mixed source kerogen is termed Type II (Tissot and Welte, 1984).

Knowledge of the origin and chemical composition of organic matter is fundamental to an assessment of the hydrocarbon potential of basins (Tissot and Welte, 1984) and also aids our understanding of the possible role that organic matter may play in sedimentary ore deposition (Maynard, 1983; Kelly and Nishioka, 1985; Parnell, 1986). The type and character of the organic matter control its ability to complex metal and metal-containing cations, possibly leading to solubilization, transport, and precipitation (Schnitzer and Kahn, 1972; Hatcher and others, 1986). The present study examines the chemical and isotopic composition of the kerogen in an effort to determine its source.

Although some components of kerogen can be identified by microscopic examination, the bulk of kerogen often lacks recognizable structures and is amorphous. Many of the same samples examined in the present study from the Hartford and Newark basins contain a large proportion of amorphous material in addition to vitrinite material in the kerogen (Braghetta, 1985).

The origin of this amorphous kerogen is generally difficult to determine chemically, as a result of the complex effects of diagenesis and thermal maturation, as well as the multiple sources from which kerogen is derived (for example, algae, bacteria, fungi, terrestrial and aquatic plant and animal debris) (Lewan, 1986; Tissot and Welte, 1984). Loss of hydrogen-rich labile components of the organic matter during thermal maturation can result in significant changes in the chemical character of kerogen. This altered kerogen can be used to estimate the degree of thermal heating the rock has experienced (Tissot and Welte, 1984). However, this technique requires an understanding of the original composition of the organic matter. For example, thermally altered Type I kerogen can have a chemical composition similar to that of less altered Type III kerogen. Thus Type III kerogen could be incorrectly identified as altered Type I kerogen, resulting in an overestimate of the thermal maturity.

A number of chemical techniques may be used to characterize kerogen, including pyrolysis gas chromatography–mass spectrometry, solid-state nuclear magnetic resonance (NMR) spectroscopy, and examination of the elemental and stable carbon isotopic ($^{13}C/^{12}C$) compositions (Tissot and Welte, 1984). NMR can determine the degree of aromaticity, that is, the percent of the total

---

[1] Lamont-Doherty Geological Observatory, Columbia University, Palisades, NY 10964.

carbon in aromatic structures (Miknis and others, 1979). In immature rocks, this measure of aromaticity is indicative of the component of aromatic-rich woody kerogen (Breger and others, 1983; Barwise and others, 1984). At a rank higher than that of bituminous coal, however, aromaticity increases with increasing maturity (Saxby and others, 1986). In contrast, the carbon isotopic compositions appear to change little from maturation (Lewan, 1986; Buchardt and others, 1986; Arneth and Matzigkeit, 1986; Deines, 1980) and appear to be the best indicator of source.

Solid-state NMR was applied by Hatcher and Romankiw (1985) to study small pieces of coalified wood, termed phytoclasts, embedded in shale from several of the Eastern United States' early Mesozoic basins. In that study, NMR and elemental data revealed a wide range in the degree of coalification. Spiker (1985) examined the stable isotopic compositions of carbon, nitrogen, and hydrogen in these phytoclasts and found that coalification had little effect on the isotopic compositions.

In this study we examined phytoclasts and the associated kerogen from the shale matrix and compared the stable carbon isotopic compositions to the aromaticity as determined by solid-state NMR. Eight of the samples examined, all Lower Jurassic, are from the Hartford basin and two are from the Newark basin, one Lower Jurassic, one Upper Triassic. Some of the same samples were also studied by Spiker (1985), Hatcher and Romankiw (1985), Braghetta (1985), Pratt and others (1986a,b), and Kotra and others (this volume).

METHODS

Preparation of the kerogen and phytoclast samples is described by Kotra and others (this volume) and the stable carbon isotope methods are described by Spiker and Hatcher (1987). The carbon isotopic compositions are reported in standard $\delta^{13}C$ notation (that is, per mil) relative to the PDB standard (Craig, 1957). Replicate sample precision for $\delta^{13}C$ is approximately 0.1 per mil. Solid-state ^{13}C NMR spectra were obtained as described previously (Hatcher and others, 1982) by using cross polarization with magic-angle spinning (CPMAS).

RESULTS AND DISCUSSION

Sample descriptions are given in table 1 and the results of NMR and stable isotope analyses are presented in table 2. The vitrinite reflectance values for most of the samples are also shown in table 2. On the basis of vitrinite reflectance analysis of the phytoclasts, all but one of the samples discussed here appear to be of relatively low rank. Corresponding kerogens are of low maturity. Vitrinite reflectance values range from about 0.4 to 0.7 percent (table 2), indicating approximately subbituminous to high-volatile bituminous rank. In contrast, the one sample of Late Triassic age from the Lockatong Formation (sample 9) has a high vitrinite reflectance value of 2.8 percent and very high aromaticity (fa = 97 percent), indicating anthracite rank (Hatcher and Romankiw, 1985). The Lockatong Formation appears to be highly mature throughout much of the Newark basin, possibly as a result of depth of burial and the thermal influence of widespread igneous intrusions.

Table 1. Description of samples from the Hartford and Newark basins

Sample number		Formation	Location
		Hartford basin—all Lower Jurassic	
1	PO–7, 8	Shuttle Meadow	Durham or Bluff Head fish bed, Bluff Head, Connecticut.
2	PO–11, 12	Shuttle Meadow	Southington limestone quarry, Southington, Connecticut.
3	PO–20C	East Berlin	Westfield fish bed, Westfield, Connecticut.
4	PO–20I	East Berlin	Westfield fish bed, Westfield, Connecticut.
5	PO–22	East Berlin	Westfield fish bed, North Branford, Connecticut.
6	PO–25, 26	East Berlin	Westfield fish bed, east side Lake Saltonstall, East Haven, Connecticut.
7	PO–28M, 28	East Berlin	Stevens locality, Parmele Brook, Durham, Connecticut.
8	PO–33, 34	Portland	Middlefield fish bed, Laurel Brook, Middlefield, Connecticut.
		Newark basin	
9	NB584–14, 15	Lockatong (Member at Skunk Hollow) (Upper Triassic)	H and K quarry Chalfont, Pennsylvania.
10	NB584–24	Towaco (Lower Jurassic)	Pompton Lakes, New Jersey.

Aromaticity of the low-rank kerogen samples ranges from 39 to 60 percent, or about 2 to 20 percent less than the aromaticity of the associated phytoclasts (table 2). The $\delta^{13}C$ values in the kerogens range from −26.9 to −30.2 per mil, or 1.8 to 3.6 per mil less than values of the associated phytoclast (table 2). The $\delta^{13}C$ values in the phytoclasts range from about −23.3 to −26.7 per mil, similar to values in modern and coalified woods (Spiker and Hatcher, 1987; Deines, 1980).

Table 2. Stable carbon isotope compositions in kerogen and lipids ($\delta^{13}C$, in per mil), NMR aromaticity (fa, in percent), vitrinite reflectance (R_o, in percent), and the fraction of algal kerogen in phytoclasts and black shale samples, Hartford and Newark basins, based on equations 1 and 2 discussed in text

[Sample numbers same as table 1; --, not analyzed]

Sample number	Formation	Phytoclast			Kerogen			Lipids	Algal kerogen	
		$\delta^{13}C$	fa	R_o	$\delta^{13}C$	fa	R_o	$\delta^{13}C$	Eq 1.	Eq. 2
Hartford basin										
1	Shuttle Meadow	−23.3	0.52	0.34	−26.9	0.46	0.64[2]	−28.1	0.32	0.48
2	Shuttle Meadow	−25.2	.65	.71	−27.2	.60	.62[2]	−28.4	.37	.20
3	East Berlin	−26.6	.71	--	−29.0	.55	--	−30.8	.67	.30
4	East Berlin	−26.0	.55	--	−29.3	.39	.50[2]	--	.72	.62
5	East Berlin	−25.3	.52	.46	−27.8	.50	.66[2]	−31.0	.47	.40
6	East Berlin	−26.7	.52	--	−28.5	.43	.73[2]	--	.58	.54
7	East Berlin	−26.5	.57	.46	−28.3	.52	.48[2]	−30.8	.55	.36
8	Portland	−26.0	.64	--	−28.9	.45	--	−30.9	.65	.50
Newark basin										
9	Lockatong	−24.3	.97	2.8[1]	−27.5	.95	--	--	.42	--
10	Towaco	−25.5	.61	.3[1]	−30.2	.41	--	--	.87	.58

[1] Neely Bostic, personal commun.

[2] Braghetta (1985).

The lower aromaticity in the kerogens, compared to the phytoclasts, indicates the presence of an additional component of aliphatic-rich kerogen from an algal source. The lower $\delta^{13}C$ values of the kerogen indicate that the kerogen is depleted in ^{13}C by several per mil relative to the phytoclasts. This algal kerogen is evidently the major source of lipids extracted from the shales. These lipids are depleted in ^{13}C, with $\delta^{13}C$ values ranging from −28.1 to −31 per mil (table 2).

Aromaticity is positively correlated with $\delta^{13}C$ in the relatively low rank phytoclasts and kerogens ($R_o < 0.8$ percent) (fig. 1). This correlation can be attributed to the mixing of autochthonous algal and allocthonous terrestrial woody derived organic matter. Kerogen containing an admixture of these two types of organic matter, termed Type II kerogen, would be expected to plot along a line between the average compositions of algal and woody kerogen.

A simple two-end-member mixing model is shown as a solid line in figure 1. In this model, woody kerogen is assumed to have about 70 percent aromaticity ($fa = 70$) and $\delta^{13}C$ of about −25 per mil. The algal kerogen is assumed to have about 20 percent aromaticity and $\delta^{13}C$ of about −31 per mil. These aromaticity values are selected on the basis of NMR studies of algal kerogen and coalified woods (Breger and others, 1983; Hatcher and others, 1982; Barwise and others, 1984; Saxby and others, 1986). It is assumed that maturation is equivalent to high-volatile bituminous coal rank, corresponding to a vitrinite reflectance value of less than 0.8 percent. The $\delta^{13}C$ assumed for the woody kerogen end-member is a typical value for coalified wood (Spiker and Hatcher, 1987; Deines, 1980). The $\delta^{13}C$ value of the algal kerogen end-member is assumed to be similar to that of the most negative lipid extract.

The percent of algal kerogen in these samples can be calculated using the $\delta^{13}C$ and aromaticity (fa) values of the model for woody kerogen ($\delta^{13}C_w$ and fa_w) and algal kerogen ($\delta^{13}C_a$ and fa_a) in the following mass balance equations:

$$C_a \delta^{13}C_a + (1 - C_a)\delta^{13}C_w = \delta^{13}C_k \qquad (1)$$

$$C_a fa_a + (1 - C_a) fa_w = fa_k \qquad (2)$$

where C_a is the fraction of algal kerogen, and $\delta^{13}C_k$ and fa_k are the measured carbon isotopic and aromaticity values of the total kerogen.

Values for the algal kerogen fraction (C_a) given in table 2 have been calculated on the basis of both the $\delta^{13}C$ values (eq. 1) and the aromaticity values (eq. 2). These calculations indicate that between about 30 and 70 percent of the kerogen is derived from algal sources or, conversely, from woody sources. The error in these calculations is probably as large as 20 percent, as a result of variation in the composition of the end-members and contributions from other sources of organic matter (for example, bacteria, fungi, and aquatic plant and animal debris).

Although this simple mixing model can account for most of the NMR and isotope values, differences in the calculated values of algal kerogen (C_a) using equations 1 and 2 range from 4 to 37 percent. Assuming the model and the end-member compositions are reasonable, these differences may provide some important clues regarding the composition of the phytoclasts and kerogens. It is noteworthy that the phytoclasts generally plot below the two end-member mixing line in figure 1 and that the kerogens generally plot above this mixing line. The

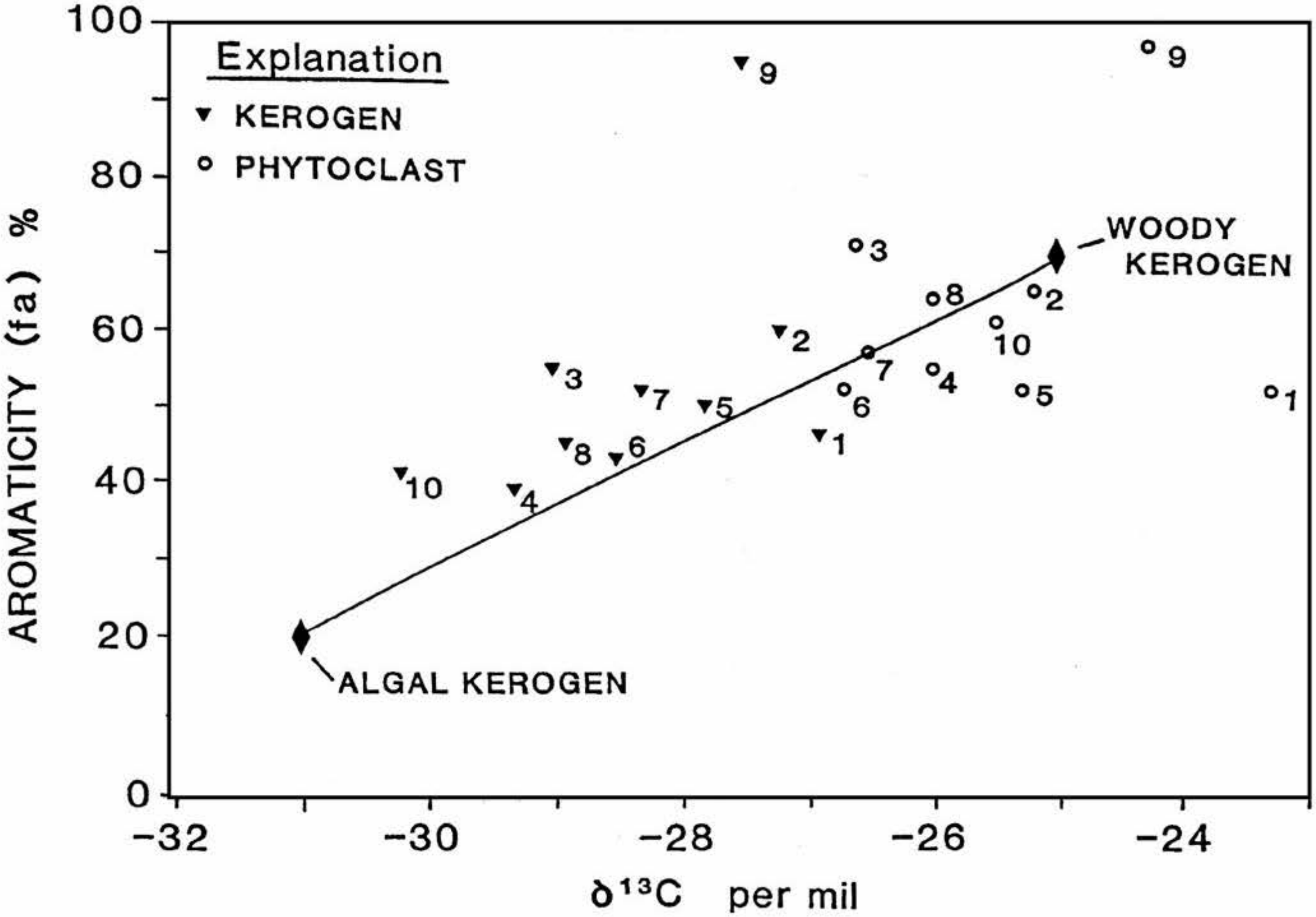

Figure 1. NMR aromaticity (fa, percent) and stable carbon isotope compositions ($\delta^{13}C$, per mil). Solid line represents a two end-member mixing model discussed in the text. $\delta\ ^{13}C$ and fa compositions of the end-members are assumed to be −25 per mil and 70 percent, respectively, for woody kerogen, and −31 per mil and 20 percent, respectively, for algal kerogen.

phytoclasts are generally less aromatic and the kerogens generally more aromatic than the model predicts.

This apparently low aromaticity of some phytoclasts may be caused by more aliphatic-rich organic matter from the sediment matrix and pore water that may have infiltrated the phytoclasts. Such a matrix effect could also explain the relatively high nitrogen content of the phytoclasts, noted by Spiker (1985), and the abundance of n-alkanes in the pyrolysis products of the phytoclasts, noted by Kotra and others (this volume).

The relatively high aromaticity of some kerogens, which plot above the two-end-member mixing line in figure 1, may be caused by the presence of highly aromatic material, such as charcoal or oxidized soil organic matter, which could significantly increase the average aromaticity of a kerogen sample. For example, the difference in the calculated algal component (C_a) using equation 1 versus equation 2 is largest for sample 3. This is because the aromaticity of kerogen in sample 3 is relatively high compared to what the model would predict. We noted that the phytoclast in sample 3 had the visual appearance of charcoal. Although this does not necessarily indicate that the associated kerogen contains significant amounts of charcoal, relatively high aromaticity values may be attributed to charcoal in this kerogen sample.

The presence of varying and significant amounts of aromatic, wood-derived kerogen may at first appear to be inconsistent with results of pyrolysis studies (Kotra and others, this volume). These studies suggest that very little of the pyrolyzable portion of the kerogen was derived from a woody source, rather that most was from an algal source. Rock-Eval pyrolysis studies by Pratt and others (1986a) indicated a uniform source of organic matter. However, it is important to note that pyrolysis techniques analyze the pyrolyzable portion and are much more sensitive to volatile components generated preferentially by algal derived components (Tissot and Welte, 1984; Larter and Senftle, 1985; Peters, 1986).

The apparent deficiency of pyrolyzable aromatic material in kerogens that contain significant amounts of wood-derived organic matter, as shown by NMR and isotopic data, indicates that some of this woody material is probably very highly aromatic. This underscores the importance of using as many analytical techniques as possible, because of inherent differences and the somewhat different insights each technique may provide. In this case, these differences indicate that the kerogen may contain significant amounts of highly aromatic material, such as oxidized soil organic matter or charcoal.

The values of the kerogens reported here are typical of values for kerogens from the Newark and Hartford basins (Spiker, unpublished data from samples not discussed here; Pratt and others, 1986b). Therefore, it appears that the kerogen from these basins may typically contain significant amounts of allochthonous, terrestrial-derived material.

CONCLUSIONS

On the basis of NMR and stable carbon isotope results, it appears that kerogens from the Hartford and Newark basins are Type II and III, containing a mixture of wood- and algal-derived organic matter. Mass balance calculations suggest that between 30 and 70 percent of the kerogen examined here was derived from allochthonous woody sources, apparently including significant amounts of oxidized soil organic matter and possibly charcoal. Although such mixed-source kerogen is common in oil source rocks, the presence of large amounts of terrestrial woody debris is deemed a potential source of natural gas (Breger and others, 1983).

ACKNOWLEDGMENTS

We thank Nicholas G. McDonald and Joseph P. Smoot for providing samples and help in the field work. We thank Dianna Mills, Lisa Romankiw, and Vicki Comer for technical assistance. We also thank Tyler B. Coplen and Carol Kendall for the isotope ratio analyses.

REFERENCES CITED

Arneth, J.D., and Matzigkeit, U., 1986, Laboratory-simulated thermal maturation of different types of sediments from the Williston basin, North America—Effects on the production rates, the isotopic and organo-geochemical composition of various pyrolysis products: Chemical Geology, v. 58, p. 339–360.

Barwise, A.J.G., Mann, A.L., Eglinton, G., Gowar, A.P., Wardroper, A.M.K., and Gutteridge, C.S., 1984, Kerogen characterization by ^{13}C NMR spectroscopy and pyrolysis-mass spectrometry: Organic Geochemistry, v. 6, p. 343-349.

Braghetta, A., 1985, A study of hydrocarbon maturity of the Hartford and Newark basins by vitrinite reflectance: Senior thesis, Princeton University, 96 p.

Breger, I.A., Hatcher, P.G., Romankiw, L.A., Miknis, F.P., and Maciel, G.E., 1983, Upper Devonian black shales of the Eastern United States—Organic geochemical studies, past and present, *in* Miknis, F.P., and McKay, J.F., eds., Geochemistry and chemistry of oil shales: American Chemical Society Symposium Series, no. 230, p. 181–198.

Buchardt, B., Clausen, J., and Thomsen, E., 1986, Carbon isotope composition of Lower Paleozoic kerogen: Effects of maturation: Organic Geochemistry, v. 10, p. 127–134.

Craig, H., 1957, Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide: Geochimica et Cosmochimica Acta, v. 12, p. 133–149.

Deines, P., 1980, The isotopic composition of reduced organic carbon, *in* Fritz, P., and Fontes, J.C., eds., Handbook of Environmental Isotope Geochemistry: v. 1, Amsterdam, Elsevier, p. 329–406.

Hatcher, P.G., Breger, I.A., Szeverenyi, N.M., and Maciel, G.E., 1982, Nuclear magnetic resonance studies of ancient buried wood—II, Observations on the origin of coal from lignite to bituminous coal: Organic Geochemistry, v. 4, p. 9–18.

Hatcher, P.G., and Romankiw, L.A., 1985, Nuclear magnetic resonance of organic-matter-rich sedimentary rocks of some early Mesozoic basins of the Eastern United States, *in* Robinson, G.R., Jr., and Froelich, A.J., eds., Proceedings of the second U.S. Geological Survey workshop on the early Mesozoic basins of the Eastern United States: U.S. Geological Survey Circular 946, p. 65–70.

Hatcher, P.G., Spiker, E.C., and Orem, W.H., 1986, Oxidative origin of sedimentary humic acids, important carriers of metals, *in* Dean, W.E., ed., Proceedings of the Denver Regional Exploration Geologists Society symposium on organics and ore deposits, April 25–26, 1985: Denver Regional Exploration Geologists Society, Wheat Ridge, Colorado, p. 57–68.

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, v. 13, p. 334–337.

Larter, S.R., and Senftle, J.T., 1985, Improved kerogen typing for petroleum source rock analysis: Nature, v. 318, p. 277–280.

Lewan, M.D., 1986, Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks: Geochimica et Cosmochimica Acta, v. 50, p. 1583–1591.

Maynard, J.B., 1983, Geochemistry of sedimentary ore deposits: Springer-Verlag, 305 p.

Miknis, F.P., Maciel, G.E., and Bartuska, V., 1979, Cross polarization magic angle spinning ^{13}C NMR spectra of oil shales: Organic Geochemistry, v. 1, p. 169–176.

Parnell, J., 1986, Hydrocarbons and metalliferous mineralization in a lacustrine rift basin: The Hartford-Deerfield basin, Connecticut Valley: Neues Jahrbuch für Mineralogie Abhandlungen, v. 154, no. 1, p. 93–110.

Peters, K.E., 1986, Guidelines for evaluating petroleum source rock using programmed pyrolysis: American Association of Petroleum Geologists Bulletin, v. 70, p. 318–329.

Pratt, L.M., Vuletich, A.K., and Burruss, R.C., 1986a, Petroleum generation and migration in Lower Jurassic lacustrine sequences, Hartford basin, Connecticut and Massachusetts, *in* Carter, L.M.H., ed., USGS research on energy resources—1986, program and abstracts: U.S. Geological Survey Circular 974, p. 57–58.

Pratt, L.M., Vuletich, A.K., and Shaw, C.A., 1986b, Preliminary results of organic geochemical and stable isotope analyses of Newark Supergroup rocks in the Hartford and Newark basins, Eastern U.S.: U.S. Geological Survey Open-File Report 86–284, 29 p.

Saxby, J.D., Bennett, A.J.R., Corcoran, J.F., Lambert, D.E., and Riley, K.W., 1986, Petroleum generation: Simulation over six years of hydrocarbon formation from torbanite and brown coal in a subsiding basin: Organic Geochemistry, v. 9, p. 69–81.

Schnitzer, M., and Khan, S.U., 1972, Humic substances in the environment: Marcel Dekker, New York, 327 p.

Spiker, E.C., 1985, Stable-isotope characterization of organic matter in the early Mesozoic basins of the Eastern United States, *in* Robinson, G.R., Jr., and Froelich, A.J., eds., Proceedings of the second U.S. Geological Survey workshop on the early Mesozoic basins of the Eastern United States: U.S. Geological Survey Circular 946, p. 70–73.

Spiker, E.C., and Hatcher, P.G., 1987, The effects of early diagenesis on the chemical and stable isotopic composition of wood: Geochimica et Cosmochimica Acta, v. 51, p. 1385–1391.

Tissot, B., and Welte, D.H., 1984, Petroleum formation and occurrence, 2d ed.: Springer-Verlag, 699 p.