

T-4180

FICHE IN POCKET

Application of biological markers, carbon isotopes and porphyrins to interpretation of deposition and preservation of organic matter in Middle Pennsylvanian rocks, western U.S.

by

Jerry L. Clayton

**ARTHUR LAKES LIBRARY
COLORADO SCHOOL OF MINES
GOLDEN, CO 80401**

ProQuest Number: 10796507

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10796507

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.

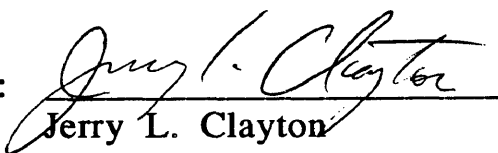
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.


ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

A thesis submitted to the faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Geochemistry).

Golden, Colorado

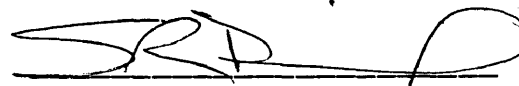
Date April 27, 1992

Signed: 
Jerry L. Clayton

Approved: 
Dr. Thomas R. Wildeman
Thesis Advisor

Golden, Colorado

Date April 27, 1992


Dr. Stephen R. Daniel
Professor and Head,
Department of Chemistry
and Geochemistry

ABSTRACT

Organic-rich (C_{org} 1-30 weight percent) black shale of Middle Pennsylvanian age (Desmoinesian and Missourian) is present in much of the west-central U.S. Black shale (or marlstones) in the northern Denver and southeastern Powder River Basins of western Nebraska and eastern Wyoming were deposited in an embayment ("restricted basin") of the Midcontinent Pennsylvanian sea. Stratigraphically equivalent Pennsylvanian black shales were deposited in northeastern Colorado on a shallow shelf of the sea and are also present over much of the midcontinent ("open marine"). On the basis of Rock-Eval pyrolysis, the bulk organic matter is type II-III. High porphyrin concentrations (as much as 40,000 ppm relative to bitumen), high total sulfur (as much as 5 weight percent), high farnesane, and high aryl isoprenoid concentrations are characteristic of shales and marlstones deposited in the embayment. Values for all of those parameters are lower in the open-marine samples. Stable carbon isotope ratios of saturated and aromatic hydrocarbons suggest a marine organic-matter source for the soluble organic matter. The isotopic composition of kerogen (C_{org}) in the rocks is from about -24 to -29 ‰, indicating mixed sources of organic matter for the insoluble organic matter. The geochemical features described above suggest that the black shales of the southeastern Powder River and northern

Denver basins were deposited in a stratified water column caused possibly by high salinity (density stratification) with euxinic conditions in the lower water layer. High preservation of primary organic matter (water-column photosynthate), fostered by the anoxic water, is indicated by unusually high amounts of porphyrins relative to C_{org} and bitumen. Some geochemical features are similar to those reported previously for hypersaline environments (even-carbon predominance, high sulfur content, abundant aryl isoprenoids); however, some exceptions to geochemical parameters thought to be characteristic of hypersaline environments are also evident such as low gammacerane and pristane/phytane greater than 1.0. These data are interpreted to indicate the salinity during deposition of the black shale or marlstones was variable and that the organic geochemistry of paleohypersaline environments is somewhat variable depending on the exact salinity conditions and the source of organic matter, particularly if allochthonous organic matter is present. In the study area, allochthonous organic matter represents a significant proportion of the organic carbon and considerable caution is necessary when attempting to interpret paleohypersalinity environments using organic geochemical data alone.

CONTENTS

ABSTRACTiii

LIST OF FIGURESvii

LIST OF TABLESxiv

ACKNOWLEDGEMENTSxv

INTRODUCTION.....1

GEOLOGIC SETTING.....3

 Stratigraphy and Structural Setting.....3

 Paleogeography and Black Shale Deposition15

SAMPLES AND ANALYTICAL METHODS19

RESULTS37

 Organic Carbon and Sulfur.....37

 Rock-Eval Pyrolysis43

 Bitumen Yield and Composition46

 Gas Chromatography-Mass Spectrometry.....46

 Porphyrins66

 Stable Carbon Isotope Ratios.....67

ORGANIC MATTER SOURCE.....67

 Evidence from Biomarkers and Sulfur.....67

 Evidence from Stable Carbon Isotopes83

	Page
ORGANIC MATTER PRESERVATION.....	104
RECOGNITION OF HYPERSALINITY.....	122
CONCLUSIONS.....	132
REFERENCES CITED	137

LIST OF FIGURES

Figure

1. Map showing paleogeography during deposition of Desmoinesian cyclothems during regressive episode and location of samples. Numbers refer to wells listed in Table 1. Restricted-basin sample locations are shown by solid dots and open-marine sample locations by solid diamonds.....5
2. Generalized stratigraphic column showing ages and names of rock units in the northern part of the study area. Inset shows a typical gamma-ray log through the Desmoinesian in Sioux County, Nebraska. Organic-rich shales and marlstones are clearly identified by the high gamma ray response on the log. Eight thin, organic-rich, radioactive black shales or marls are present in the restricted basin of western Nebraska and eastern Wyoming as indicted by the gamma ray log . The age of the uppermost organic-rich unit may be Missourian rather than Desmoinesian as indicated on the figure. Gamma ray log is given in API units.....7
3. Generalized sequence of lithologies contained in a complete cyclothem in the northern Denver basin

(western Nebraska) and relation to sea level
(modified from Doyle, 1987). A, limestone; B, black shale
or marlstone; C, limestone and anhydrite;
D, anhydrite.....14

4. Hydrogen Index (mg hydrocarbons/g organic carbon
versus Oxygen Index (mg CO₂/g organic carbon) for
single cuttings chips (approximately 10-20
mg each) handpicked from 1-33 Brunkhardt well (7,000-
7,010 ft).....21

5. Tmax (°C) from Rock-Eval pyrolysis for single cuttings
chips (approximately 10-20 mg each) handpicked from
1-33 Brunkhardt well (7,000-7,010 ft).....23

6. Weight percent organic carbon (C_{org}) for single cuttings
chips (approximately 10-20 mg each) handpicked from
1-33 Brunkhardt well (7,000-7,010 ft).....25

7. C_{org}/S_T ratio for rock samples.....40

8. Total iron content versus total sulfur for rock samples
from the "restricted-basin" (top) and "open-marine"
(bottom) environments. The dashed lines indicate the
stoichiometric amounts of iron and sulfur
in FeS₂ and FeS.....42

9. Hydrogen Index (mg HC/g C_{Org}) versus Oxygen Index (mg CO₂/g C_{Org}) from Rock-Eval pyrolysis for Desmoinesian rock samples.....45
10. Extractable organic matter compared with C_{Org} for rock samples.....48
11. Typical gas chromatograms of saturated hydrocarbons from rock extracts. Sample numbers refer to Table 2. Relative amounts of isoprenoids vary markedly between samples of similar thermal maturity as indicated by the 1-26 Hilton and 14-3 Murphy samples. In most samples, isoprenoids are abundant (see Table 2). 1-33 Brunkhardt was run under slightly different GC conditions than other samples, and some evaporative loss of light hydrocarbons occurred during sample preparation.....50
12. Mass chromatogram of *m/z* 133 showing a typical molecular distribution of aryl isoprenoids in restricted basin samples and example mass spectrum of the C₁₃ compound obtained from scanning a whole aromatic fraction (mass resolution of 3,000 at 5% valley, background subtracted).....53
13. GC-MS (total ion current) of representative aromatic hydrocarbon fractions from open marine and restricted basin shales from northeastern Colorado and western

- Nebraska, respectively. See Table 2 and Figure 1 for well locations. Chromatograms on right show enlargement of scans 499-530. Aryl isoprenoid compounds, indicated by asterisks or carbon number, are major peaks in restricted basin samples, but are present in trace amounts in open marine samples and are commonly not detectable.....55
14. Example chemical structures of carotenoids found in photosynthetic sulfur bacteria that are believed to be the precursor compounds for aryl isoprenoids detected in sedimentary organic matter.....59
15. GC-MS of steranes (m/z 217) and terpanes (m/z 191) in whole bitumens from rock extractions. Carbon numbers of steranes refer to compounds with $\alpha\alpha\alpha$ (H) stereochemical configuration. Sterane peaks labeled 1, 2, 3, $\alpha\alpha\alpha$ C₂₇, $\alpha\beta\beta$ 20R C₂₇ + minor C₂₉ diasterane, and $\alpha\beta\beta$ 20S C₂₇, respectively. T_m = 17 α (H)-trisnorhopane. T_s = 18 α (H)-trisorneohopane.....61
16. Relative abundance of pristane (C₁₉) versus farnesane (C₂₀) determined from GC of saturated hydrocarbon fractions from open-marine (triangles) and restricted-basin (asterisks) settings. Amounts shown are

	normalized percentages of the C ₁₅ -C ₂₀ isoprenoid fraction.....	79
17.	Hydrogen index (mg hydrocarbons/g C _{Org}) from Rock-Eval versus $\delta^{13}\text{C}$ of C _{Org} (kerogen).....	87
18.	C _{Org} versus $\delta^{13}\text{C}$ (C _{Org}).....	89
19.	Carbon isotopic composition of saturated and aromatic hydrocarbons. Line separating marine from non-marine sources of organic matter from Sofer (1984).....	96
20..	$\delta^{13}\text{C}$ (kerogen, or C _{Org}) - $\delta^{13}\text{C}$ (saturates) versus $\delta^{13}\text{C}$ (kerogen, or C _{Org}) - $\delta^{13}\text{C}$ (aromatics).....	99
21.	Comparison of kerogen (C _{Org}) $\delta^{13}\text{C}$ values and Δ values (difference in $\delta^{13}\text{C}$ values between C _{Org} and hydrocarbon fractions).....	103
22.	Concentration of tetrapyrroles (pheopigments) in organic matter from surface sediments in offshore California basins versus height of water column for the $\leq 10 \mu$ sediment particle size fraction. From Lewan et al. (1982) and Orr et al. (1958).....	106
23.	Hydrogen Index (mg hydrocarbons/g C _{Org}) for rock samples from Rock-Eval pyrolysis versus total porphyrin concentration (VOP + NiP) relative to bitumen (ppm).....	110

24. C_{org} versus total porphyrin concentration (VOP + NiP) relative to bitumen (ppm). Squares indicate restricted basin samples, +'s indicate open marine samples from northeastern Colorado, x's indicate open-marine samples from Kansas and Oklahoma.....113
25. Comparison of $\delta^{13}C$ (C_{org}) and porphyrin concentration normalized to C_{org} and bitumen.....117
26. Geochemical parameters of cores samples collected at approximately 1-cm intervals through a single black shale bed in the Mitchell 34-12 Seegrst well (samples 9-18, Table 2). Parameter abbreviations and units of measurement are described in Table 2.....120
27. GC of saturated hydrocarbon fraction of rock extract containing high amounts of the proposed hypersaline indicator *n*-C₂₂. The odd carbon preference and high pristane to phytane ratio are interpreted to indicate input of terrestrial organic matter.....130

28. Summary of interpreted water column conditions in the "restricted basin" part of the study area in Nebraska during deposition of organic-rich rocks. The upper water column contained oxygen in sufficient amounts to support aerobic photosynthesis, but was possibly thinner than the lower anoxic water layer in which sulfate reduction and anoxygenic photosynthesis were taking place.....136

LIST OF TABLES

Table

1. Elemental analysis of selected black shale and marlstone samples, northern Denver basin and southeastern Powder River basin.....9
2. Organic geochemical data for rocks, northern Denver Basin and southeastern Powder River Basin.....28
3. List of aromatic hydrocarbons identified by GC and GC-MS. Numbers refer to peaks identified in the TIC traces of Figure 15.....65
4. Stable carbon isotopic ratios for kerogen, saturated and aromatic hydrocarbons, and carbonate carbon in rock samples northern Denver Basin and southeastern Powder River Basin.....68
5. Sulfur isotope ratios of Desmoinesian black shale samples from the western Nebraska panhandle (Sioux County).....81
6. Geochemical characteristics of rocks and oils contained in hypersaline sequences.....126

ACKNOWLEDGMENTS

The assistance of T.R. Wildeman throughout the preparation of this thesis is greatly appreciated. The following companies and individuals provided samples: Bird Oil Corporation, Conoco Inc., J. Hatch, Hunt Oil, Mitchell Energy, and Sun Exploration and Production Company. Analytical work by the following U.S. Geological Survey colleagues is gratefully acknowledged: P.H. Briggs, T.A. Daws, J.D. King, P.G. Lillis, G.E. Michael, A. Warden, and M.D. Wasserman. Helpful comments on an earlier draft by D. Anders, M. Lewan, and J. Palacas are appreciated. Many discussions with F.F. Meissner contributed significantly to this research.

INTRODUCTION

Recently, considerable research has been directed toward improved applications of organic geochemistry in assessment of paleoenvironment (Brassell et al., 1987). Various multiparameter approaches have been used to interpret paleoenvironments based on analysis of rocks and crude oils (Moldowan et al., 1986; Brassell et al., 1987; Mello et al., 1988). Successful paleoenvironmental assessment of ancient rocks or crude oils requires an understanding of the reaction pathway(s) linking the organic components of recent sediments or biological systems and their diagenetic or catagenetic products in ancient sediments (Brassell et al., 1987) and an understanding of environmental factors controlling the distribution of organisms in the sedimentary environment and the preservation of organic matter

One purpose of the present study is to apply organic geochemistry to interpretation of paleoenvironment (water, sediment chemistry and source of organic matter) of ancient rocks having low to moderate present-day levels of thermal maturity (vitrinite reflectance \approx 0.4-0.6 percent). The objective is to test the use of organic geochemical techniques for interpreting paleoenvironment during deposition of organic-rich rocks contained in a stratigraphically narrow interval (about 30-100 m thick) of Middle Pennsylvanian (Desmoinesian and Missourian) age in the northern Denver and southeastern Powder River Basins (north of the

Transcontinental Arch, Fig. 1) in an embayment of the Midcontinent Pennsylvanian sea in which above normal salinities existed at times in the water column. For comparative purposes, a few samples of Desmoinesian-age organic-rich rocks from Kansas, Missouri, and Oklahoma are included in the study.

The term hypersaline is used in this paper according to the terminology of Lang (1937) as discussed by Hite and Anders (1991). According to Lang's (1973) scheme, hypersaline refers to all salinities above normal marine salinity (i.e., 35-350+ ‰). The salinity range over which carbonate precipitation occurs is called "vitasaline" and the point at which anhydrite precipitation begins (approximately 142 ‰) is called "penesaline". For convenience in the present paper, the term hypersaline is used throughout and no distinction is made between the various stages of hypersalinity.

GEOLOGIC SETTING

Stratigraphy and Structural Setting

During Middle Pennsylvanian (Desmoinesian, above 310 Ma) time, the area of the present-day northern Denver basin and southeastern Powder River Basin (Figure 1) was a shallow embayment of the Midcontinent sea (Heckel, 1977; Wilson, 1978; Cardinal and Holmes, 1984). The area including the Nebraska panhandle, southeastern Wyoming, and southwestern South Dakota is the site of the Lusk Embayment of Pennsylvanian age (Bates, 1955) and the Alliance basin of Permian age (MacLachlan and Bieber, 1963; Rascoe and Baars, 1972). Numerous previous reports have discussed the Pennsylvanian stratigraphy and tectonics of the northern Denver and southeastern Powder River Basins in detail (e.g. Agatston, 1954; Bates, 1955; Cardinal and Holmes, 1984; Desmond et al., 1984; Foster, 1958; Hoyt, 1962, 1963; MacLachlan and Bieber, 1963; Mallory, 1958, 1960, 1967, 1972; Momper, 1963; Rascoe and Baars, 1972; Tranter and Petter, 1963; Tromp, 1981; Tromp et al., 1981; Wilson, 1978) and only a brief summary of the stratigraphy and tectonics is given here.

Formation names and ages for rocks of Mississippian through Permian age in the northern Denver and southeastern Powder River Basins are given in Figure 2. The top of the Pennsylvanian occurs at the Red Shale Marker (Cardinal and Holmes, 1984; Foster, 1958; Mallory, 1967; Maughan, 1978), a distinctive red shale and mudstone. The rocks of Atokan through Missourian age consist predominantly of

Figure 1. Map showing paleogeography during deposition of Desmoinesian cyclothem during regressive episode and location of samples. Numbers refer to wells listed in Table 1. Restricted basin sample locations are shown by solid dots and open-marine sample locations by solid diamonds.

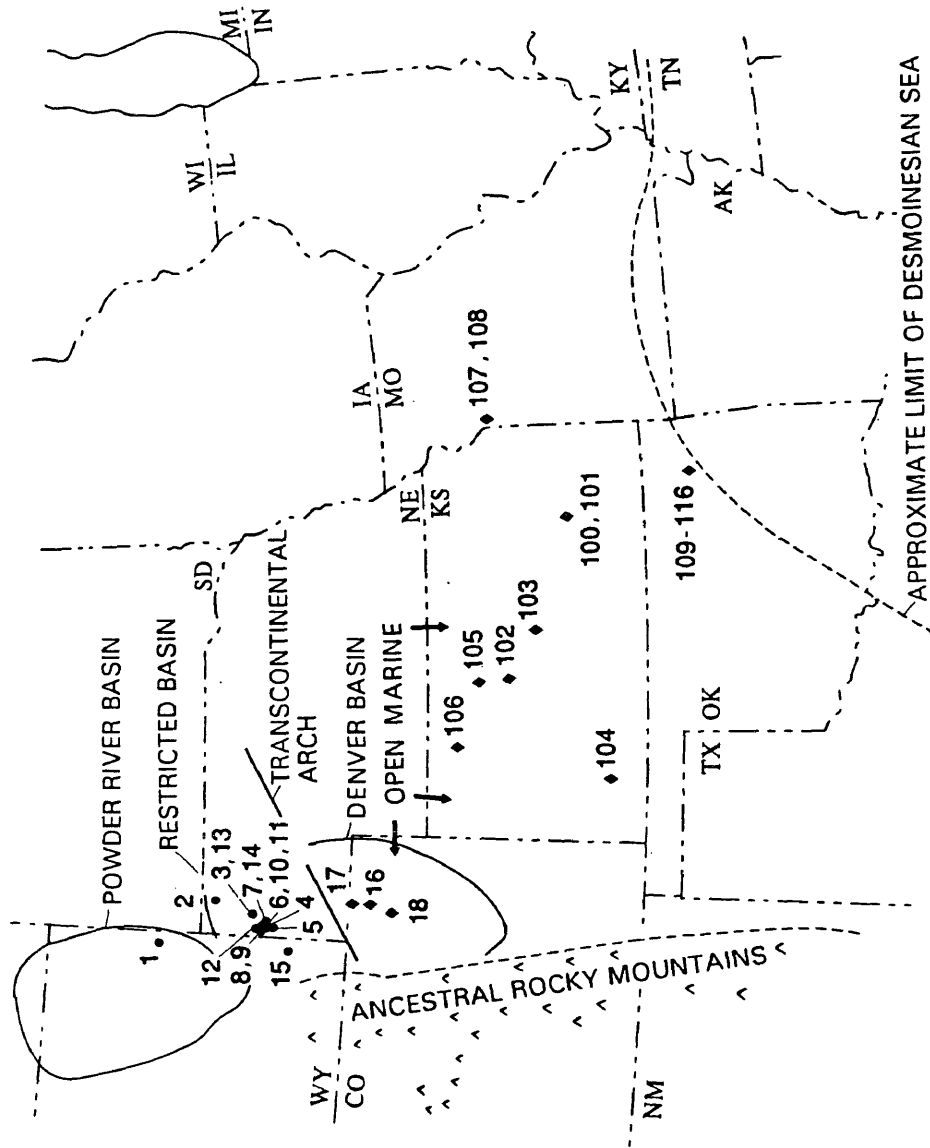
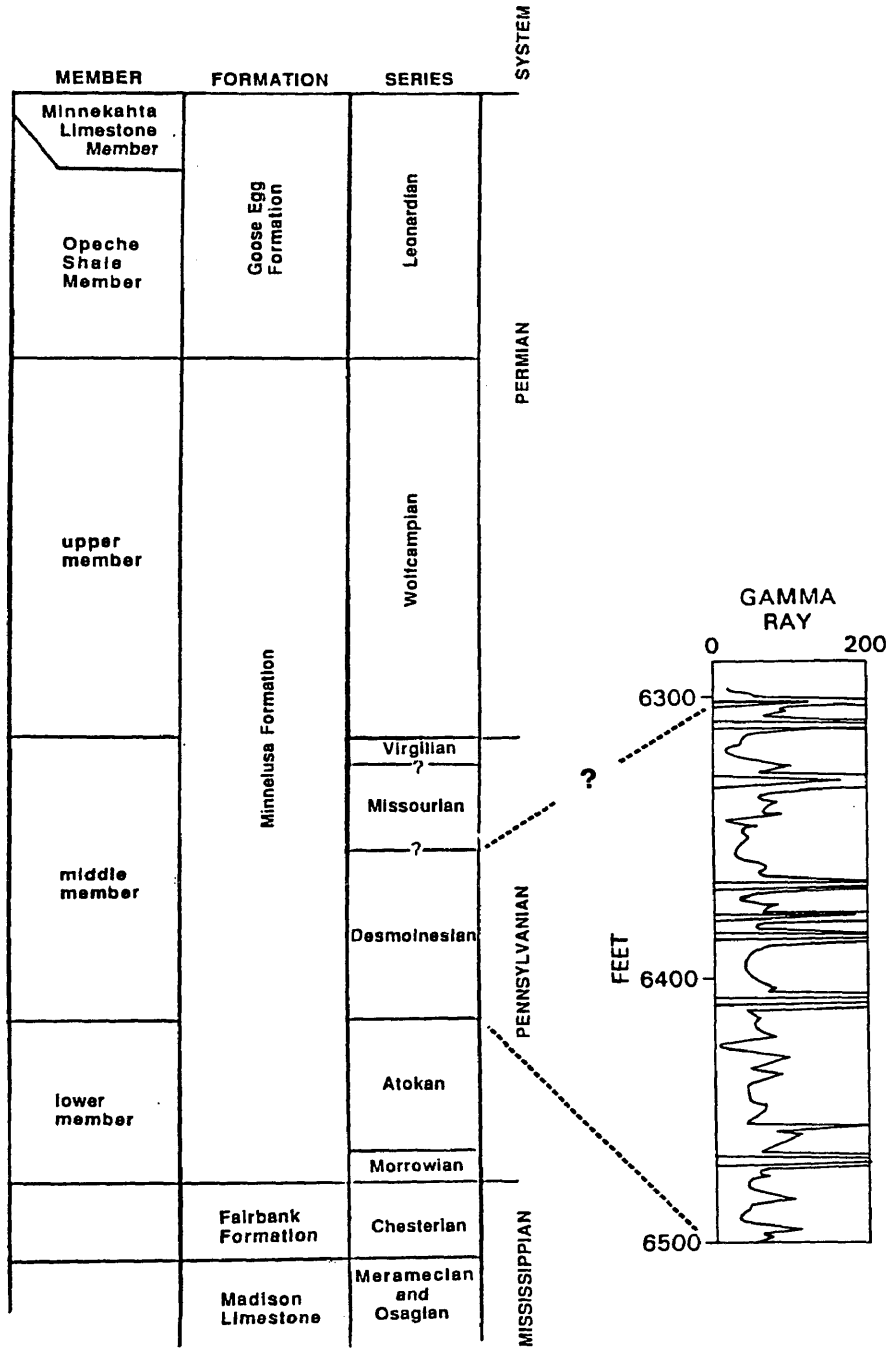


Figure 2. Generalized stratigraphic column showing ages and names of rock units in the northern part of the study area. Inset shows a typical gamma-ray log through the Desmoinesian in Sioux County, Nebraska. Organic-rich shales and marlstones are clearly identified by the high gamma ray response on the log. Eight thin, organic-rich, radioactive black shales or marls are present in the restricted basin of western Nebraska and eastern Wyoming as indicated by the gamma ray log . The age of the uppermost organic-rich unit may be Missourian rather than Desmoinesian as indicated on the figure. Gamma ray log is given in API units.



shallow marine carbonates, anhydrite, chert, sandstone, and marlstone (Cardinal and Holmes, 1984).

The black shales and marlstones of Desmoinesian and Missourian age, the focus of this study, are highly radioactive and can be correlated with gamma-ray logs over a broad area of the northern Denver and southeastern Powder River Basins. Tromp (1982) reported that the black shales and marlstones contain from 40 to 60% quartz, a few percent to 50% dolomite, generally less than 10% illite, and as much as 10% pyrite. Results of elemental analysis (inductively coupled plasma-emission spectrometry) on 22 shale and marlstone samples from the northern part of the study area (Table 1) agree, in general, with those of Tromp (1981), although carbonate minerals are significant components of all of the samples analyzed in the present study. The high Mg values suggest that dolomite is an important constituent of the carbonate mineral fraction. Total carbonate carbon was determined separately for five samples (samples 60-65, Table 1), the amount of CaO and MgO required to account for the measured carbonate carbon was calculated. With the exception of one sample (sample 65), the carbonate carbon values determined directly compare closely with the calculated values. In other words, essentially all of the MgO and CaO must be present as carbonate minerals to account for the directly-measured carbonate carbon. Assuming that the situation is similar for the other samples, carbonate content was determined assuming that all of the CaO and

Table 1

Elemental analysis of selected black shale and marlstone samples of Desmoinesian and Missourian age, northern Denver and southeastern Powder River Basins [values are weight percent of the whole rock].

Sample Number	SiO ₂ ¹	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	S ²	OM ³	Carbonate ⁴
2. Mitchell 34-12 Seegrift (Sec. 12, T.33N.-R.52W.)												
8	26.4	7.9	3.1	11.5	15.4	0.39	3.0	0.27	0.21	3.3	10.4	50
3. Bird 2-4 Murphy (Sec. 2, T.27N.-R.54W.)												
23	38.7	8.5	4.2	4.5	8.3	0.58	3.2	0.30	0.52	2.9	23.1	23
24	32.7	7.6	3.2	8.1	12.9	0.45	3.1	0.23	0.45	2.9	14.4	41
25	47.3	10.9	3.1	4.5	12.9	0.70	4.4	0.35	0.53	1.4	1.3	30
26	43.2	9.6	4.3	5.6	9.9	0.61	3.8	0.32	0.52	2.9	8.8	29
27	43.9	9.1	3.2	5.0	10.2	0.54	3.8	0.28	0.55	2.6	10.0	29
4. Bird 18-8 Downer (Sec. 18, T.24N.-R.56W.)												
29	38.3	9.5	3.5	5.1	16.8	0.58	3.6	0.38	0.59	2.0	3.6	39
31	33.8	8.9	4.6	9.0	12.9	0.57	3.2	0.32	0.29	2.9	8.4	40
7. Bird 11-16 Corman (Sec. 11, T.25N.-R.56W.)												
48	37.8	7.9	3.5	8.0	11.5	0.51	3.1	0.25	0.39	2.3	11.3	37
49	33.6	6.6	2.2	11.0	16.4	0.46	2.8	0.23	0.55	1.4	6.2	49
50	44.4	11.7	3.1	6.5	8.8	0.66	5.0	0.45	0.25	2.2	6.2	28

Table 1 (continued)

51	15.2	7.8	3.4	8.1	11.8	0.46	3.2	0.27	0.41	2.5	33.8	50
52	38.1	7.9	4.4	5.0	9.8	0.50	3.4	0.27	0.57	nd	19.9	31
53	40.2	10.6	4.4	4.5	7.7	0.78	4.1	0.38	0.61	3.8	14.1	24
55	34.8	7.9	4.6	3.8	9.5	0.39	3.6	0.30	0.66	4.1	20.7	29
56	47.5	10.0	5.7	4.8	5.0	0.35	4.2	0.35	0.29	3.0	12.6	18
57	34.6	5.5	2.1	13.3	18.5	0.35	2.4	0.17	0.20	nd	1.7	54
9. Conoco 35-1 Duncan (Sec. 35, T.25N.-R.57W.)												
60	27.7	6.6	2.7	11.1	16.1	0.50	2.6	0.17	0.25	2.3	8.2	53 (50)
61	26.3	6.1	2.2	10.6	15.5	0.41	2.5	0.18	0.43	2.2	13.7	53 (51)
63	30.6	6.8	2.8	10.0	15.4	0.41	3.0	0.18	0.43	2.1	11.7	48 (49)
64	38.0	10.2	4.9	4.0	6.7	0.69	4.1	0.33	0.82	4.1	19.9	21 (22)
65	44.5	6.2	3.1	5.5	11.3	0.32	2.9	0.22	0.52	nd	20.2	28 (36)
15. Sun M. Segelke 1 (Sec. 26, T.11N.-R.53W.)												
91	47.4	8.5	4.0	6.5	8.1	0.42	3.5	0.32	0.43	2.2	9.2	26

Table 1 (continued)

17. Hunt 1-33 Brunkhardt (Sec 33, T.5N.-R.54W.)

93	41.0	11.5	3.5	3.7	12.5	0.61	3.5	0.38	0.70	1.5	9.3	31
5)		15.5	2.5	2.5	3.1	1.3	3.3	0.65	0.17	0.82	nd	nd
6)		15.4	2.5	2.4	3.1	1.3	3.2	0.65	0.17	nd	nd	nd
7)		0.81	nd	7.9	42.6	0.05	0.33	0.06	0.04	nd	nd	nd
8)		9.8	nd	2.0	21.7	0.64	2.2	0.37	0.23	0.19	<0.5	nd

1) SiO₂ determined by difference.

2) Percent total sulfur determined by Leco Sulfur Analyzer.

3) Total organic matter calculated from organic carbon content (C_{org}/0.9).

4) Weight percent of mineral matter composed of carbonate minerals, determined on organic-matter free basis. Values in parenthesis are separate carbonate determinations based on carbonate carbon content determined by acid digestion of the rock.

5) Average shale of Clarke (1915).

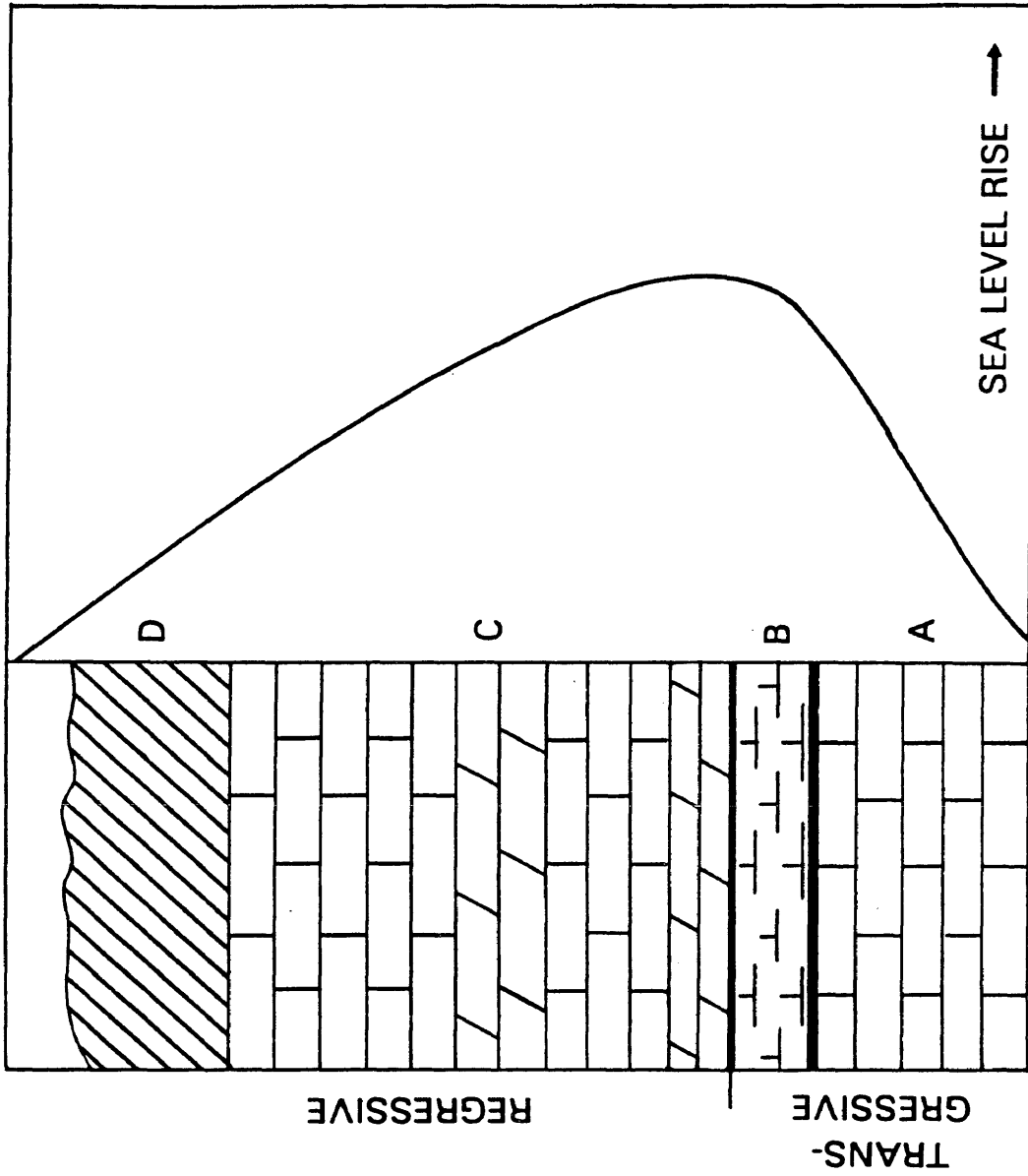
6,7) Average shale and limestone, respectively, according to Mason (1965).

8) Example marlstone of Cretaceous age (Pierre Shale) Tourtelot, 1962).

MgO occur as carbonates (last column of Table 1). Siderite was not considered a significant constituent because the generally high sulfur values suggest that most of the iron is present as iron sulfides. In many cases, sulfur is present in these rocks close to or in excess of the stoichiometric requirement for FeS₂ or FeS and, therefore, very little iron would be available for formation of siderite.

The overall stratigraphic sequence in the Desmoinesian and Missourian consists of a repetitive sequence of sediments, or cyclothems, analogous to those described by Heckel (1977, 1980, 1984) for the Midcontinent and the black shales or marlstones occur in the transgressive phase of each cycle. The sedimentary sequence in the Nebraska panhandle and adjacent areas is thinner, however, than equivalent rocks of the Midcontinent (Cardinal and Holmes, 1984). Many of the cycles in the northern Denver and southeastern Powder River Basins are incomplete and in some cases are apparently separated by periods of erosion or nondeposition (Cardinal and Holmes, 1984; Momper, 1966). The total thickness of Desmoinesian-age rocks in this area is from about 30 to 100 m (Wilson, 1978; Doyle, 1987). A typical idealized cycle from the Desmoinesian or Missourian age rocks of Nebraska panhandle is illustrated in the gamma-ray log of Figure 2 and in Figure 3.. In a typical cycle of Desmoinesian or Missourian rocks of the Nebraska panhandle, organic-rich black shales and marlstones are overlain by a regressive series of carbonate rock types with anhydrite at the top of each cycle. As many as nine

Figure 3. Generalized sequence of lithologies contained in a complete cyclothem in the northern Denver basin (western Nebraska) and relation to sea level (modified from Doyle, 1987). A, limestone; B, black shale or marlstone; C, limestone and anhydrite; D, anhydrite.



cyclothems containing organic-rich black shales or marlstones have been identified in the study area of the northern Denver and southeastern Powder River Basins.

Two of the most important structural elements in the area during Paleozoic time were the Ancestral Rockies and the Transcontinental Arch, a northeast-southwest trending feature that was a positive element at times during the Paleozoic (Momper, 1963; Weimer, 1978). Based on isopach maps of Paleozoic strata, a number of workers have concluded that the Transcontinental Arch influenced sedimentation during much of Paleozoic time (Cardinal and Holmes, 1984; Hoyt, 1963; Momper, 1963; Wilson, 1978; Weimer, 1978) and may have affected Mesozoic sedimentation (Weimer, 1978). Cardinal and Holmes (1984) suggested that the Transcontinental Arch caused nondeposition and erosion over a large portion of the Nebraska panhandle during Mississippian time and that subsidence of the Arch during Pennsylvanian time allowed the sea to advance northward into the northern Denver Basin.

Paleogeography and Black Shale Deposition

From the geologic evidence presently available, it is not clear to what extent, if any, the Transcontinental Arch affected sedimentation during Desmoinesian and Missourian time. Geologic studies indicate that during Desmoinesian time the Lusk Embayment, or Alliance Basin, was a shelf that sloped gently (less than about 0.3 m/km) to the present-day south (Cardinal and Holmes, 1984). Water circulation

on the shelf is thought to have been restricted (Hoyt, 1963; Momper, 1963; Desmond et al., 1984) owing to shallow water and the large areal extent of the relatively flat topographic surface (Desmond et al., 1984). It is possible that a low-relief topographic high was present at the location of the Transcontinental Arch where Cardinal and Holmes (1984) observed a thinning of Desmoinesian strata, or a slight break in the shelf slope may have been present although insufficient geologic data are presently available to adequately test either of these two hypothesis.

Nevertheless, the presence of evaporite rocks (carbonate-anhydrite sequence) indicates that oceanic circulation was restricted at times during Desmoinesian and Missourian time. According to Doyle (1987) and Desmond et al. (1984), most of the black shales or marlstones in western Nebraska and eastern Wyoming are subtidal deposits with supratidal, sabkha, and eolian deposits along the margins of the shelf area in parts of South Dakota and Nebraska along the northern and eastern Depositional edge of Desmoinesian rocks. Water depths may have been about 20 m or less during black shale deposition in the Nebraska panhandle during Desmoinesian time (Doyle, 1987).

The high carbonate content of the black shales and marlstones and absence of fossils (Desmond et al., 1984) are consistent with, but do not prove, that salinities were above normal during deposition although this cannot be determined unequivocally from the data

presently available. Anhydrite nodules common in many of the shale and marlstone beds are probably mostly secondary in origin, although petrographic work by D. Masse (oral communication, 1991) indicates that some primary anhydrite is present. This finding indicates that hypersaline (>35‰) conditions existed during deposition of at least some of the shales and marlstones, and that very high salinities occurred at times. However, it should be emphasized that the geological and geochemical data presently available are insufficient to derive any unequivocal conclusions about water salinities during deposition of most of the black shales or marlstones.

In contrast, deposition of black shales in northeastern Colorado and the Midcontinent region is likely to have occurred in a shallow marine environment with normal marine salinities (Heckel, 1977). Heckel (1977, 1980, 1984) concluded that the black shales of the Midcontinent cyclothem are the most basinward deposits of the transgressive part of each transgressive-regressive episode represented by individual cyclothem sequences. He proposed that the organic-rich black shales were deposited in an anoxic environment below a thermocline with water depths from about 50 to 100 m.

In the present study, the area to the south including northeastern Colorado and the broad Midcontinent region studied by Heckel is referred to as "open marine" and the shelf area or embayment to the north is referred to as a "restricted-basin". The

term restricted basin is meant to imply that restricted water circulation occurred on the shelf area (Lusk Embayment), but does not necessarily require a topographic barrier, or sill, as the restricting mechanism as discussed above.

An alternative model for cyclothem deposits has recently been proposed for Pennsylvanian rocks of the eastern United States (Cecil, 1990). According to this model, cyclic deposits represent climatic changes wherein carbonate and (or) evaporite rocks are deposited during dry periods and siliclastic rocks represent periods of greater rainfall. During times of continually wet conditions, chemically precipitated rocks are dominant including high amounts of organic matter derived from abundant plant growth on adjacent land masses. Siliclastic rocks are of minor importance during continually wet periods because erosion is impeded by dense vegetation. Although this model of paleoclimatic control has not yet been tested for cyclothems of the western U.S., it does have some appeal because some of the stratigraphic relationships observed in the cyclothem deposits of the Nebraska panhandle and southeastern Powder River Basin are more easily explained with this model than by a model of tectonic or eustatic sea-level changes alone. For example, at some locations organic-rich black shales are interbedded with sandstones of eolian origin. This stratigraphic relationship is difficult to explain by the transgressive-regressive model above. Instead, geologically-rapid changes in climate could produce this stratigraphic sequence.

Presently, insufficient data are available to adequately test the role of climate in the deposition of the cyclothem deposits. Further studies are needed to investigate the importance of climate in controlling the deposition of the cyclothem.

SAMPLES AND ANALYTICAL METHODS

The location of wells from which samples were used in this study are shown in Figure 1. Only subsurface core samples were used except for the 1-33 Brunkhardt well, for which only cuttings samples were available. Cuttings samples were handpicked, and selected samples were analyzed in duplicate to minimize the possibility of contamination by caving or from organic-poor rock types such as limestone and dolomite that are stratigraphically adjacent to the thin organic-rich black shale beds. Samples were handpicked by placing the bulk cuttings samples in a culture dish and individual grains were selected using forceps under a binocular microscope.

To test the amount of variability among individual rock grains picked by this procedure, Rock-Eval pyrolysis was performed on single grains selected from one sample (eight individual grains of about 10-20 mg each, collected from a 10-foot interval in the 1-33 Brunkhardt well). Hydrogen Index (HI), Oxygen Index (OI), Tmax, and organic carbon (Corg) for these eight individual grains are shown in Figures 4-6. With the exception of one grain that has a low Corg and HI, the individual grains have fairly consistent HI and Tmax values. The Corg values have a range of about 5 weight percent,

Figure 4. Hydrogen Index (mg hydrocarbons/g organic carbon versus Oxygen Index (mg CO₂/g organic carbon) for single cuttings chips (approximately 10-20 mg each) handpicked from 1-33 Brunkhardt well (7,000-7,010 ft).

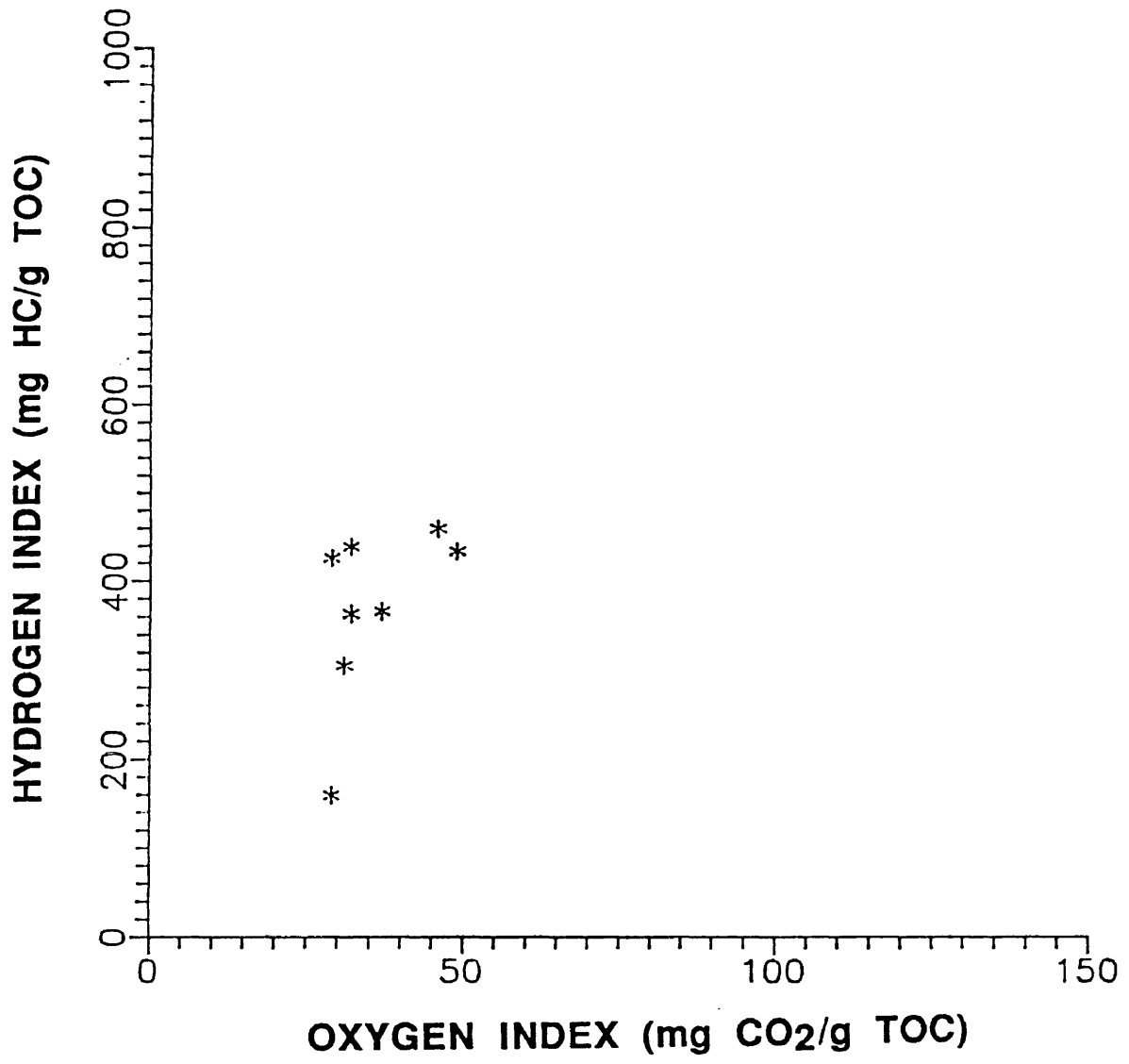


Figure 5. Tmax (°C) from Rock-Eval pyrolysis for single cuttings chips (approximately 10-20 mg each) handpicked from 1-33 Brunkhardt well (7,000-7,010 ft).

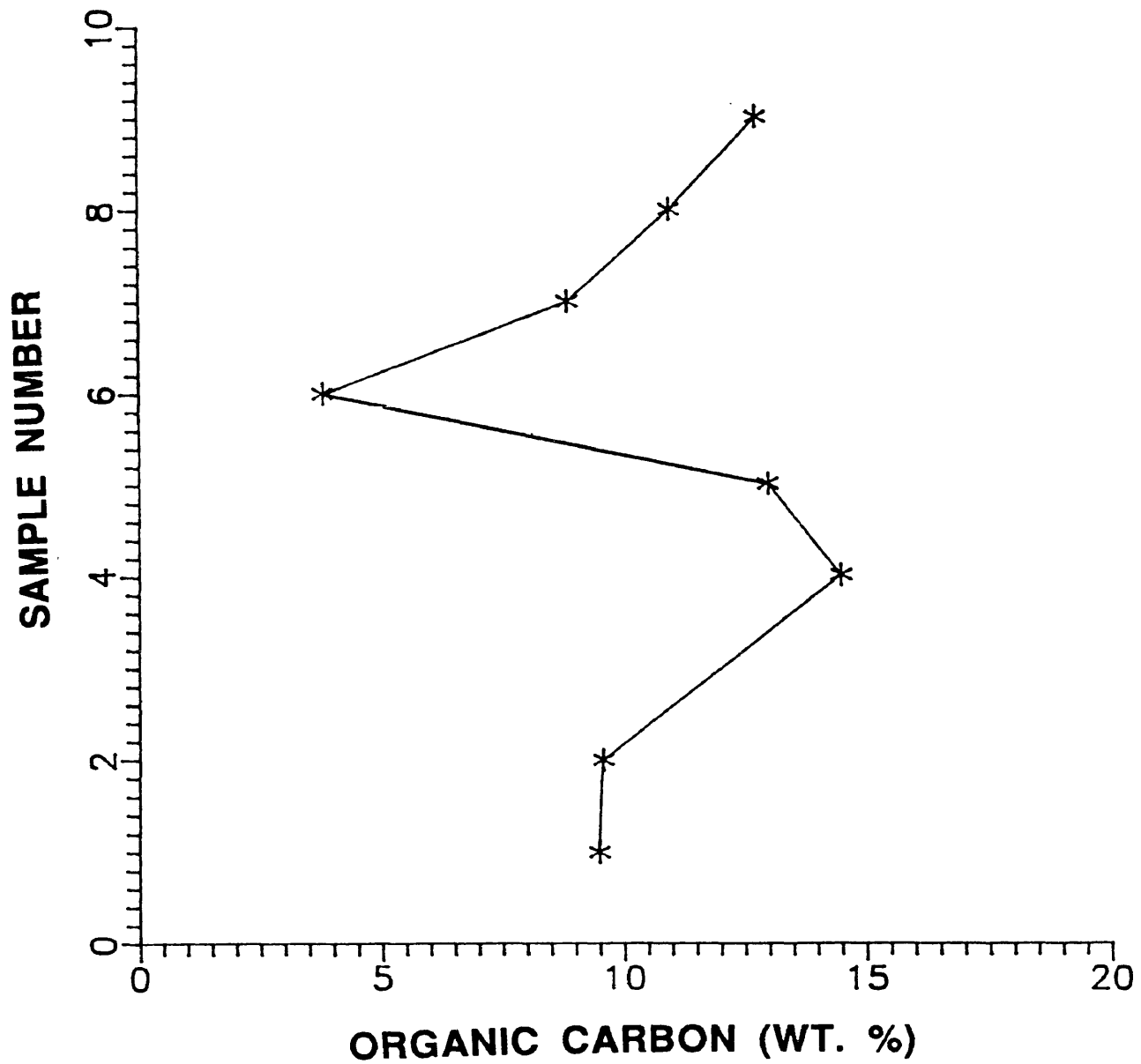
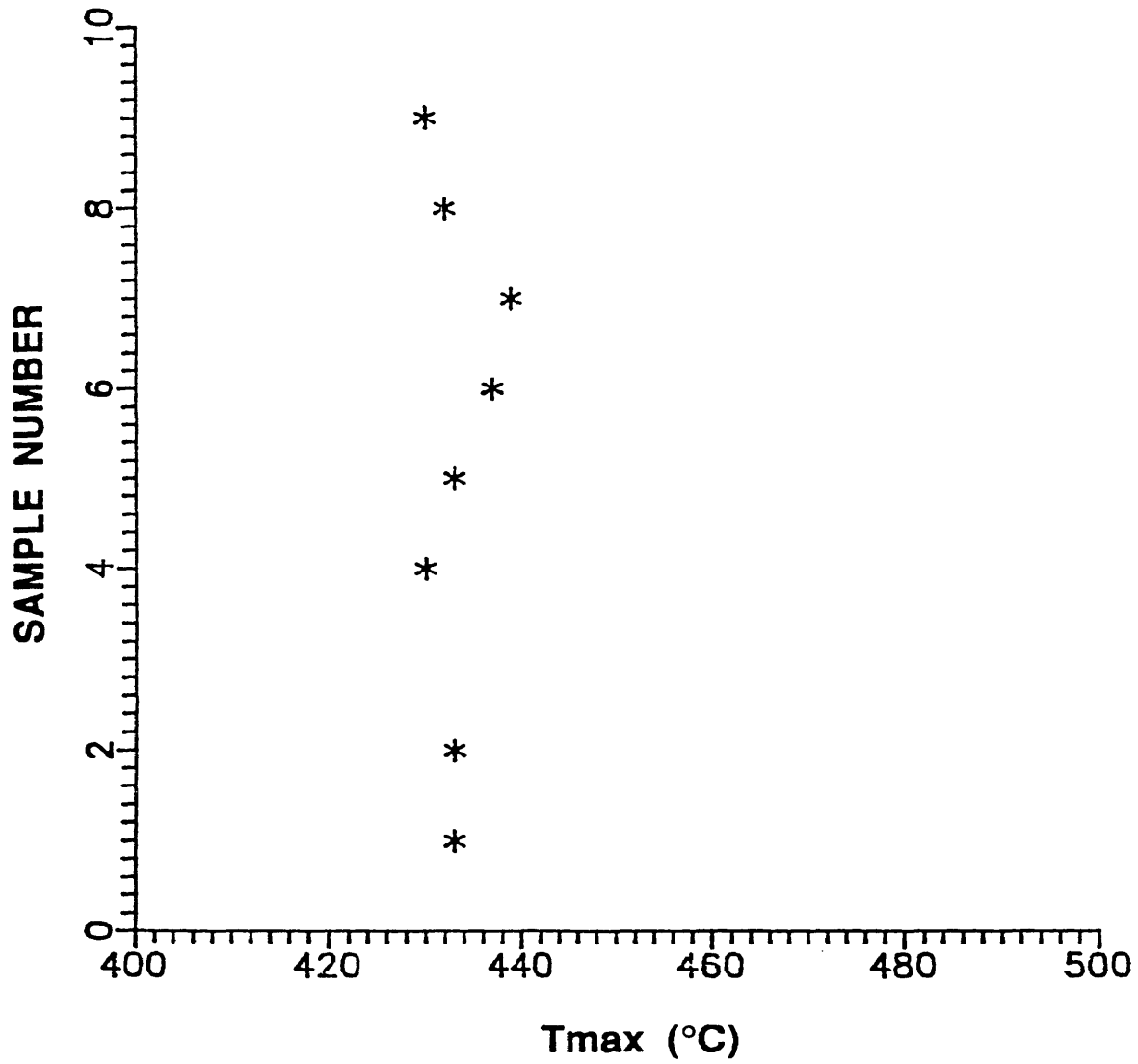


Figure 6. Weight percent organic carbon (Corg) for single cuttings chips (approximately 10-20 mg each) handpicked from 1-33 Brunkhardt well (7,000-7,010 ft).



excluding the spurious value of 5 weight percent noted above. Although the relative variability of the Corg data is greater than the HI or Tmax values, the individual grains are all recognizable as very organic-rich compared to shales generally and this amount of variability would not significantly affect the interpretations of the present study.

The Tmax data would be expected to exhibit the least variability unless cavings from much shallower depths were present in the sample because Tmax is dependent mainly on thermal maturity and only secondarily on the type or amount of organic matter. Therefore, Tmax reflects the thermal maturity at or near the burial depth from which the sample was taken and should not vary unless cuttings from a significantly shallower depth interval were included in the sample (because of caving in the drill hole). In contrast, measurements sensitive to organic matter content and type of organic matter (Corg, HI, OI) have slightly greater variability because mixing of cuttings from several thin, black shale units separated vertically by as little as 10-20 feet is likely.

These data illustrate the difficulty of using cuttings samples for geochemical analysis and the importance of handpicking samples. Bulk cuttings samples (that is, not handpicked) from the 1-33 Brunkhardt well have Corg contents and HI values less than 1.0 and 100, respectively, owing to inclusion of the very organic-lean nature

of the rocks that are interbedded with the organic-rich black shales (J. Clayton, unpublished data).

In the present study, rocks in the restricted-basin setting and the adjacent open-marine setting in northeastern Colorado are the main focus. Samples of equivalent rocks were collected from the open-marine environment of Kansas, Missouri, and Oklahoma for comparison of certain geochemical parameters. Seventeen such latter samples were analyzed previously for other studies: samples 100-108 (Table 2) were analyzed by J. R. Hatch (U.S. Geological Survey, unpublished data) and samples 109-116 by Wenger and Baker (1986).

Thermal maturity of the Desmoinesian and Missourian interval is about the same throughout the study area. Vitrinite reflectance (percent R_0), or vitrinite reflectance equivalent determined from other thermal maturation parameters, is 0.4-0.6 percent. These rocks have apparently experienced a fairly low temperature history so that only limited thermal maturation has taken place in the black shales and marlstones, despite their advanced age and fairly deep burial (as much as about 3,000 m prior to erosion in the restricted basin of western Nebraska). Therefore, geochemical differences between samples reflect primarily variation in organic-matter source or early diagenesis rather than variation in thermal history.

Rock samples were pulverized to approximately 100-mesh particle size, and a split was removed for determination of C_{org} and

Table 2

Organic geochemical data for rocks, northern Denver basin and southeastern Powder River basin. [Wells shown by number in figure 1. Sample depth in meters. T, trace amount, too small for detection. Leaders (--), not determined.]

Sample member	Sample depth (m)	Corg ¹	EOM ²	SAT. ³ HC	S/A ⁴	Pr/Ph ⁵	Pr/nC ¹⁷	NIP ⁶	VOP ⁷	V/V+Ni ⁸	S _T ⁸	Corg/S _T ⁸	S ₁ ⁹	S ₂ ¹⁰	Hf ¹¹	Tmax
RESTRICTED-BASIN SAMPLES (Nebraska, Wyoming)																
1	1,831	27.0	8,700	2,100	0.7	1.33	0.21	7	241	0.99	3.8	7.1	5.7	188.4	696	459
2	1,835	9.0	13,200	5,500	0.4	0.91	0.24	T	53	--	2.4	3.8	2.2	21.9	243	42
3	1,855	18.0	10,400	1,600	0.2	1.29	0.36	613	35,293	0.98	4.5	4.0	4.7	89.5	496	433
4	1,860	15.0	10,700	1,500	0.2	1.20	0.43	--	--	--	3.2	4.7	2.8	64.9	432	438
5	1,879	7.7	1,579	505	1.0	1.30	0.28	--	--	--	2.6	2.9	1.7	0.9	129	437
6	1,887	8.4	3,900	360	0.3	1.05	0.63	549	8,244	0.92	1.9	4.4	1.2	49.5	435	--
2. Mitchell 34-12 Seegrst (sec. 16, T.33N., R52 W.)																
7	1,389	2.6	381	86	0.6	1.40	0.14	--	--	--	0.5	5.2	0.2	1.3	49	431
8	1,394.5	9.4	9,443	1,640	0.6	1.08	0.81	T	16,109	1.00	3.3	2.8	2.5	29.3	310	427
9	1,394.54	10.4	8,949	--	--	--	--	63	22,805	1.00	--	--	3.1	43.0	412	433
10	1,394.57	9.1	8,036	--	--	--	--	122	24,596	1.00	--	--	2.9	33.6	369	435
11	1,394.60	9.3	8,874	--	--	--	--	217	29,972	0.99	--	--	2.9	32.9	355	434
12	1,394.63	9.4	8,181	--	--	--	--	411	31,813	0.99	--	--	2.8	35.5	378	434
13	1,394.66	9.7	8,035	--	--	--	--	327	23,801	0.99	--	--	2.9	35.7	366	434
14	1,394.69	9.5	8,635	--	--	--	--	234	18,294	0.99	--	--	2.9	34.5	362	434
15	1,394.7210.4		9,893	--	--	--	--	293	30,620	0.99	--	--	3.1	36.4	349	435

Table 2 (continued)

16	1,394.75	10.7	8,010	--	--	--	47	19,222	1.00	--	--	3.7	43.9	409	436	
17	1,394.78	10.9	8,327	--	--	--	55	22,408	1.00	--	--	3.9	46.1	425	431	
18	1,394.81	11.1	7,946	--	--	--	99	21,140	1.00	--	--	--	46.4	419	432	
19	1,395	5.5	5,835	1,072	0.6	1.04	0.94	274	17,742	0.98	2.1	2.6	2.5	29.3	310	427
20	1,395.4	--	1,195	639	2.1	--	--	--	--	--	--	--	--	--	--	--
21	1,399	--	5,553	2,163	1.0	--	T	301	1.00	--	--	1.6	18.2	330	427	
22	1,402	8.5	5,155	1,265	0.6	1.04	0.42	39	1,690	0.97	2.5	3.4	2.4	29.8	351	425

3. Bird 2-4 Murphy (sec. 2, T.27N., R.54W.)

23	1,942	20.8	14,435	2,387	0.4	0.90	0.38	53	39,731	0.99	2.9	7.2	5.5	77.1	371	430
24	1,946	13.0	7,732	1,323	0.5	1.13	0.40	19	16,582	0.99	2.9	4.5	2.9	57.6	442	432
25	1,948	1.2	293	46	0.5	0.71	0.28	--	--	--	1.4	0.9	0.1	0.5	40	--
26	1,955.4	7.9	6,913	1,318	0.5	1.00	0.58	88	18,320	0.99	2.9	2.7	2.0	31.6	399	434
27	1,955.7	9.0	6,506	1,014	0.4	0.83	0.59	T	22,041	--	2.6	3.5	2.1	37.5	416	434

4. Bird 18-8 Downer (sec. T.24N., R.56W.)

28	2,363.7	2.4	2,500	600	0.5	1.07	0.67	--	--	--	1.8	1.3	1.1	7.9	333	427
29	2,364	3.2	2,400	400	0.4	--	--	--	--	--	2.0	1.6	1.2	15.9	495	430
30	2,364.6	1.7	1,500	200	0.3	1.13	0.59	T	3,041	1.00	0.7	2.4	--	--	314	437
31	2,380	7.6	6,700	1,000	0.3	0.95	0.45	179	7,628	0.97	21.9	2.6	2.4	36.5	423	--
32	2,393	4.4	2,900	300	0.2	1.25	0.18	T	266	1.00	2.3	1.9	1.3	14.8	337	--

5. Bird 2-3 Laucomer (sec. 5, T.24N., R.55W.)

33	2,256	10.0	5,830	926	0.3	1.00	0.44	211	13,617	0.98	3.4	2.9	2.3	42.3	423	428
34	2,26-	15.9	6,545	1,095	0.4	1.07	0.51	358	11,846	0.97	3.0	5.3	3.6	77.1	485	428

Table 2 (continued)

35	2,281	8.1	7,025	1,208	0.4	1.00	0.46	69	15,953	0.99	3.1	2.6	2.3	28.1	346	422
36	2,303	--	--	--	--	--	--	38	12,103	1.00	--	--	--	--	--	--
6. 13-18 Laucomer (sec. 8, T.25N., R.55W.)																
37	2,267	8.5	--	--	--	--	--	--	--	--	--	--	1.4	41.7	493	447
38	2,271.9	0.5	--	--	--	--	--	--	--	--	--	--	0.2	4.7	347	445
39	2,272.3	0.7	--	--	--	--	--	--	--	--	--	--	0.2	4.0	556	445
40	2,272.9	6.4	--	--	--	--	--	--	--	--	--	--	0.9	0.8	219	431
41	2,275	1.4	--	--	--	--	--	--	--	--	--	--	0.4	3.0	46	418
42	2,291	0.7	--	--	--	--	--	--	--	--	--	--	0.2	0.3	468	434
43	2,302.7	15.0	--	--	--	--	--	--	--	--	--	--	3.4	70.0	337	435
44	2,303	11.0	--	--	--	--	--	--	--	--	--	--	2.6	37.0	371	437
45	2,303.4	3.9	--	--	--	--	--	--	--	--	--	--	0.9	14.3	435	429
46	2,313	0.8	--	--	--	--	--	--	--	--	--	--	4.3	0.4	447	431
9. Conoco 35-1 Duncan (sec. 35, T.25N., R.57W.)																
60	2,416	7.4	5,000	800	1.3	--	--	--	--	--	2.3	3.2	2.6	24.9	335	439
61	2,417	12.3	6,500	1,400	0.4	--	--	9	3,704	1.00	2.2	5.6	4.4	56.0	458	441
62	2,418	12.3	5,800	860	0.9	--	--	--	--	--	--	--	3.7	55.0	445	442
63	2,428	10.5	5,300	1,300	1.6	--	--	105	8,670	0.99	2.1	5.0	2.8	52.0	491	440
64	2,431	17.9	7,800	1,700	1.3	--	--	222	18,143	0.99	4.1	4.4	6.9	98.0	546	437
65	2,441	18.2	11,500	3,000	0.6	--	--	--	--	--	--	--	6.8	100.0	548	439
10. True Spear Diamond Ranch 32-9 (sec. 8, T.25N., R.55W.)																
66	2,129	10.3	--	--	--	--	--	--	--	--	--	--	1.4	62.2	605	436

Table 2 (continued)

67	2,149	3.2	--	--	--	--	--	--	--	0.7	14.1	441	427
68	2,169	3.3	--	--	--	--	--	--	--	0.9	16.8	501	430
69	2,175.9	2.8	--	--	--	--	--	--	--	0.3	3.8	134	427
70	2,176.2	3.1	--	--	--	--	--	--	--	0.5	4.7	150	434
71	2,176.5	2.8	--	--	--	--	--	--	--	0.5	7.1	254	431

11. Hrubetz 1-26 Hilton (sec. 26, T.26N., R.56W.)

72	2,378	10.0	10,700	--	--	442	31,326	0.99	3.1	3.2	1.8	32.8	327	435
73	2,391	24.4	24,800	--	--	514	15,560	0.97	5.0	4.9	5.5	108.6	444	429
74	2,405	25.2	24,600	--	--	371	21,010	0.98	4.6	5.5	4.2	75.0	296	430
75	2,413	4.9	13,700	--	--	807	7,569	0.90	1.7	2.9	0.4	15.8	321	440

12. True 14-3 Murphy (sec. 3, T.27N., R.54W.)

76	1,964.3	12.9	15,600	--	--	365	25,861	0.99	2.8	4.6	4.4	62.3	481	424
77	1,964.9	10.5	8,600	--	--	442	26,340	0.98	2.0	5.3	3.0	46.6	443	423
78	1,965.2	7.9	7,500	--	--	473	18,239	0.97	2.4	3.3	2.2	35.6	452	426
79	1,980	10.9	5,800	--	--	823	11,711	0.93	2.9	3.8	2.5	60.7	555	424
80	2,007	1.3	--	--	--	--	--	--	--	--	0.1	0.7	52	427

13. Bird 11-16x Corman (sec. 11, T.25N., R.56W.)

81	2,360	21.5	25,300	--	--	981	32,648	0.97	3.9	5.5	5.0	106.9	496	428
82	2,924	3.0	--	--	--	--	--	--	--	--	2.1	9.2	312	439
83	2,924	5.3	--	--	--	--	--	--	--	--	2.5	16.3	311	434
84	2,924	6.8	--	--	--	--	--	--	--	--	2.8	28.2	415	432
85	2,925	7.3	--	--	--	--	--	--	--	--	1.9	23.3	318	434

Table 2 (continued)

86	2,925	6.4	--	--	--	--	--	--	--	1.9	24.3	380	434			
87	2,925	6.0	--	--	--	--	--	--	--	1.4	25.3	422	435			
88	2,927	17.2	--	--	--	--	--	--	--	5.6	69.3	402	426			
OPEN-MARINE SAMPLES (Colorado, Kansas)																
15. Sun M. Segelke I (sec. 26, T.11N., R.52W.)																
89	2,304.5	3.3	--	--	--	--	--	0.3	11.0	1.5	8.9	274	443			
90	2,304.810.1	--	--	--	--	--	--	--	--	3.2	38.2	378	440			
91	2,396	8.3	--	--	--	--	--	2.2	3.8	2.0	31.5	381	443			
16. Sun Roelle I (sec. 25, T.12N., R.53W.)																
92	2,272	5.8	--	--	--	--	--	0.7	8.3	1.9	22.4	382	439			
17. Hunt 1-33 Brunkhardt (sec. 33, T.5N., R.54W.)																
93	2,195	8.4	4,316	896	0.82	1.44	0.36	T	359	--	1.6/1.4	5.3	1.3	22.5	268	426
94	2,253	13.3	--	--	--	--	--	148	11,839	0.98	2.3	5.8	3.0	63.1	464	426
95	2,256	13.6	--	--	--	--	--	--	--	--	1.6	8.5	2.9	52.1	382	427
96	2,268	--	--	--	--	--	--	T	4,638	--	1.4	--	--	--	--	--
97	2,277	3.6	--	--	--	--	--	--	3,770	--	--	--	0.6	7.4	204	432
98	2,284	3.3	--	--	--	1.95	1.66	--	3,107	--	1.2/1.1	2.8	0.1	6.9	212	430
99	2,378	23.3	--	--	--	--	--	T	285	--	3.7	6.3	2.3	57.9	248	431
MISCELLANEOUS CORES AND OUTCROPS FROM KANSAS, OKLAHOMA, ILLINOIS																
100	637	21.6	6,300	--	--	--	1.7m	202	436	0.68	--	--	--	64m	280m	440m
101	678	14.9	3,800	--	--	--	1.9m	18	448	0.96	--	--	--	41m	260m	449m
102	964	8.2	3,850	--	--	--	--	959	4,774	0.83	--	--	--	--	--	330
103	889	12.8	7,720	--	--	--	--	381	4,141	0.92	2.2	5.8	--	--	--	340

Table 2 (continued)

104	1382	11.1	6,120	--	--	--	776	--	1.8	5.0	--	360
105	1004	10.0	8,190	--	--	1,215	2,790	0.70	1.8	5.6	--	--
106	1130	6.9	3,640	--	--	2,209	584	0.21	--	--	--	270
107	Outcrop	15.4	6,250	--	--	328	1,314	0.80	--	--	--	438
108	Outcrop	13.2	5,700	--	--	781	2,374	0.75	--	--	--	360
109		16.9	--	--	--	--	181	--	3.7	4.6	--	--
110		9.95	--	--	--	--	339	--	1.5	6.6	--	--
111		18.3	--	--	--	--	609	...	2.6	7.0	--	--
112		13.1	--	--	--	--	580	--	1.8	7.3	--	--
113		16.6	--	--	--	--	1,232	--	1.2	13.8	--	...
114		20.1	--	--	--	--	1,141	--	--	--	--	--
115		15.7	--	--	--	--	993	--	2.6	6.0	--	--
116		9.15	--	--	--	--	815	--	--	--	--	--

- 1) Weight percent organic carbon.
- 2) Chloroform-extractable organic matter (ppm relative to dry rock weight).
- 3) C₁₅+ saturated hydrocarbons (parts per million relative to dry rock weight).
- 4) Saturated to -aromatic hydrocarbon ratio.
- 5) Pristane to phytane ratio.
- 6) Nickel porphyrins (ppm in extractable organic matter).
- 7) Vanadium porphyrins (ppm in extractable organic matter).
- 8) Ratio of VOP/NiP+VOP
- 9) Total sulfur from Leco combustion.
- 10) S1 from Rock-Eval pyrolysis (mg/g Corg).
- 11) S2 from Rock-Eval pyrolysis (mg/g Corg).
- 12) Temperature of maximum pyrolysis yield (oC).
- 13) Data from Hatch and others (1989); S1+S2 yields combined.

sulfur. C_{Org} values were determined for 101 samples using a Delsi Model II Rock-Eval instrument equipped with a C_{Org} module. Sulfur values were determined for selected samples using a Leco sulfur analyzer.

Based on the pyrolysis assay, 59 samples were selected for extraction. Bitumen was obtained by extraction for 24 h with $CHCl_3$ in a Soxhlet apparatus. Asphaltenes were removed from the bitumens obtained above by $CHCl_3$ elution of the maltene fraction from a 250- μm macroporous silica gel column prepared in cyclohexane. The maltene fraction (i.e. the bitumen remaining after removal of asphaltenes) was taken to dryness using a rotary evaporator and nickel porphyrins (NiP) and vanadyl porphyrins (VOP) were isolated using column chromatography by successive elution with 0.35% ethyl acetate in cyclohexane and 8.0 percent ethyl acetate in cyclohexane (Freeman et. al., 1987). Quantitation of the porphyrin fractions was accomplished using an HP8542 ultraviolet/visible diode array spectrophotometer. The VOP and NiP absorbances were determined by taking the second derivative of the absorption spectrum to correct for background (nonporphyrin) absorbances.

A separate aliquot of the bitumen obtained by Soxhlet extraction was separated by liquid chromatography (silica gel), eluting successively with iso-octane, benzene:iso-octane (3:1 v/v), and benzene:methanol (1:1 v/v). These fractions contained saturated hydrocarbons, aromatic hydrocarbons, and nonhydrocarbons

("resins"), respectively. Each of the three eluates was dried under N₂ to remove the solvent and weighed to determine the amounts of each fraction. A small aliquot (≈5 ml.) of the saturated hydrocarbon fraction was removed for gas chromatography prior to complete removal of the solvent for gravimetric determination.

Gas chromatography (GC) analysis was performed using an HP 5880A GC equipped with a 50 m by 0.32 mm SE-54 fused silica capillary column. The GC was programmed from 50 to 320°C at 4°C min⁻¹ using hydrogen as the carrier gas. The detector output was digitized and stored on computer disk using the Nelson chromatography software.

GC-mass spectrometry (GC-MS) was performed using the GC described above coupled to a Kratos MS 30 mass spectrometer. GC-MS analysis was performed on whole bitumens at a mass resolution of 3,000 (5 percent valley). The MS source was operated in electron impact mode at 70 eV at a pressure of 10⁻⁶ torr at 250°C. Multiple ion detection was accomplished by switching the accelerating voltage with a constant magnetic field. For determination of aryl isoprenoid distributions and relative abundances, aromatic fractions were analyzed using GC-MS. Relative abundances of aryl isoprenoids and other biological markers (from whole bitumen analyses) were determined from peak areas of diagnostic ions (base peak). Peak identifications were based on retention times and fragmentation patterns compared to literature spectra.

Carbon isotope ratios of saturated and aromatic hydrocarbons and kerogens were determined by placing the sample in a quartz tube with cupric oxide and a silver strip, then sealing the tube under a vacuum. The tube was heated at 840 °C for 4 hrs. The CO₂ formed was collected and purified using a cryogenic vacuum line. Carbonate carbon was collected as CO₂ by digestion of the samples in 100 percent anhydrous phosphoric acid at 25 °C. The CO₂ generated by acid digestion was collected according to the procedure above.

Carbon isotope ratios of the CO₂ collected above were measured using Finnigan MAT 251, 90° sector isotope ratio mass spectrometer. Isotopic compositions were determined by comparison with a working reference standard prepared from NBS-19 calcite. Isotope ratios are reported in the standard delta notation in units of parts per thousand (‰) relative to the Peedee belemnite standard (PDB).

$$\delta^{13}\text{C} (\text{‰}) = [(R_{\text{sample}}/\text{PDB}) - 1] \times 10^3,$$

$$R = {}^{13}\text{C}/{}^{12}\text{C}$$

Instrumental reproducibility for isotope ratios is 0.5 ‰. Duplicates of several samples were analyzed including duplicate CO₂ preparation to monitor reproducibility. $\delta^{13}\text{C}$ values of kerogen and carbonate carbon were reproducible with 0.13 ‰ and 0.85 ‰, respectively

Total sulfur was separated into various forms (pyrite, anhydrite, acid-volatile, organic) using the method of Tuttle et al. (1986) and sulfur isotope ratios were measured on selected samples.

Twenty-four samples were selected for elemental analysis using inductively coupled plasma (ICP) emission spectroscopy. For ICP analysis about 0.200 g of powdered rock was dissolved using a low-temperature multi-acid digestion (con HCl, HF, HClO₃, and HNO₃, successively). The solution was dried and redissolved in 1.0 ml. aqua regia and diluted to 10.0 g with 1.0 percent HNO₃. The precision and accuracy of the method is 5-10 percent maximum relative standard deviation. Amounts of major elements are expressed as weight percent of their oxides in Table 1. SiO₂ was determined by difference.

RESULTS

Organic Carbon and Sulfur

Total organic carbon content (C_{Org}) of the black shales is about 1-30 weight percent (Table 2). Black shales in the restricted-basin and open-marine setting have markedly higher C_{Org} contents than rocks deposited on the sill separating these two areas and around the margins of the seaway for which C_{Org} values are all less than about 2.0 weight percent. Between individual black shale units at any given location, the C_{Org} content is somewhat variable, but by comparison it is mostly invariant for vertical profiles within a single bed (samples 9-18; Table 2). Because insufficient well data are available to

unequivocally correlate individual black shale beds across the entire study area, from the restricted-basin to the open-marine environment, it was not possible to evaluate the lateral variability in C_{org} for individual black shale beds on a regional scale.

Total sulfur content of the shale is from 0.13 to 5.0 weight percent, and most values are between 2 and 4.5 percent (Table 2). Carbon/sulfur ratios (C_{org}/S_T) of restricted basin samples (average 3.7) are generally lower than those of the open-marine samples (average 6.5) (Figure 7). One restricted-basin sample has an anomalously high C/S ratio (sample 51, 11-16 Corman, 2,364 m; $C/S = 12.2$). Excluding this sample, the restricted-basin samples have an average C/S ratio of 3.4. Many of the restricted-basin samples have ratios lower than those reported for normal marine sediments ($C/S \approx 3$) (Berner, 1970; Sweeney, 1972; Goldhaber and Kaplan, 1974; Leventhal, 1983), whereas the open-marine samples generally have higher ratios.

Whole-rock iron content correlates weakly with total sulfur content (Figure 8). The average iron content for black shales from the restricted basin is 2.8 weight percent ($N = 24$, range = 1.7-4.4), less than the stoichiometric amount required for samples containing greater than 3.1 weight percent sulfur if all the sulfur were present as FeS_2 . Although degree of pyritization (DOP) was not determined,

Figure 7. C_{org}/S_T ratio for rock samples.

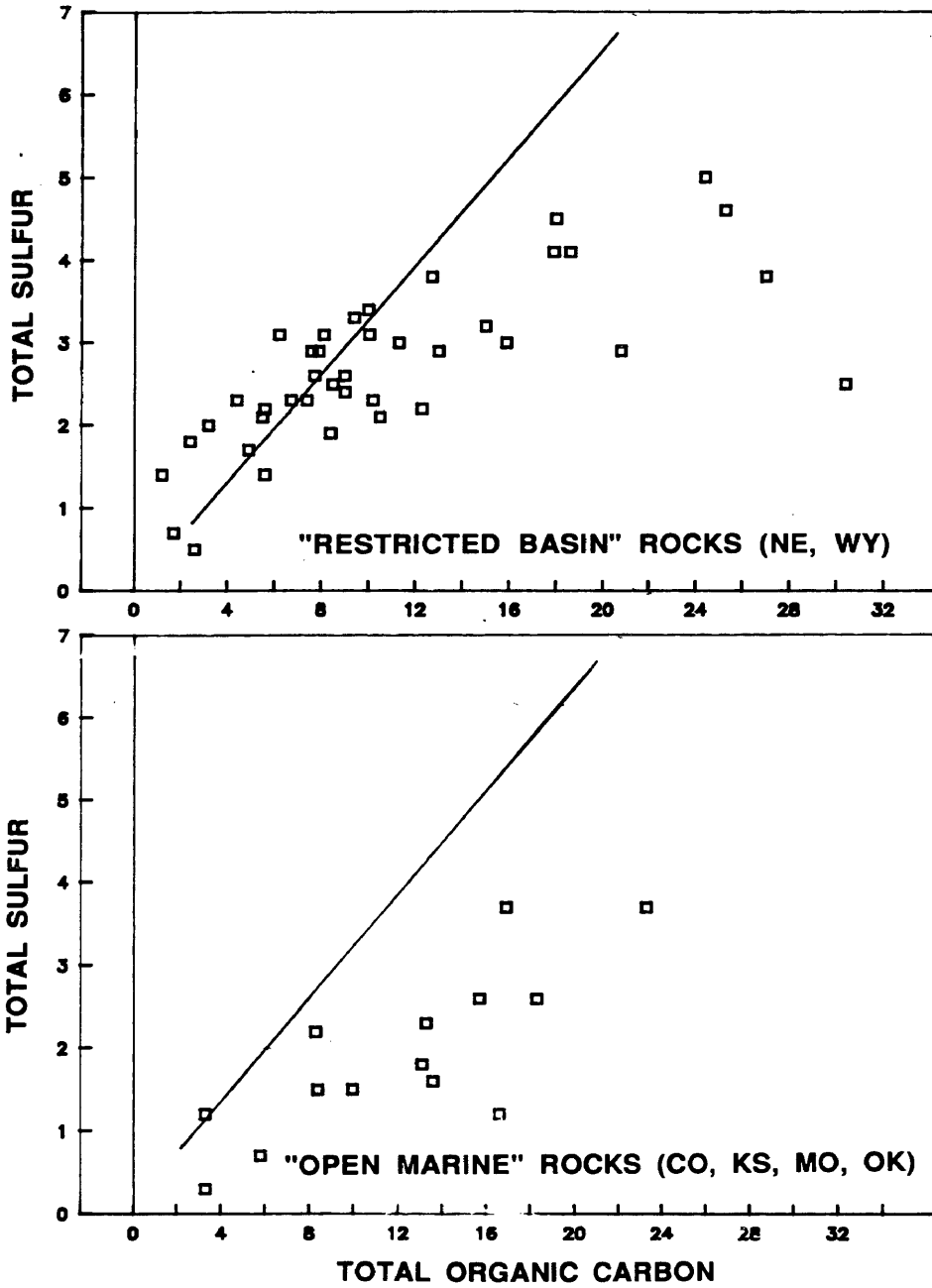
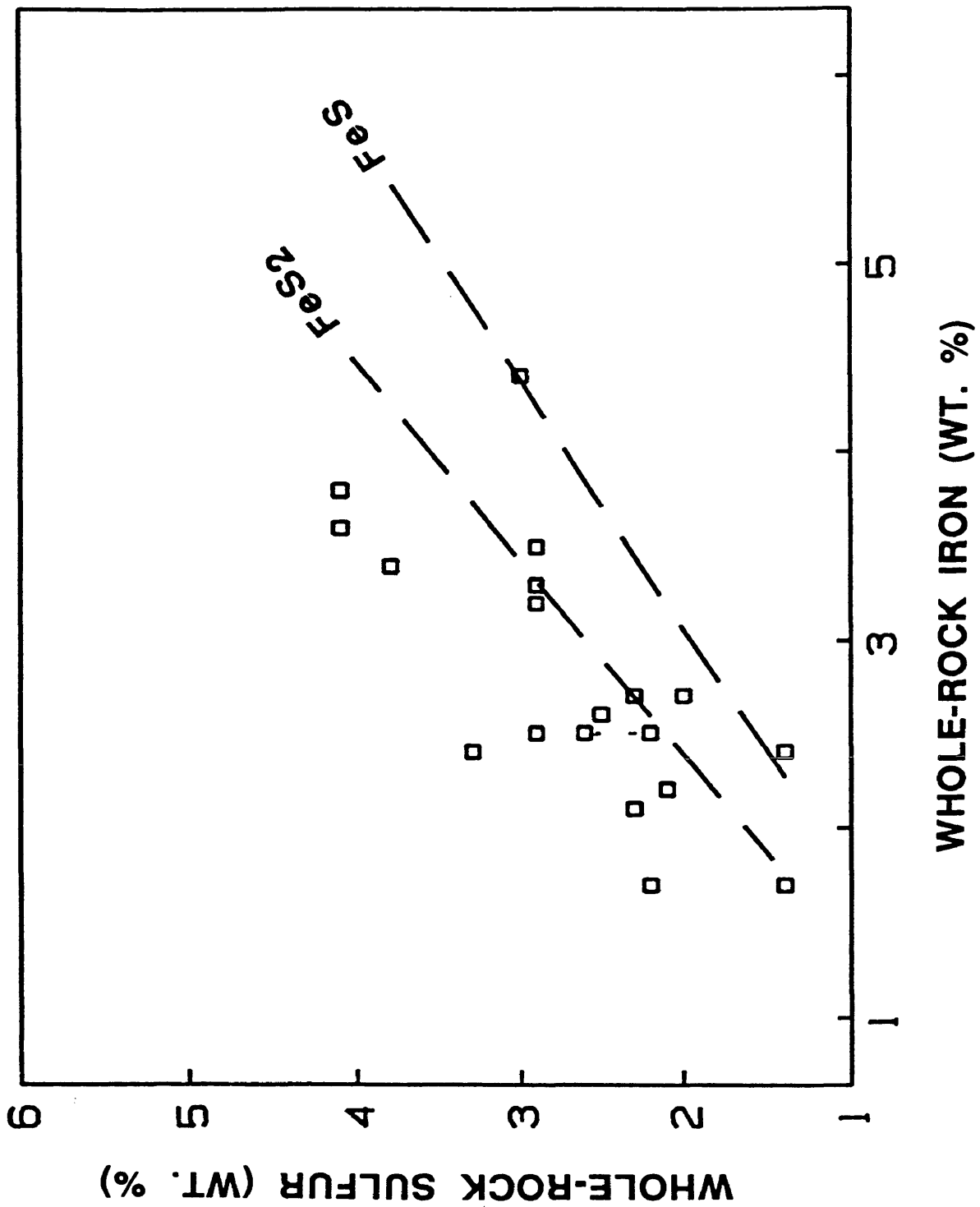


Figure 8. Total iron content versus total sulfur for rock samples from the "restricted-basin" (top) and "open-marine" (bottom) environments. The dashed lines indicate the stoichiometric amounts of iron and sulfur in FeS_2 and FeS .



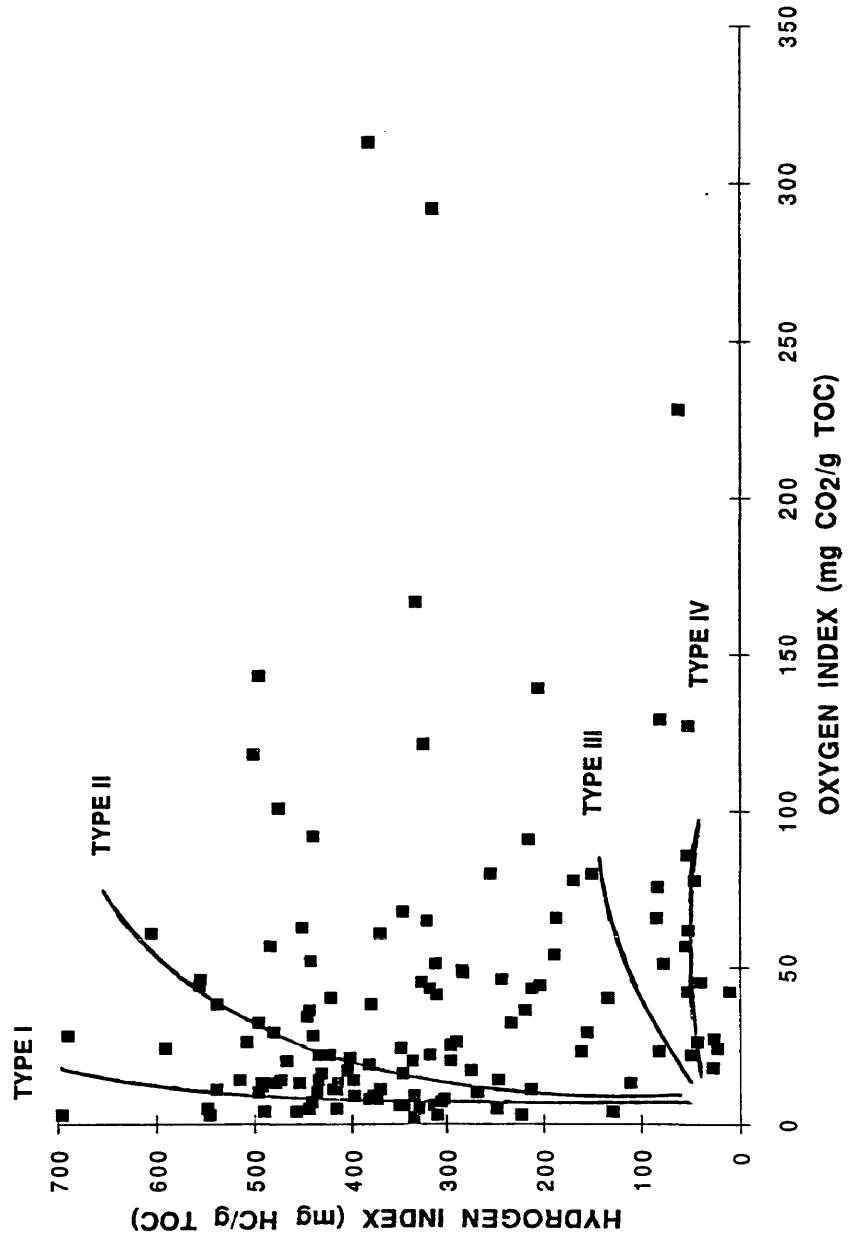
these data suggest that most of the available reactive iron is incorporated in sulfide minerals (that is, DOP of 1.0). In other words, (sulfur) sulfide is present in excess in some samples relative to iron for formation of iron sulfide minerals. The average sulfur content of restricted-basin samples is 2.9 percent.

Rock-Eval Pyrolysis

Pyrolysis results are highly variable between separate shale beds but notably invariant among a series of closely spaced (approximately 1-cm interval) samples from an individual black shale bed (samples 9-18, Table 2). Total S_1+S_2 yields are quite high, and some values exceed 100 kg/ton (100,000 ppm). The ratio of S_1/S_1+S_2 is less than 0.1 for most samples that contain more than about 2.0 weight percent C_{org} .

The hydrogen index (HI) ranges from less than 100 to about 700 mg hydrocarbons(HC)/g C_{org} ; restricted-basin samples have slightly higher indices (average 399 mg HC/g C_{org}) than open-marine samples (average 301 mg HC/g C_{org}). Overall, organic matter in most samples from both areas is types II and III (Figure 9) (Tissot et al., 1974; Espitalié et al., 1977). Rocks from the margins of the seaway and the shelf between the restricted basin and open sea have much lower HI values (<200 mg HC/g C_{org}) (Clayton and Ryder, 1984; J. L. Clayton, unpublished data) and contain predominantly type III organic matter.

Figure 9. Hydrogen Index (mg HC/g C_{Org}) versus Oxygen Index from Rock-Eval pyrolysis for Desmoinesian rock samples.



Bitumen Yield and Composition

Yields of extractable organic matter, or bitumen, are generally low (less than about 10 percent by weight) relative to C_{Org} (1-30 weight percent) (Figure 10), although on an absolute basis bitumen concentrations are as high as about 25,000 ppm (relative to rock weight) because of the high total amounts of C_{Org} . With few exceptions, the bitumens are enriched in aromatic hydrocarbons. Saturated to aromatic hydrocarbon ratios are mostly less than 0.5.

Gas Chromatography-Mass Spectrometry

Saturated hydrocarbons extracted from organic-rich black shale samples contain predominately low-molecular-weight compound (<C₂₀), and isoprenoids are present in high amounts relative to *n*-alkanes in most samples (Figure 11). The hydrocarbon distributions in extracts from organic-rich rocks from the restricted-basin (samples 75,78) and open-marine settings (sample 93) are quite similar (Figure 11). Rocks containing low amounts of organic matter (C_{Org} <1.0 percent) are interbedded with the black shales, and the black shales grade into organic-lean rocks along the shoreward margins of the restricted basin (Clayton and Ryder, 1984). The organic-lean rocks (not shown in Figure 11) typically contain relatively greater amounts of higher molecular-weight *n*-alkanes (C₂₅₊), are depleted in isoprenoids relative to *n*-alkanes, and, in some cases, exhibit an odd-carbon preference (C₂₅-C₃₁).

Figure 10. Extractable organic matter compared with C_{org} for rock samples.

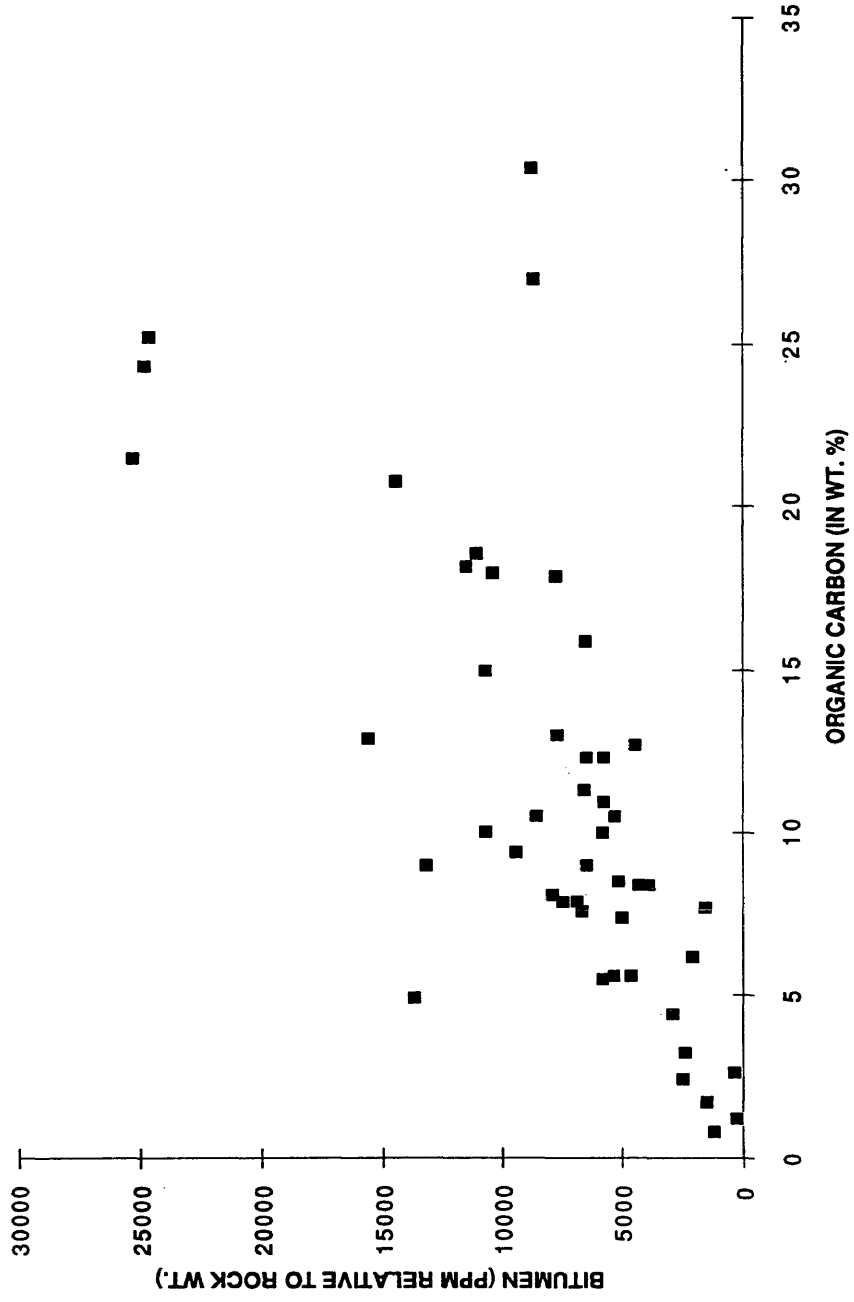
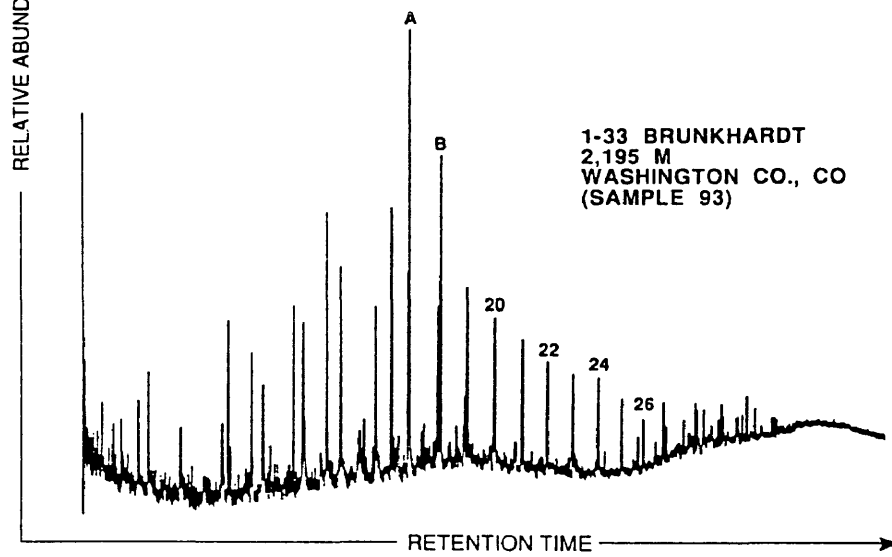
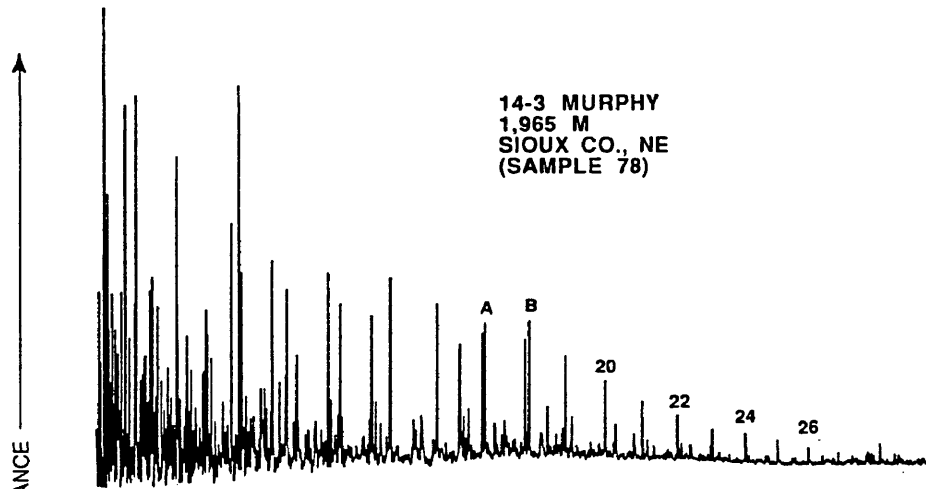
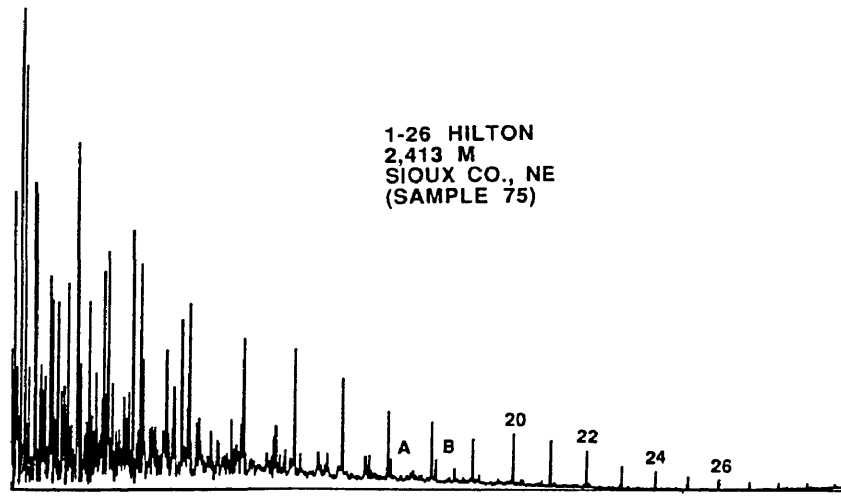


Figure 11. Typical gas chromatograms of saturated hydrocarbons from rock extracts. Sample numbers refer to Table 2. Relative amounts of isoprenoids vary markedly between samples of similar thermal maturity as indicated by the 1-26 Hilton and 14-3 Murphy samples. In most samples, isoprenoids are abundant (see Table 2). 1-33 Brunkhardt was run under slightly different GC conditions than other samples, and some evaporative loss of light hydrocarbons occurred during sample preparation.



Figures 12 and 13 show GC-MS results for aromatic hydrocarbons extracted from black shales of the restricted-basin and open-marine settings. Peak identifications (Table 3) are based on mass spectra and comparison of retention times with standards and literature values. A homologous series of compounds with m/z 133 base peak are abundant among the aromatic hydrocarbons extracted from restricted basin shales but are minor components of the open-marine rocks. Comparison of mass spectra of these compounds (Figure 12) with literature spectra (Summons and Powell, 1987) indicates that the compounds are a series of aryl isoprenoids. The MS fragmentation pattern indicates a methyl substitution pattern similar to that reported by Summons and Powell (1987) for presumed isorenieratene degradation products (Figure 14); however, all of the samples in the present study are predominated by homologues of lower carbon number (Figure 12) than samples studied by Summons and Powell (1986).

Results of GC-MS analysis of steranes (m/z) and terpanes (m/z 191) extracted from organic-rich, black shales of the restricted-basin and northernmost open-marine setting in Colorado are compared in Figure 15. Based on relative ion intensities, steranes are apparently subordinate to terpanes in all of the samples analyzed from the restricted-basin. The same is true for the open-marine samples, although GC-MS analysis was performed on open-marine samples

Figure 12. Mass chromatogram of m/z 133 showing a typical molecular distribution of aryl isoprenoids in restricted basin samples and example mass spectrum of the C₁₃ compound obtained from scanning a whole aromatic fraction (mass resolution of 3,000 at 5% valley, background subtracted).

DS-55 CROSS SCAN REPORT, RUN: 7824
11-16 CORMAN AROMATICS [7824 FT]
* 133

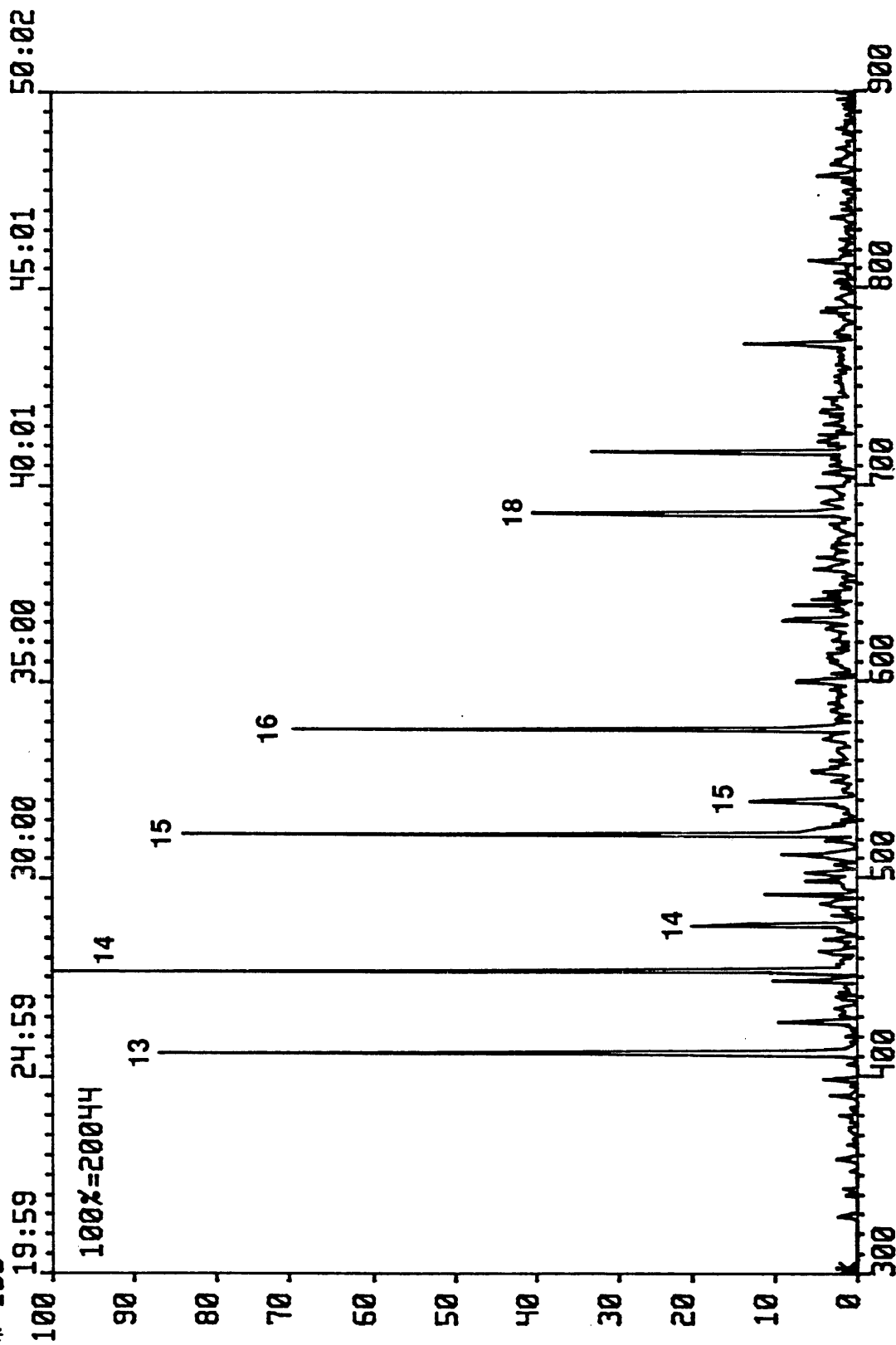
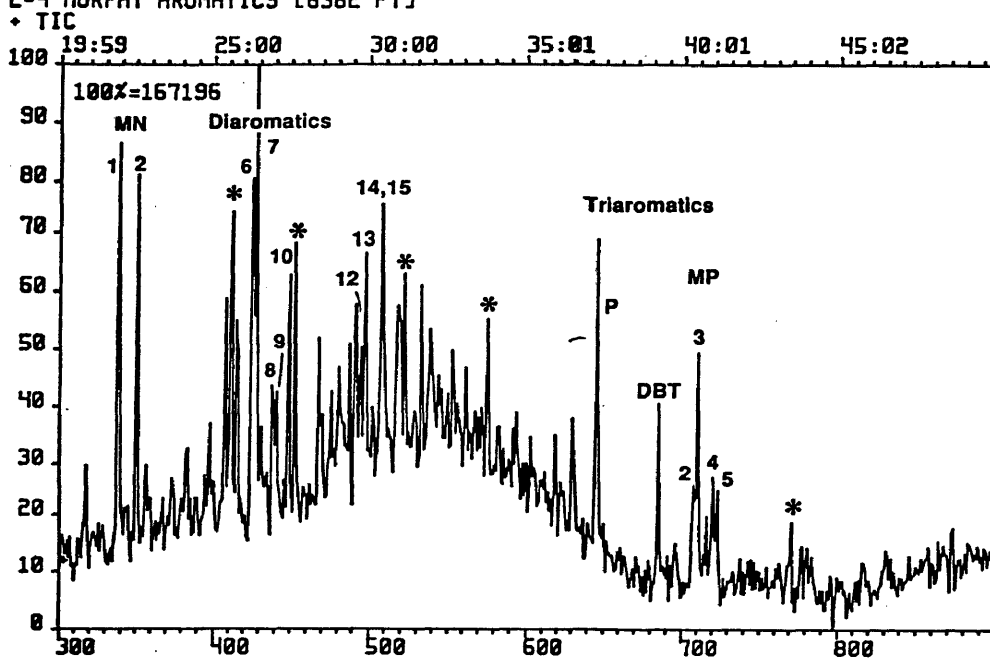
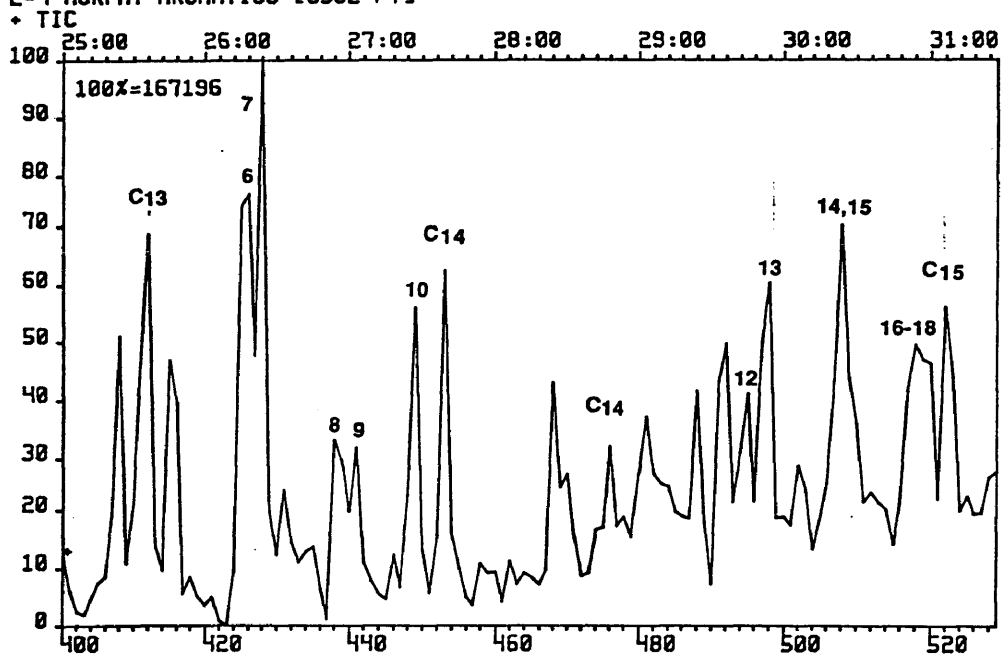


Figure 13. GC-MS (total ion current) of representative aromatic hydrocarbon fractions from open marine and restricted basin shales from northeastern Colorado and western Nebraska, respectively. See Table 2 and Figure 1 for well locations. Chromatograms below show enlargement of scans 499-530. Aryl isoprenoid compounds, indicated by asterisks or carbon number, are major peaks in restricted basin samples, but are present in trace amounts in open marine samples and are commonly not detectable.

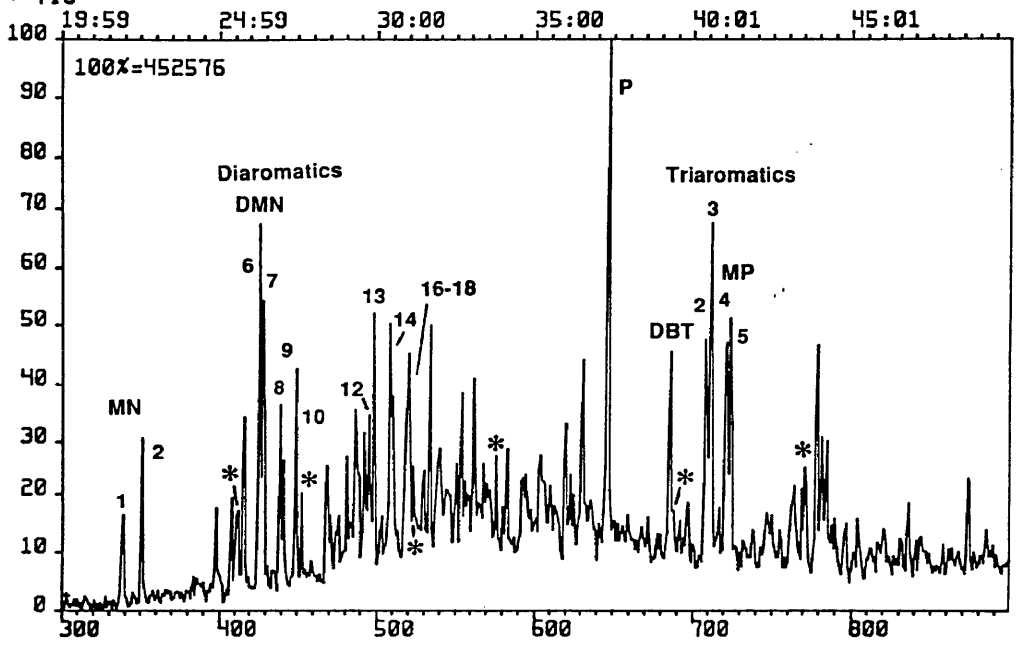
DS-55 CROSS SCAN REPORT, RUN: 6382
2-4 MURPHY AROMATICS [6382 FT]



DS-55 CROSS SCAN REPORT, RUN: 6382
2-4 MURPHY AROMATICS [6382 FT]



DS-55 CROSS SCAN REPORT, RUN: 7824
11-16 CORMAN AROMATICS [7824 FT]
+ TIC



DS-55 CROSS SCAN REPORT, RUN: 7824
11-16 CORMAN AROMATICS [7824 FT]
+ TIC

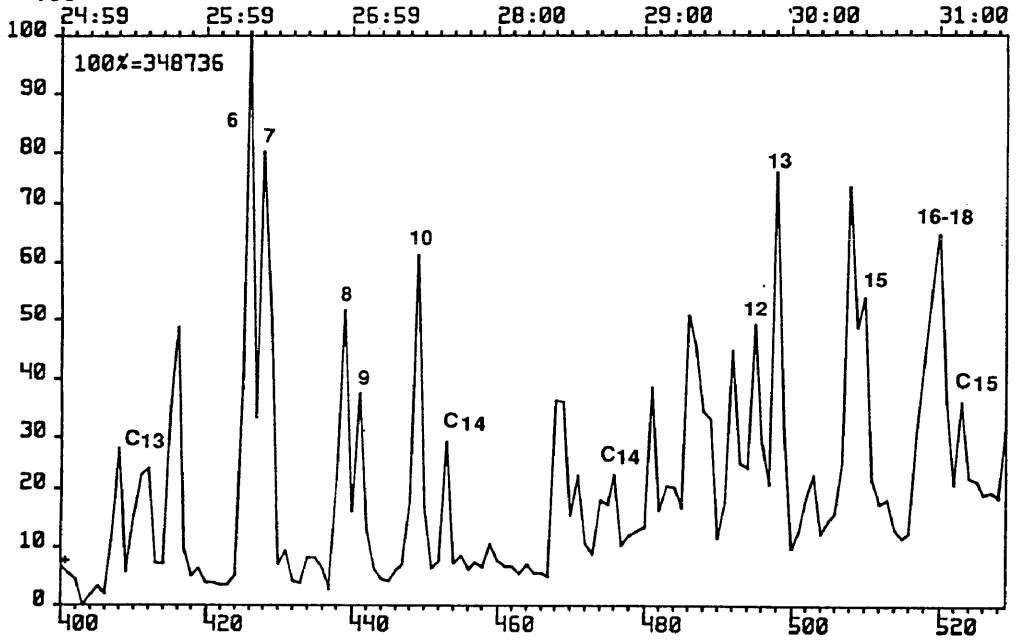


Figure 13. (continued)

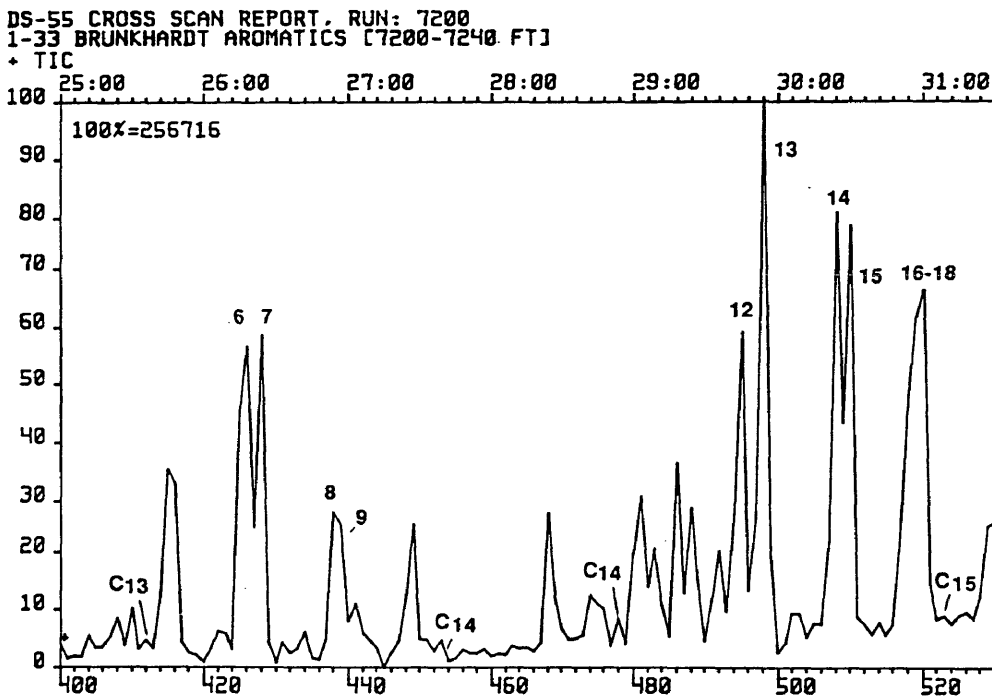
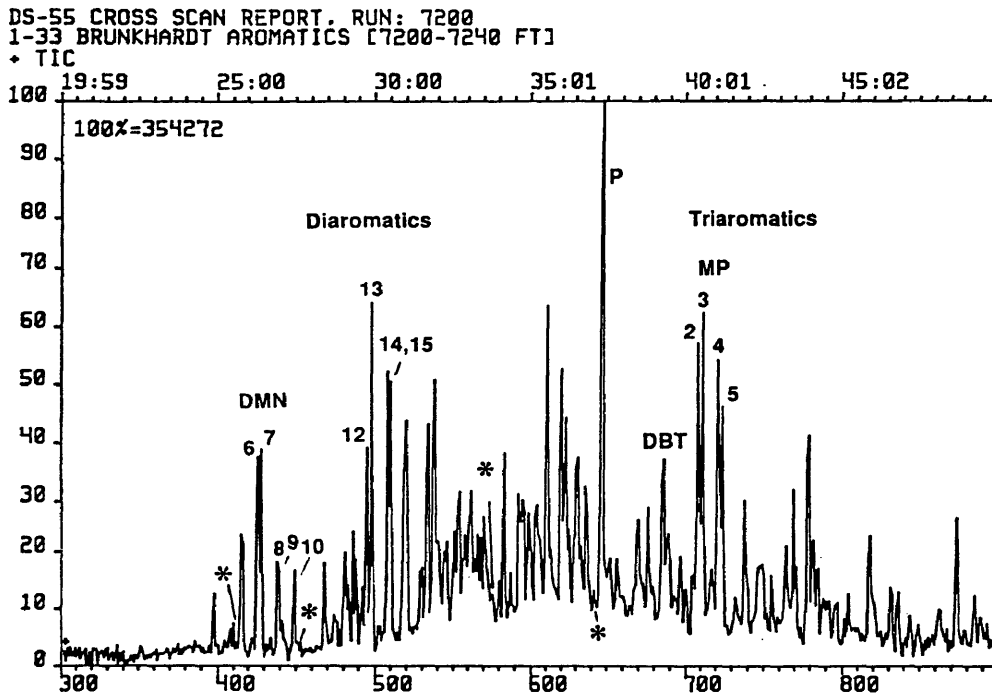
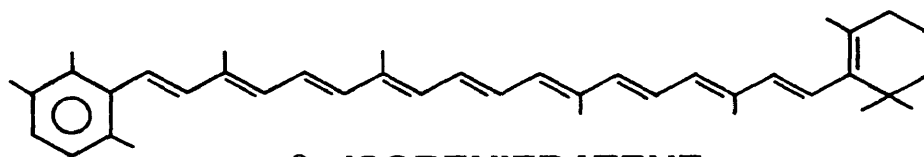
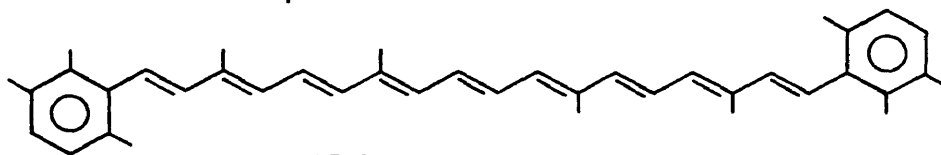


Figure 13. (continued)

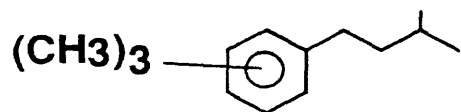
Figure 14. Example chemical structures of carotenoids found in photosynthetic sulfur bacteria that are believed to be the precursor compounds for aryl isoprenoids detected in sedimentary organic matter.



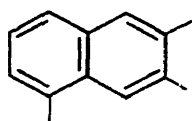
β -ISOENIERTENE



ISOENIERTENE



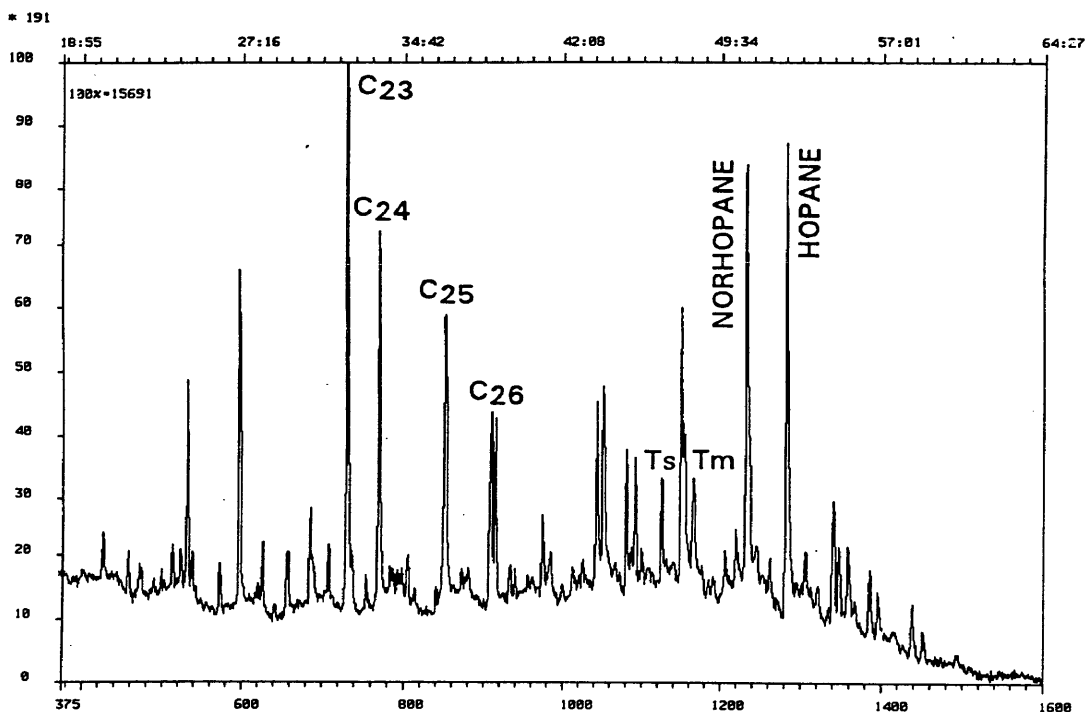
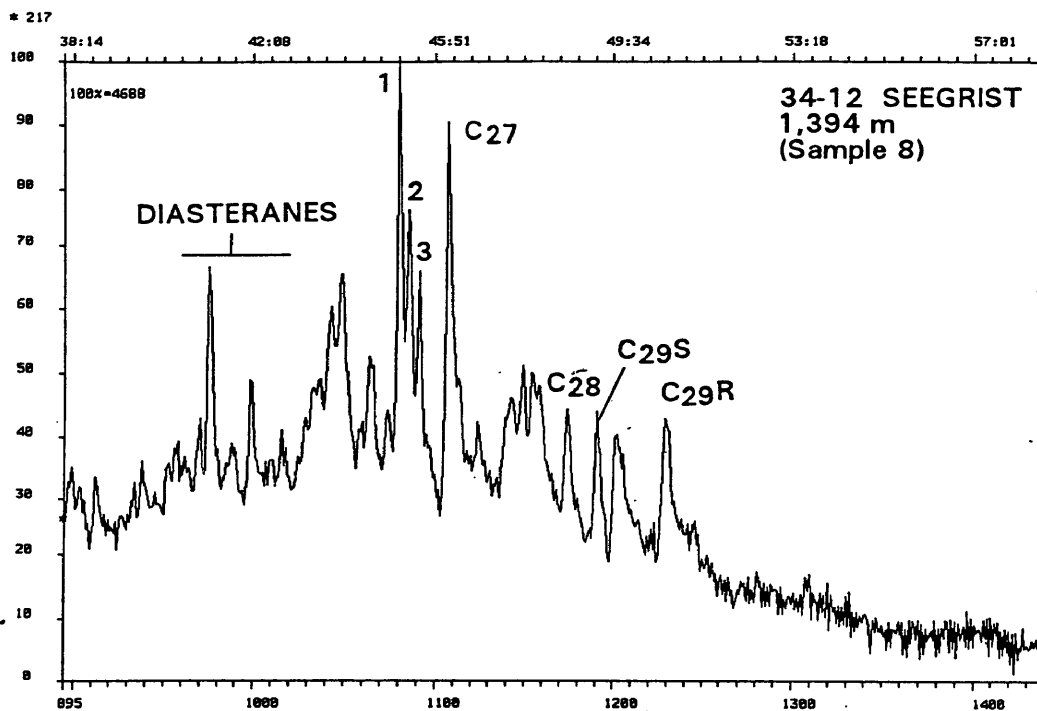
(SUMMONS & POWELL,
1987)



2,3,5-TRIMETHYL-
NAPHTHALENE

Figure 15. GC-MS of steranes (m/z 217) and terpanes (m/z 191) in whole bitumens from rock extractions. Carbon numbers of steranes refer to compounds with $\alpha\alpha\alpha$ (H) stereochemical configuration. Sterane peaks labeled 1, 2, 3, $\alpha\alpha\alpha$ C₂₇, $\alpha\beta\beta$ 20R C₂₇ + minor C₂₉ diasterane, and $\alpha\beta\beta$ 20S C₂₇, respectively. T_m = 17 α (H)-trisnorhopane. T_s = 18 α (H)-trisnorneohopane.

RESTRICTED BASIN



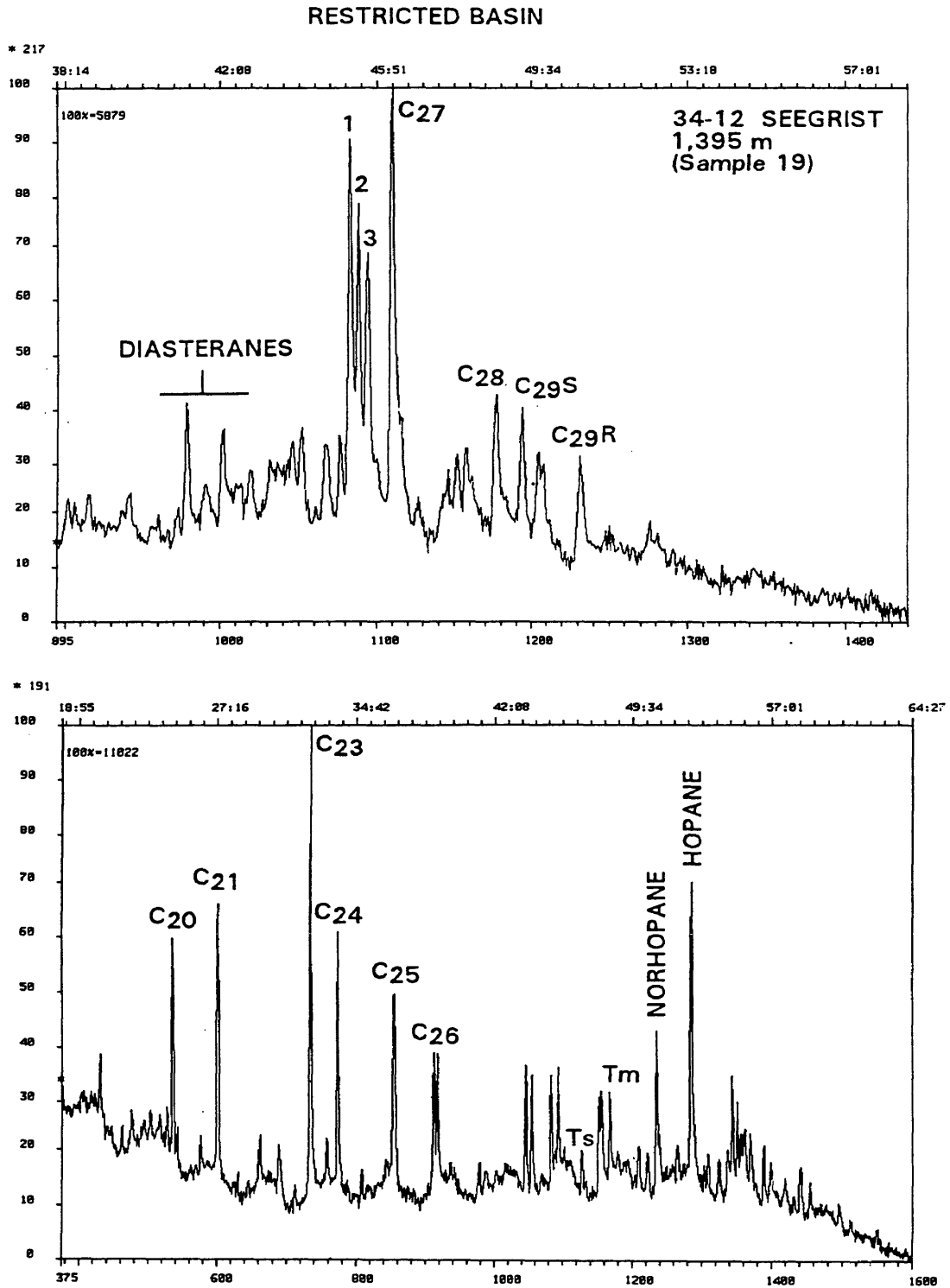


Figure 15. (continued)

RESTRICTED BASIN

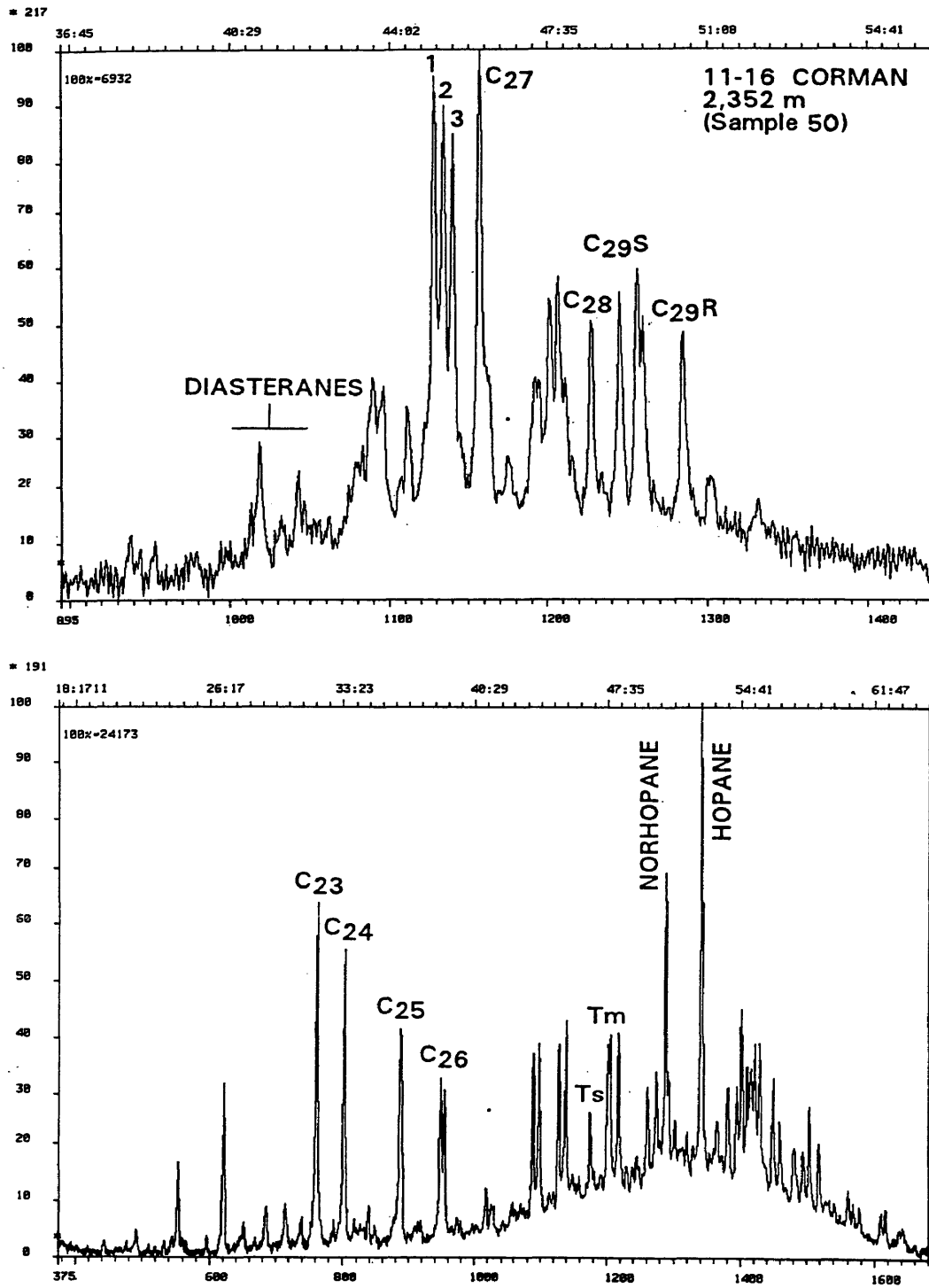


Figure 15. (continued)

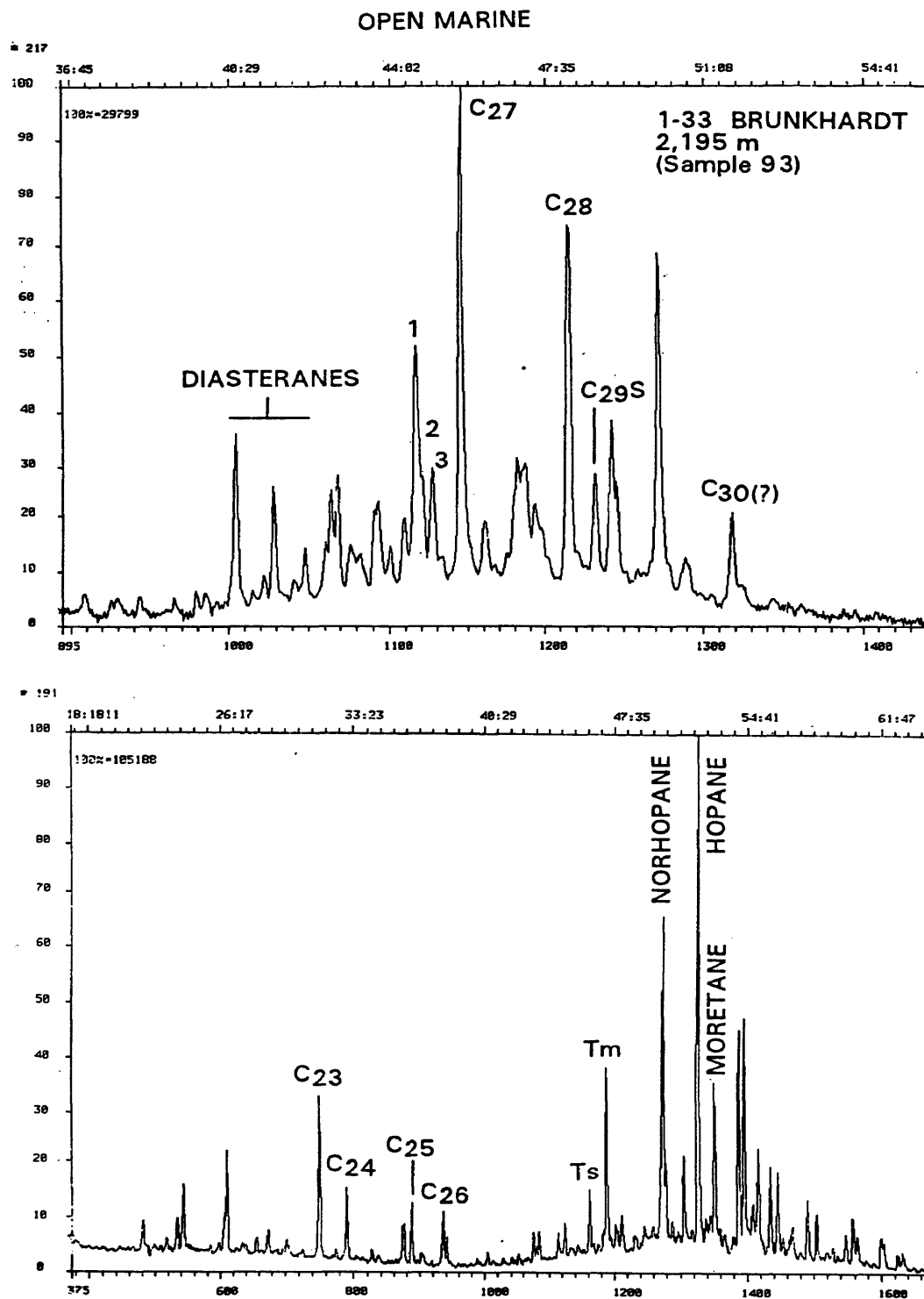


Figure 15. (continued)

Table 3

List of aromatic hydrocarbons identified by GC and GC-MS. Numbers refer to peaks identified in the GC traces of Figure 13.

Peak No.	Compound Name
Diaromatic Hydrocarbons	
1.	2-methylnaphthalene
2.	1-methylnaphthalene
3.	2-ethylnaphthalene
4.	1-ethylnaphthalene
5.	2,6- and 2,7-dimethylnaphthalene
6.	1,3- and 1,7-dimethylnaphthalene
7.	1,6-dimethylnaphthalene
8.	1,4- and 2,3-dimethylnaphthalene
9.	1,5-dimethylnaphthalene
10.	1,2-dimethylnaphthalene
11.	1,8-dimethylnaphthalene
12.	1,3,7-trimethylnaphthalene
13.	1,3,6-trimethylnaphthalene
14.	1,3,5- and 1,4,6-trimethylnaphthalene
15.	2,3,6-trimethylnaphthalene
16.	1,2,7-trimethylnaphthalene
17.	1,6,7-trimethylnaphthalene
18.	1,2,6-trimethylnaphthalene
19.	1,2,4-trimethylnaphthalene
20.	1,2,5-trimethylnaphthalene
Triaromatic Hydrocarbons	
1.	phenanthrene (P)
2.	3-methylphenanthrene
3.	2-methylphenanthrene
4.	9- and 4-methylphenanthrene
5.	1-methylphenanthrene

only from northern Colorado. Diasteranes are present in secondary amounts relative to regular steranes, and C₂₇ compounds are the most abundant regular steranes present in the C₂₇-C₂₉ fraction. C₃₀ steranes were not analyzed in the present study.

The terpene distributions are quite variable with respect to relative amounts of tricyclic and pentacyclic compounds (Figure 15) (see also Clayton and Ryder, 1984), although in most samples the pentacyclic compounds are more abundant than the tricyclic compounds. The hopanes are predominantly of 17 α , 21 β stereochemistry, although small amounts of 17 β , 21 α compounds (moretanes) are present in some samples (Figure 15, top).

Porphyryns

Total porphyrin concentration (relative to bitumen) in restricted-basin samples are as high as about 40,000 ppm, and most samples contain more than 10,000 ppm (Table 2). Similarly high porphyrin concentrations have been reported in the Cretaceous La Luna Formation of Venezuela (Didyk et al., 1975), and the Permian Kuperschiefer Formation of Germany (Eckardt et al., 1989). A porphyrin concentration of 19,000 ppm (VOP+NiP) was reported in bitumen from a single sample of the Devonian and Mississippian New Albany Shale (Indiana) (Van Berkel et al., 1989). With the exception of one sample (number 94) from northeastern Colorado, the total porphyrin concentration of black shale samples from the open-marine setting is less than about 5,000 ppm.

Vanadyl porphyrins are predominant in the restricted-basin samples; VOP/VOP+NiP ratios are all greater than 0.9. In open-marine samples, the relative amounts of VOP and NiP are more variable (VOP/VOP+NiP = 0.2-1.0).

Stable Carbon Isotope Ratios

Stable carbon isotope ratios were determined for kerogen, saturated and aromatic hydrocarbons (C₁₅+) and carbonate carbon for selected samples (Table 4). $\delta^{13}\text{C}$ values for kerogens are from -23.70 to -28.97 ‰ $\delta^{13}\text{C}$ values for saturated and aromatic hydrocarbons are from -25.76 to -29.55 ‰ and -26.41 to -29.68 ‰, respectively. These values are similar to those reported by Wenger and Baker (1986) and Wenter et al. (1988) for black shales of Pennsylvanian age in Oklahoma. Values in carbonate carbon are from -3.48 to +3.82 ‰, and most are near 0 ‰, the normal value for bicarbonate in modern oceans (Craig, 1953).

ORGANIC-MATTER SOURCE

Evidence from Biomarkers and Sulfur

In bulk, organic matter contained in the organic-rich black shales of both the restricted-basin and open-marine settings is types II and III according to pyrolysis assay, indicating a mixed origin for the parent organic matter or moderate oxidation of the organic matter during early diagenesis in the water column or upper layers of sediment. Similarly, Tromp (1982) reported a predominance of wood fragments, resin, charcoal, cuticles and other higher plant fragments

Table 4

Stable carbon isotopic ratios for kerogen, saturated and aromatic hydrocarbons, and carbonate carbon in rock samples, northern Denver and southeastern Powder River basins. [Wells shown by number in Figure 1. Sample depth in meters. nd indicates not determined]

$\delta^{13}\text{C}$ (‰ versus PDB)

Sample number	Sample depth (M)	Kerogen	Saturated hydrocarbons	Aromatic hydrocarbons	Carbonate carbon
1. Shell 31-16 (sec. 16, T.42 N.,R.62 W.)					
1	1,831	-25.36	-27.42	-26.83	+0.07
2	1,835	-25.62	-27.33	-27.03	-1.91
3	1,855	-28.69	nd	-28.84	+0.13
4	1,860	-28.89	-29.42	-29.68	+0.57
5	1,879	-24.98	nd	nd	+0.57
6	1,887	-27.84	-28.32	-28.13	+1.27
2. Mitchell 34-12 Seegrist (sec. 12, T.33 N.,R.52 W)					
7	1,389	-24.25/-24.17	-26.44	-26.64	-1.71
8	1,394.5	-28.93	-29.43	-29.65	-0.84
9	1,394.54	-28.88	nd	nd	+1.51
10	1,394-57	-28.90	nd	nd	-1.59
11	1,394.60	-28.97	nd	nd	-1.68
12	1,394.63	-28.62	nd	nd	-1.94
13	1,394.66	-28.74	nd	nd	-1.97
14	1,394.69	-28.84	nd	nd	-1.58

Table 4 (continued)

15	1,394.72	-28.97	nd	nd	-1.47
16	1,394.75	-28.72	nd	nd	-1.52
17	1,394.78	-28.94	nd	nd	-1.50
18	1,394.81	-28.53	nd	nd	-1.49
19	1,395	-28.92	-29.55	-29.60	-1.98
20	1,395.4	nd	-29.50	-29.32	nd
22	1,402	-25.69/-25.56	-25.76	-26.48	-0.15
----- 3. Bird 2-4 Murphy (sec. 2,T.27 N.,R.54 W.) -----					
24	1,946	-26.28	nd	nd	+1.46
25	1,948	-25.47	nd	nd	-0.16
26	1,955.4	-27.88	nd	nd	+0.95
27	1,955.7	-27.54	nd	nd	+0.39
----- 4. Bird 18-8 Downer (sec. 18, T.24 N.,R.56 W.) -----					
28	2,363.7	-26.22	-28.59	-28.86	-0.60
29	2,364	nd	-28.77	-28.45	nd
30	2,364.6	-28.72	-29.05	-28.66	-0.76
30a	2,378	-25.72	-26.51	-26.66	+3.82
31	2,380	-26.67	-27.04	-26.41	+1.98
31a	2,390	nd	-27.95	nd	nd
32	2,393	-26.58	-27.18	-26.89	+0.03

Table 4 (continued)

5 . Bird 2-3 Laucomer (sec. 5, T.24 N.,R.55 W)						
33	2,256	-26.29	nd	nd	+1.55/+1.54	
34	2,260	-26.23	nd	nd	+1.38/+1.42	
34a	2,263	-25.12	nd	nd	+0.80	
34b	2,267	-26.28	nd	nd	-1.91/+1.90	
35	2,271	-27.82	md	md	+ -0.27/+0.31	
35a	2,292	-24.11/-24.06	nd	nd	-1.29	
35b	2,293	-23.82/-23.70	nd	nd	-1.00/-1.06	
36	2,303	-28.83	nd	nd	-0.21	
37a	2,303.4	-28.72	nd	nd	-0.20	
6 . True 13-18 Laucomer (sec. 8, T.25 N., R.55 W.)						
37	2,267	-26.28	nd	nd	+1.91	
44	2,303	-28.83	nd	nd	-0.07	
45	2,303.4	-28.72	nd	nd	-0.70	
7 . Bird 11-16 Corman (sec. 11, T.25 N.,R.56 W.)						
47	2,350.9	-28.76	nd	nd	-0.64/-0.29	
48	2,351.2	-28.80	nd	nd	-0.58/-1.29	
49	2,351.5	-28.51	nd	nd	-0.47	
50	2,351.8	-28.16	nd	nd	-0.26/-0.27	
51	2,364.0	-27.95	nd	nd	-0.22	
52	2,364.3	-26.73/-26.65	nd	nd	+1.39/+1.19	

Table 4 (continued)

53	2,367	-25.95	-28.58	-27.80	+1.32
53a	2,370	-25.46	-28.79	-29.05	+0.14
54	2,376.5	-26.49	-28.84	-27.82	+0.22
55	2,376.8	-27.84	nd	nd	+0.54/+0.11
56	2,385.4	-27.89	nd	nd	+0.65
57	2,385.6	-27.46	nd	nd	+0.91
57a	2,386	-27.02	nd	nd	+0.76/+0.75
57b	2,395	-25.58	nd	nd	+1.09/+0.24
----- 8. Conoco 23-1 Perkins (sec. 23, T.25 N., R.57 W.) -----					
58	2,461	-26.05	nd	nd	+1.60
59	2,462	-25.30	-27.60	-26.98	+1.83
----- 9. Conoco 35-1 Duncan (sec. 35, T.25 N., R.57 N.) -----					
60	2,416	-28.83/-28.84	nd	nd	+1.15
61	2,417	-28.66	-29.36	-29.35	-1.30
62	2,418	-28.80	nd	nd	-1.14/-1.12
63	2,428	-24.74	nd	nd	+1.56
63a	2,428.4	-23.92	-27.11	-27.40	+1.62
64	2,431	-25.88	nd	nd	-1.15
65	2,441	-27.74/-27.78	-28.49	-28.75	+0.07
----- 15. Sun M. Segelke 1 (sec. 26, T.11 N., R.53 W.) -----					
89	2,304.5	-26.37	nd	nd	-0.73

Table 4 (continued)

90	2,304.8	-26.51	nd	nd	-0.49
91	2,306	nd	-27.47	-27.15	nd
----- 16. Sun Roelle 1 (sec. 24, T.12 N.,R.53 W.) -----					
92	2,272	-26.31	-27.21	-27.24	-0.97
92a	2,271	nd	-28.61	-27.27	nd
----- 17. Hunt 1-33 Brunkhardt (sec. 33, T.5 N.,R.54 W.) -----					
93	2,195	-28.21	nd	nd	-3.48
95	2,256	-26.94	nd	nd	-2.70
96	2,268	-26.72	nd	nd	-0.84
97	2,277	-26.61	nd	nd	-1.56
98	2,284	-26.48	nd	nd	-1.29
99a	2,381	-24.85	-28.85	-28.78	-2.82

in organic matter contained in samples of equivalent black shale beds. In the present study, visual kerogen analysis was performed on only a limited number of samples, but macerals of the vitrinite group are predominant (M. L. Pawlewicz, U.S. Geological Survey, unpublished data).

The molecular distribution of saturated hydrocarbons extracted from black shales both from the restricted basin and from northeastern Colorado is dominated by low molecular-weight components and acyclic isoprenoids (Figure 11). For samples at low levels of thermal maturity, both of these features are suggestive of significant input of algal and bacterial organic matter and thus an original composition of type II. The predominance of C₂₇ compounds in the sterane fraction supports this interpretation (Huang and Meinschein, 1979). Further, the abundance of aryl isoprenoid compounds in the restricted-basin samples suggests that photosynthetic sulfur bacteria were major contributors to the organic matter contained in these rocks (Summons and Powell, 1987).

The relatively low hydrogen indices of the black shales, particularly for the restricted-basin samples, appear contradictory to the observed distribution of soluble organic matter, which suggests input of mainly algal and bacterial organic matter. Two possible explanations for this paradox are (1) that oxidation of labile organic matter may have occurred at the depositional site and thus

concentrated any nonreactive organic matter that was transported to the depositional site or (2) that a significant component of hydrogen-deficient organic matter (nonreactive) may have been added through erosion of a soil profile or was transported from adjacent land masses (by water and possibly air) during transgression of the sea when the black shales were deposited. This latter process was discussed by Wenger and Baker (1986) to explain the presence of various higher-plant-derived organic constituents in Middle Pennsylvanian shales of Oklahoma. The same or similar process probably occurred during deposition of the Desmoinesian and Missourian black shales from the northern part of the epicontinental sea in Colorado and the restricted-basin in western Nebraska and eastern Wyoming. Erosion of the underlying soil or deposition of allochthonous organic matter would not only contribute nonreactive organic constituents but also could provide nutrients to support high primary organic productivity in the warm shallow sea (Hallam, 1981; Meissner et al., 1984; Wenger and Baker, 1986). One problem with the interpretation of erosion of coal is that coal occurrence within the Middle Pennsylvanian rocks in northeastern Colorado and Nebraska is poorly documented. Although one coal of Desmoinesian age was sampled in the present study from the Sun Fay 1 State well (sec. 36, T. 1 S., R. 46 W., Yuma County, Colorado) (64 percent Corg), the regional and stratigraphic distribution of coals in the area is unknown because of lack of

outcrops and paucity of drill holes that have penetrated Pennsylvanian-age rocks.

During Desmoinesian and Missourian time, stratigraphically equivalent rocks (middle member of the Minnelusa Formation) include sabkha-eolian dune-peritidal deposits (Tromp, 1981). Therefore, clastic input into the restricted basin was limited and would not account for the high contents of C_{org} consisting of substantial proportions of hydrogen-deficient (terrestrially-derived) organic constituents. It is possible, however, that the eolian deposits may not be exactly time-equivalent with the most organic-rich black shales and marlstones. If a very humid (everwet) climate existed during the deposition of the black shales and marlstones, dense terrestrial vegetation and transport of high amounts of organic matter from runoff would be possible without associated clastic material (Cecil, 1990). Subsequent climatic change to an arid regime could account for both the organic-matter type contained in the organic-rich rocks and the stratigraphic relationships between these organic-rich lithologies and eolian deposits (Cecil, 1990). This hypothesis cannot be adequately tested with the geochemical and stratigraphic data presently available.

The presence of soluble organic matter containing a substantial contribution from algal and bacterial sources in rocks containing a predominance of organic constituents derived from higher plant debris and reworked organic matter illustrates the importance of a

multi-parameter approach (including both chemical and geological considerations) for characterization of organic matter dispersed in rocks. The observation of high amounts of vitrinite in these rocks coupled with the relatively low hydrogen indices could easily lead to the prediction that the soluble organic matter would consist of a vastly different composition than is actually present in the rocks. Significant contribution of soluble organic matter from the water-column flora would not be expected based solely on characterization of the organic matter in bulk using visual and pyrolysis procedures.

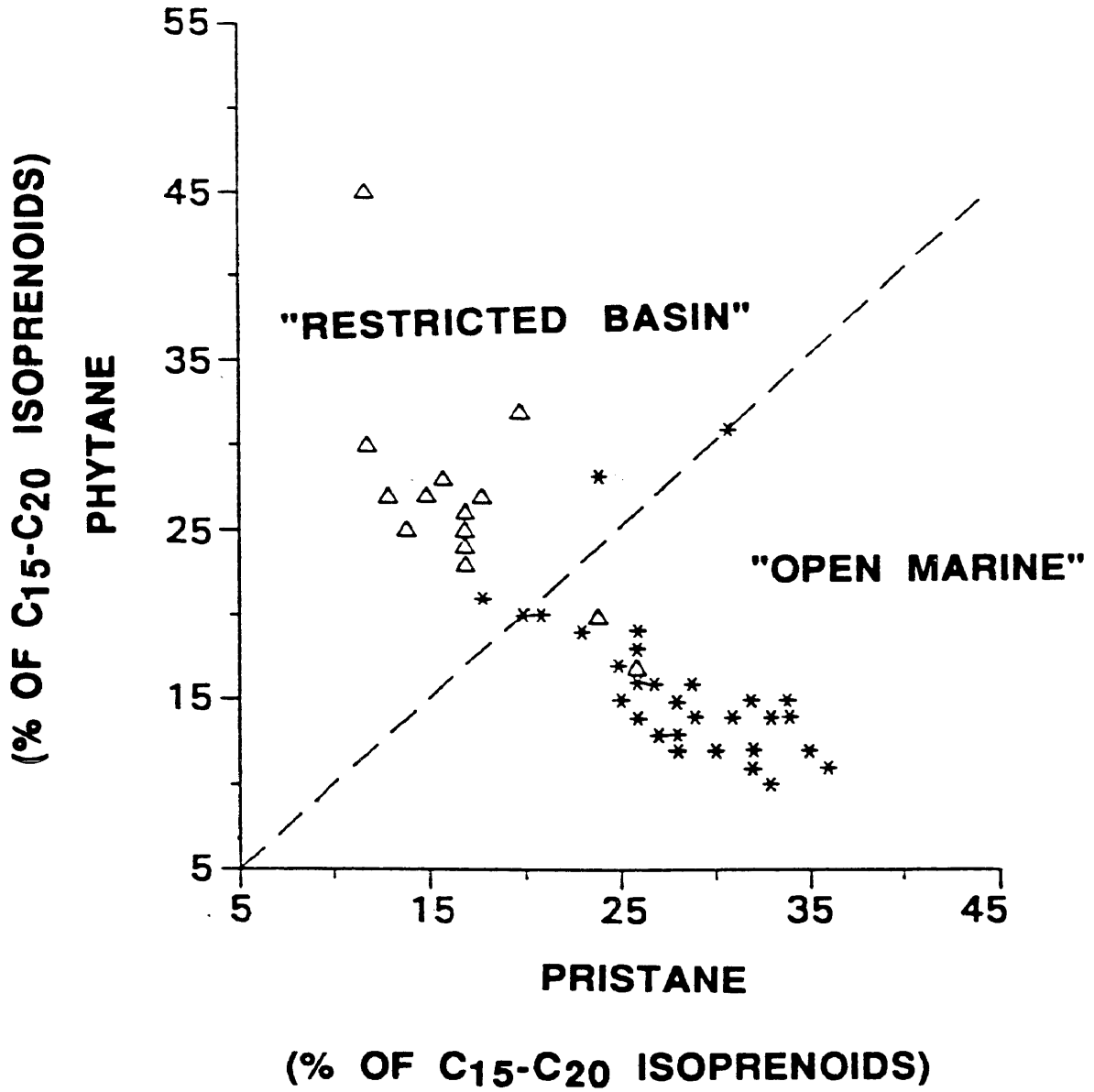
The presence of high relative amounts of aryl isoprenoids in the restricted-basin shales suggests that photosynthetic sulfur bacteria were present in the Desmoinesian sea or uppermost sediment layer (Summons and Powell, 1986, 1987). Photosynthetic sulfur bacteria belong mainly to two genera-*Chlorobiaceae* (green bacteria) and *Chromatiaceae* (purple bacteria). Bacteria of both genera earn their living by obtaining light energy to synthesize organic matter using reduced sulfur species as the reducing agent to incorporate CO₂ in cellular material. Photosynthetic sulfur bacteria contain bacteriochlorophyll instead of the more common chlorophylls a-c found in algae and higher plants. Bacteriochlorophylls absorb light in a different part of the visible region than chlorophylls a-c, and the reduction of CO₂ through oxidation of sulfide is energetically more favorable (more negative ΔG) than is photosynthesis in which H₂O is the hydrogen donor. Photosynthetic sulfur bacteria are able to live in

areas of low light penetration, including the upper few millimeters of sediments (Jørgensen, 1982) and at the lower limit of the photic zone in the water column. In addition, photosynthetic sulfur bacteria are obligate anaerobes and require a replenishable supply of reduced sulfur because they are incapable of storing sulfur for metabolic purposes.

Additional evidence for the presence of a significant population of photosynthetic sulfur bacteria in the restricted basin setting is the high farnesane to pristane ratios. Because bacteriochlorophyll contains farnesyl as the esterifying alcohol instead of phytyl, high amounts of farnesane could be an indication of the presence of a large population of photosynthetic sulfur bacteria. Figure 16 compares relative abundances of farnesane and pristane in restricted-basin and open-marine samples. The open-marine samples include several from wells in Kansas (Figure 1).

Previous workers have shown that photosynthetic sulfur bacteria can be important primary producers of organic matter. For example, Takahashi and Ichimura (1968) presented evidence that photosynthetic sulfur bacteria synthesized from 9 to 25 percent of the total annual organic matter produced in some Japanese lakes containing sulfidic waters. Likewise, Kepkay et al. (1979) reported that chemoautotrophic fixation of CO_2 by sulfur bacteria constituted an appreciable proportion of the organic carbon present in sulfidic marine waters of Nova Scotia. Guerrero et al. (1985) found that

Figure 16. Relative abundance of pristane (C₁₉) versus farnesane (C₂₀) determined from GC of saturated hydrocarbon fractions from open-marine (triangles) and restricted-basin (asterisks) settings. Amounts shown are normalized percentages of the C₁₅-C₂₀ isoprenoid fraction.



purple sulfur bacteria (*Chromatium*) accounted for 92 percent of the microbial biovolume in the anaerobic zone in two lakes of northern Spain.

Considering the ecological factors necessary for growth of photosynthetic sulfur bacteria, it is likely that the water column in the restricted basin was stratified during deposition of the organic-rich black shales. The requirement of a replenishable supply of reduced sulfur suggests that the lower water layer was not only anoxic but was also euxinic. Besides photosynthetic sulfur bacteria, sulfate-reducing bacteria (SRB) were likely present in the lower water column or uppermost sediment layer.

According to Summons and Powell (1986, 1987), aryl isoprenoids may indicate that hypersaline conditions existed in the water column during sedimentation. Similarly, Schwark and Püttman (1990) reported high amounts of aryl isoprenoids in the organic-rich Permian Kupferschiefer of Germany, which they attributed to photosynthetic sulfur bacteria and deposition under hypersaline conditions. Hypersaline conditions are clearly not an ecological requirement for photosynthetic sulfur bacteria but rather can provide a mechanism for water-column stratification and development of euxinic conditions. In addition to high content of sulfur, the sulfur isotopic composition of pyrite in the organic-rich rocks supports the hypothesis that SRB were present (Table 5). $\delta^{34}\text{S}$ values of anhydrite are similar to that reported by Claypool et al. (1980) for

Table 5

Sulfur isotope ratios of Desmoinesian black shale samples from the western
Nebraska panhandle (Sioux County)

Sample description	$\delta^{34}\text{S}$ (‰ versus CDM)
11-16 Corman (2,377 m)	
Bitumen	-15.6
Anhydrite	+13.7
Pyrite	-31.2
Organic sulfur	-23.7
22-14 Houghson (2,369 m)	
Anhydrite	+14.3
Pyrite	-25.9

Pennsylvanian seawater, but the isotopically light (^{34}S depleted) values for pyrite suggest that bacterial sulfate reduction occurred in an "open" system (that is, not sulfate limited) (Goldhaber and Kaplan, 1974). The sulfate reducers, in consortium with various anaerobic fermentative bacteria necessary to produce metabolizable organic substrates for the SRB, could have contributed significantly to the composition of soluble organic matter preserved in the sediments both by altering organic materials falling through the water column and by contributing their own anabolic products to the sediments. The high relative amounts of hopanes and high amounts of phytane, presumably derived from bacterial cells, supports the notion of significant input of bacterial organic matter including archaeobacteria (Michaelis and Albrecht, 1979).

Biomarker compounds indicative of methanogens such as diphytanyl (Tornabene et al., 1978, 1979, 1980; Holzer et al., 1979) are not present in detectable amounts in any of the shales examined. The organic-rich black shales are very thin (generally less than 0.5 m) and contain uniformly high amounts of sulfur. It is probable that because of slow rates of sedimentation and low thicknesses of organic-rich detritus, sulfate reduction was predominant during accumulation of the black organic-rich facies and methanogenesis never became an important enough process to generate large amounts of methane. The sulfur isotope data support the interpretation that sulfate-reduction occurred in the presence of

excess amounts of sulfate ("open system") (Table 5). Further, petroleum exploration drilling in black shales in both the restricted basin and open-marine settings has not revealed the presence of significant quantities of methane-rich gas. It should be emphasized, however, that although some microbial gas has been reported in Pennsylvanian strata (Jenden et al., 1988) preservation of gas formed during early diagenesis is unlikely in such old rocks.

The relatively high sulfur contents and generally low carbon/sulfur ratios of the restricted-basin samples (Figure 7) are consistent with the interpretation of euxinic water conditions (Leventhal, 1983). In contrast, the higher carbon/sulfur ratios in the open-marine samples (Figure 7 and Table 2), along with the low aryl isoprenoid and farnesane contents, suggests that the water column in the open-marine environment may not have contained significant quantities of sulfide. It should be noted, however, that iron contents of the restricted-basin samples are fairly low and may have been a limiting factor for sulfur incorporation in the sediments. The same is likely true for the open-marine sediments. Iron concentrations are less than 3.0 weight percent in open-marine shales of northeastern Colorado, although only two samples were analyzed.

Evidence from Stable Carbon Isotopes

An important objective of carbon isotope studies in organic geochemistry is to interpret the biological source(s) of sedimentary organic matter (kerogen). Although the $\delta^{13}\text{C}$ values for various living

organisms are well known (Galimov, 1974, 1970; Fuex, 1977), isotope fractionation may occur during deposition of sedimentary organic matter and during the formation of kerogen (e.g. Fuex, 1977; Dean et al., 1986; Hayes et al., 1989). Thus, the carbon isotope ratio of the original organic source material may not be preserved in kerogen, although the general trends for various groups of organisms are usually still evident. For example, terrestrial plants are depleted in ^{13}C ($\delta^{13}\text{C}$ about -25 to -30 ‰) relative to marine plants ($\delta^{13}\text{C}$ about -20 to -23 ‰), but this difference can be as small as 3 ‰ in kerogens (Galimov, 1980). An additional complicating factor for interpreting source of organic material using isotopic data is that the degree of isotope fractionation during photosynthesis depends on the concentration of CO_2 available and the temperature at which photosynthesis occurs (Park and Epstein, 1960; Deuser et al., 1968; Sackett et al., 1965; Calder and Parker, 1973; Wong and Sackett, 1978; Fontugne and Duplessy, 1981). Moreover, the source of CO_2 available for photosynthesis may vary, and therefore the starting $^{12}\text{C}/^{13}\text{C}$ ratio of CO_2 fixed during photosynthesis can vary (McKenzie, 1982; Schoell, 1984; Lewan, 1986).

Dean and others (1986) and Dean and Anders (in prep.) proposed that comparison of $\delta^{13}\text{C}$ of kerogen and hydrogen index allows separation of the effects of parent organic-matter source and environment - that is alteration of $^{13}\text{C}/^{12}\text{C}$ by various chemical and biological processes during sedimentation and early diagenesis -

although it is unclear to what extent the isotopic composition might be altered during diagenesis (Gearing et al., 1984). The underlying assumptions in this approach are that (1) hydrogen index reflects the source of organic matter and (2) that bacterial organic matter is not an important contributor to sedimentary organic matter. Dean et al. (1986) argued, therefore, that a correlation should exist between $\delta^{13}\text{C}$ values and the hydrogen index of kerogen because higher hydrogen indices correlate with greater proportional input of algal organic matter and attendant shift in $\delta^{13}\text{C}$ values.

In their study of Cretaceous rocks, Dean et al. (1986) hypothesized that a positive correlation should exist between these parameters; that is $\delta^{13}\text{C}$ values should become more positive as the hydrogen index increases assuming that algal organic matter is ^{12}C depleted relative to terrestrial organic matter. Instead they found a negative correlation where marine $\delta^{13}\text{C}$ values were about -27 ‰. Similarly, Lewan's (1986) data on amorphous ("algal") kerogens of Phanerozoic age show uniformly light values. A compilation of isotope data for kerogens of various origins by Schoell (1984) shows values of about -26 ‰ for type III kerogen and about -28 ‰ for type II kerogen. Type I kerogens showed the widest range of values (-23 to 33 ‰).

In the present study, kerogen isotopic composition does not show any correlation with either hydrogen index or C_{org} content in the Desmoinesian shale samples (Figures 17 and 18). It might be

Figure 17. Hydrogen index (mg hydrocarbons/g C_{Org}) from Rock-Eval versus $\delta^{13}\text{C}$ of C_{Org} (kerogen).

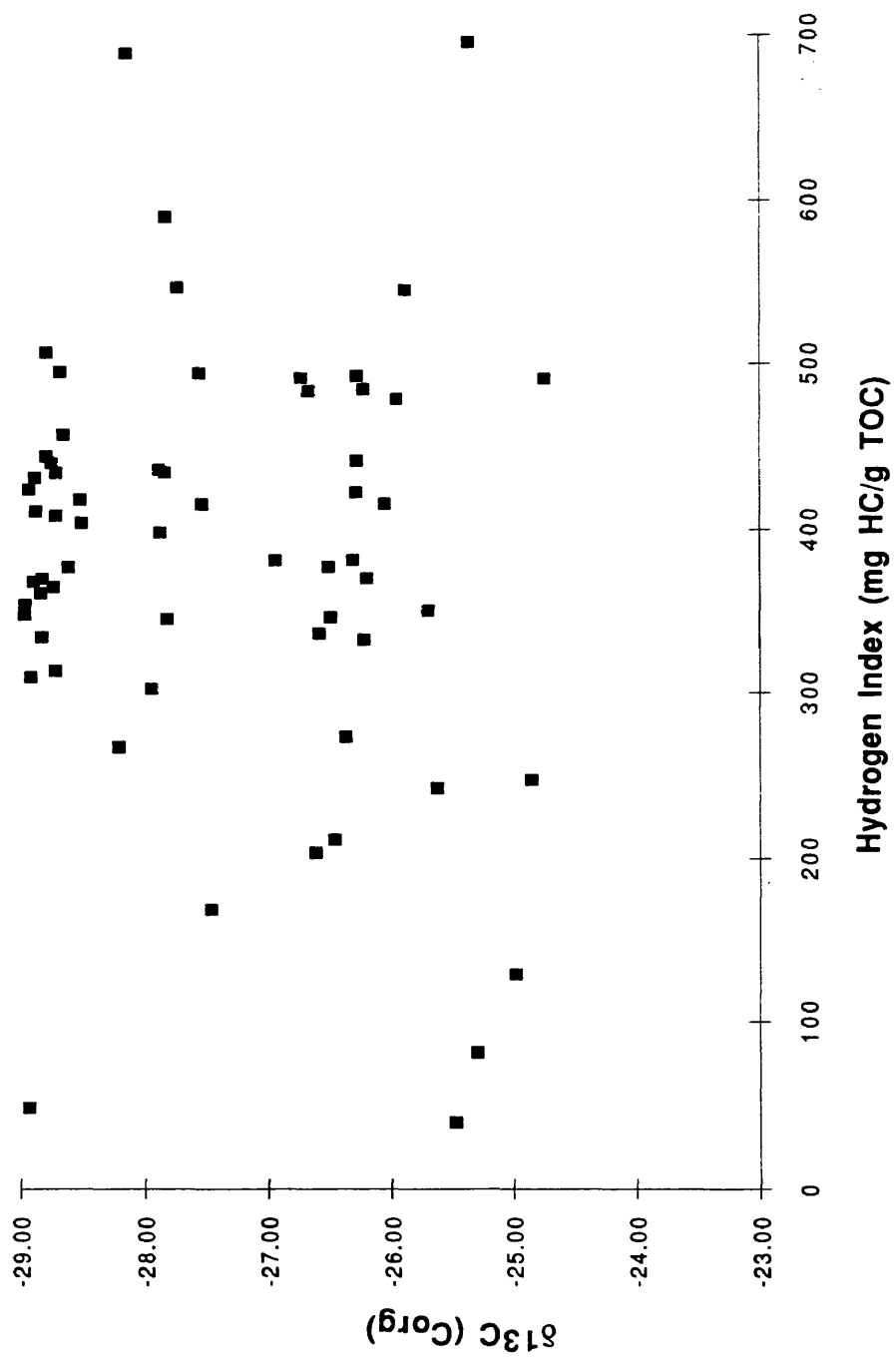
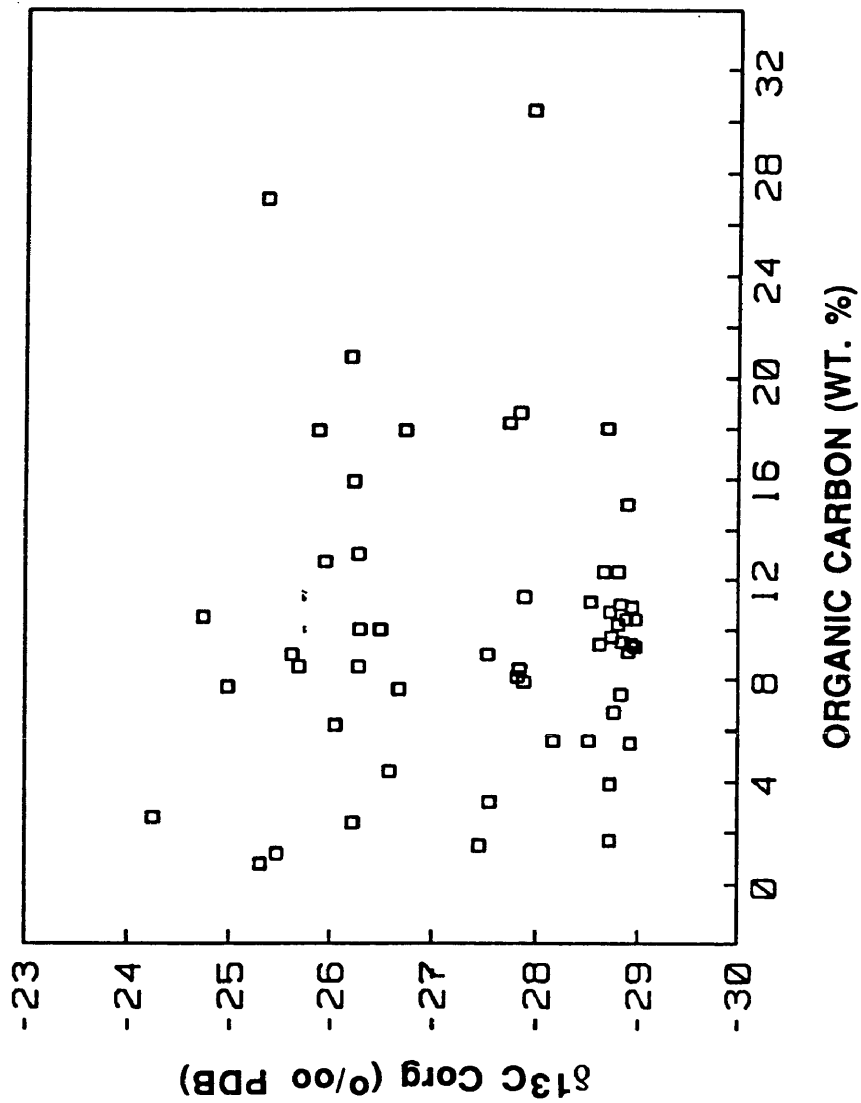


Figure 18. C_{org} versus $\delta^{13}C$ (C_{org}).



expected that lower C_{Org} values would be accompanied by isotopically heavier kerogen values because shales containing low amounts of C_{Org} commonly contain a greater proportion of terrestrial organic matter than organic-rich rocks. The lack of correlation between kerogen isotope composition and either hydrogen index or C_{Org} is undoubtedly due to a number of interrelated factors that are discussed in the succeeding paragraphs.

First, bacteria have apparently been major contributors to the extractable organic matter of these rocks as indicated by the abundance of biological markers characteristic of photosynthetic sulfur bacteria (aryl isoprenoids) and by the sulfur isotope data, which indicate the presence of sulfate-reducing bacteria. Moreover, high amounts of phytane could be due to a high population of archaebacteria during sedimentation (Michaelis and Albrecht, 1979). It is unlikely that bacteria play a significant role in determining the isotopic composition of kerogen, although at present insufficient data are available in the literature to satisfactorily assess these potential effects. Little is known about the isotopic composition of lipids contained in bacteria or how bacteria alter the isotopic composition of other organic materials in the water column or upper layers of sediments. It is known, however, that bacterial production of methane is accompanied by large isotope fractionations (Schoell, 1984), and recent studies of isotopic compositions of individual biological marker compounds indicate that similarly large isotope

fractionations may accompany bacterial anabolic processes (Freeman et al., 1990; Hayes et al., 1990). Coffin et al., (1989) reported a wide range of $\delta^{13}\text{C}$ values in bioassays of bacteria harvested from a marine estuary (-11.5 to -27.4 ‰), but experimental data showed that bacteria had $\delta^{13}\text{C}$ values within 2 ‰ of their growth substrates. Therefore, Coffin et al. (1989) suggested that $\delta^{13}\text{C}$ values of bacteria could be used as tracers for assessing growth substrates.

Second, as noted previously, the organic matter contained in these Desmoinesian and Missourian shales is apparently derived from two distinct sources. The bitumen fraction contains predominantly algal and (or) bacterial compounds, whereas the kerogen probably has a significant component of refractory organic material (low hydrogen index) presumably derived from terrestrial organisms, although some decrease of hydrogen index through oxidation of algal or bacterial organic matter cannot be discounted entirely. In a study of isotopic composition of amorphous organic matter (presumably algal and bacterial), Lewan (1986) reported $\delta^{13}\text{C}$ values of about -28 to -30 ‰ for Pennsylvanian-age samples collected from Colorado and Montana (Marmaton, Paradox, and Tyler Formations). He interpreted these isotope ratios to indicate that algal organic matter derived from the photic zone of marine waters where atmospheric CO_2 is not in equilibrium with oceanic bicarbonate ($\delta^{13}\text{C}$ about 0 ‰) was the predominant source of CO_2 . Wenger et al. (1988) reported $\delta^{13}\text{C}$ values of about -27 ‰ for kerogen in Pennsylvanian-age black

shales from Kansas and Oklahoma. Approximately half of the samples analyzed in the present study have $\delta^{13}\text{C}$ values between -28 and 30 ‰.

The importance of source of CO_2 is that a large $\delta^{13}\text{C}$ variation is possible for CO_2 derived from different sources. For example, bacterial decomposition of organic matter may produce CO_2 as light as about -7 to -22 ‰ (Oana and Deevey, 1960; McKenzie, 1982). In a shallow stratified water column diffusion of isotopically light CO_2 derived from degradation of organic matter could contribute significantly to the CO_2 reservoir available for photosynthesis in the upper photic zone, particularly in organic-rich sediments, and result in primary production of isotopically light organic matter (Lewan, 1986). This explanation of ^{13}C -depleted CO_2 could account for the samples that have both isotopically light kerogen (about -29 ‰) and relatively high hydrogen indices (about 500-600 mg/g) (Figure 17). Wenger et al. (1988) proposed that isotopically light algal organic matter in Pennsylvanian black shales is the result of erosion of peat swamps and coals during oceanic transgression providing isotopically light CO_2 . The model proposed herein for a stratified water column with anoxic bottom waters during deposition of the Desmoinesian organic-rich rocks is consistent with this interpretation. However, hydrogen indices in the 500-600 mg/g range suggest that some input of terrestrial (isotopically light) organic matter occurred because pure algal, undegraded organic matter has much higher hydrogen indices

(about 800-900 mg HC/g C_{org}). Therefore, the $\delta^{13}\text{C}$ -hydrogen index relationship above is best explained by the additive effects of ^{13}C -depleted CO_2 and a component of terrestrial organic matter input.

Microscopic analysis of two samples of the organic-rich shale to assess the kerogen composition revealed the presence of large amounts of vitrinite (M. L. Pawlewicz, written communication, 1990), and Tromp (1981) previously reported the presence of predominantly higher plant and recycled macerals in Desmoinesian black shales in the Minnelusa Formation.

Samples with more ^{13}C enrichment (-24 to -27 ‰ in Figures 17 and 18) could be explained by a greater proportional contribution of terrestrial organic matter or a source of isotopically heavier CO_2 . More ^{13}C -enriched CO_2 could be caused by an oceanic CO_2 reservoir containing predominantly dissolved atmospheric CO_2 . According to Lewan's (1986) model, this situation should occur where water depths are great enough (greater than about 500 m) to impede diffusion of bottom-water CO_2 derived from organic matter decay and circulation is sufficient to allow equilibration between atmospheric CO_2 and dissolved bicarbonate. In the present study, this explanation is unlikely because water depths were probably never greater than about 50 m (Doyle, 1987; present study).

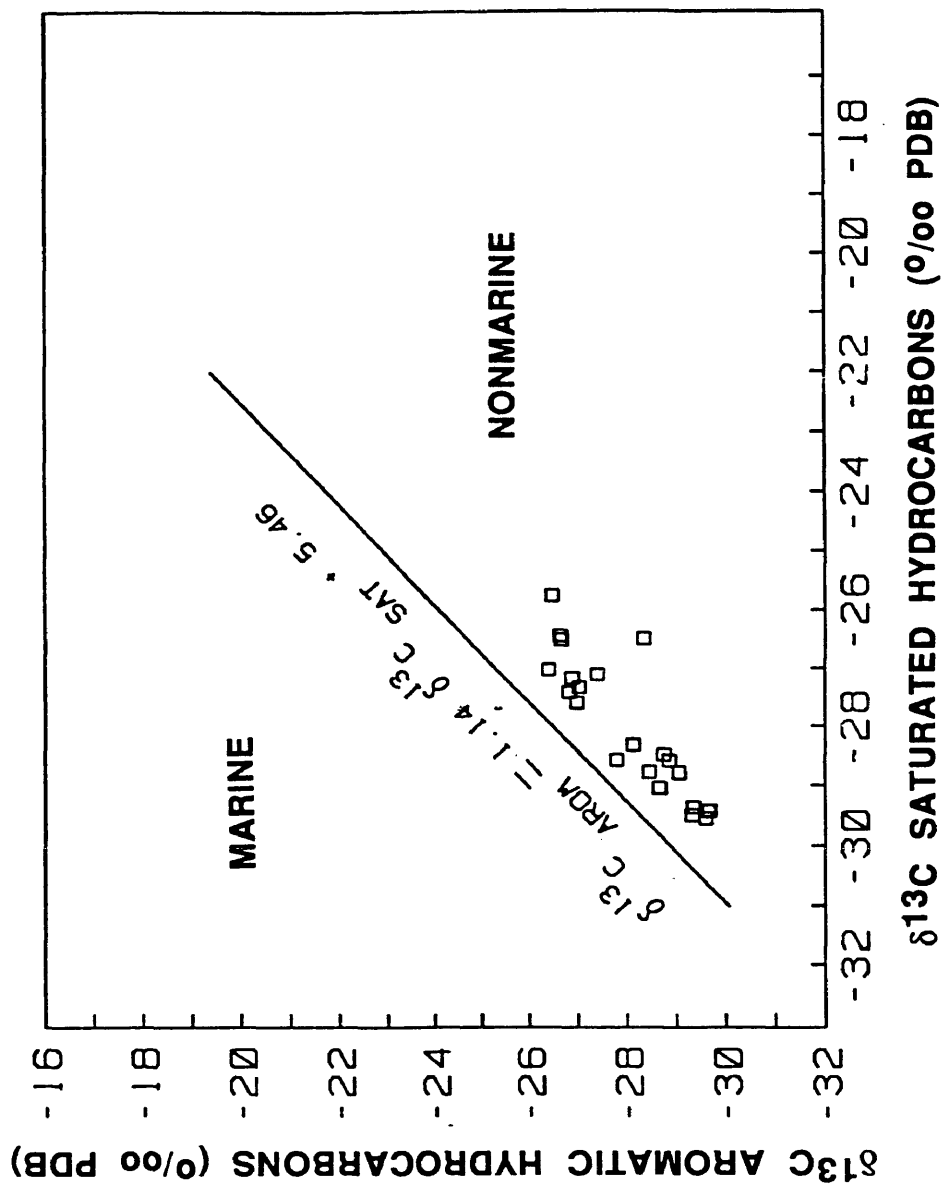
Invoking input of greater proportions of terrestrial organic matter as an explanation for the relative ^{13}C -enrichment is supported by the hydrogen index and visual kerogen data discussed

above, which indicate the presence of substantial amounts of terrestrial organic matter. Alternatively, the ^{13}C -enriched samples could indicate periods of greater bacterial activity. If bacterial alteration is accompanied by isotopic fractionation wherein ^{12}C bonds are preferentially cleaved, then ^{13}C enrichment might occur in the residual organic matter. At present, insufficient data are available to adequately evaluate this hypothesis.

The concentration of dissolved CO_2 in seawater could also theoretically affect the organic matter $\delta^{13}\text{C}$. Fractionation between the CO_2 reservoir and primary photosynthate decreases at low pCO_2 values (Deuser et al. 1968). Periodic decreases in pCO_2 in the atmosphere or independent decreases in seawater CO_2 concentrations at high salinity values -- for example, during Desmoinesian black shale deposition -- could cause concomitant shifts in $\delta^{13}\text{C}$ values of the organic matter. Alternatively, very high atmospheric CO_2 levels and concomitant increases in seawater CO_2 could enhance photosynthetic fractionation (Arthur et al. 1985).

Figure 19 shows a comparison of $\delta^{13}\text{C}$ values of C_{15+} saturated and aromatic hydrocarbons. Sofer (1984) reported that waxy oils (presumed from terrestrial organic matter sources) could be distinguished from nonwaxy oils (presumed from marine sources) by comparison of the carbon isotopic composition of saturated and aromatic hydrocarbons. Assuming that Sofer's (1984) approach is valid for hydrocarbons contained in shales ("non-migrated oil") as

Figure 19. Carbon isotopic composition of saturated and aromatic hydrocarbons. Line separating marine from non-marine sources of organic matter from Sofer (1984).

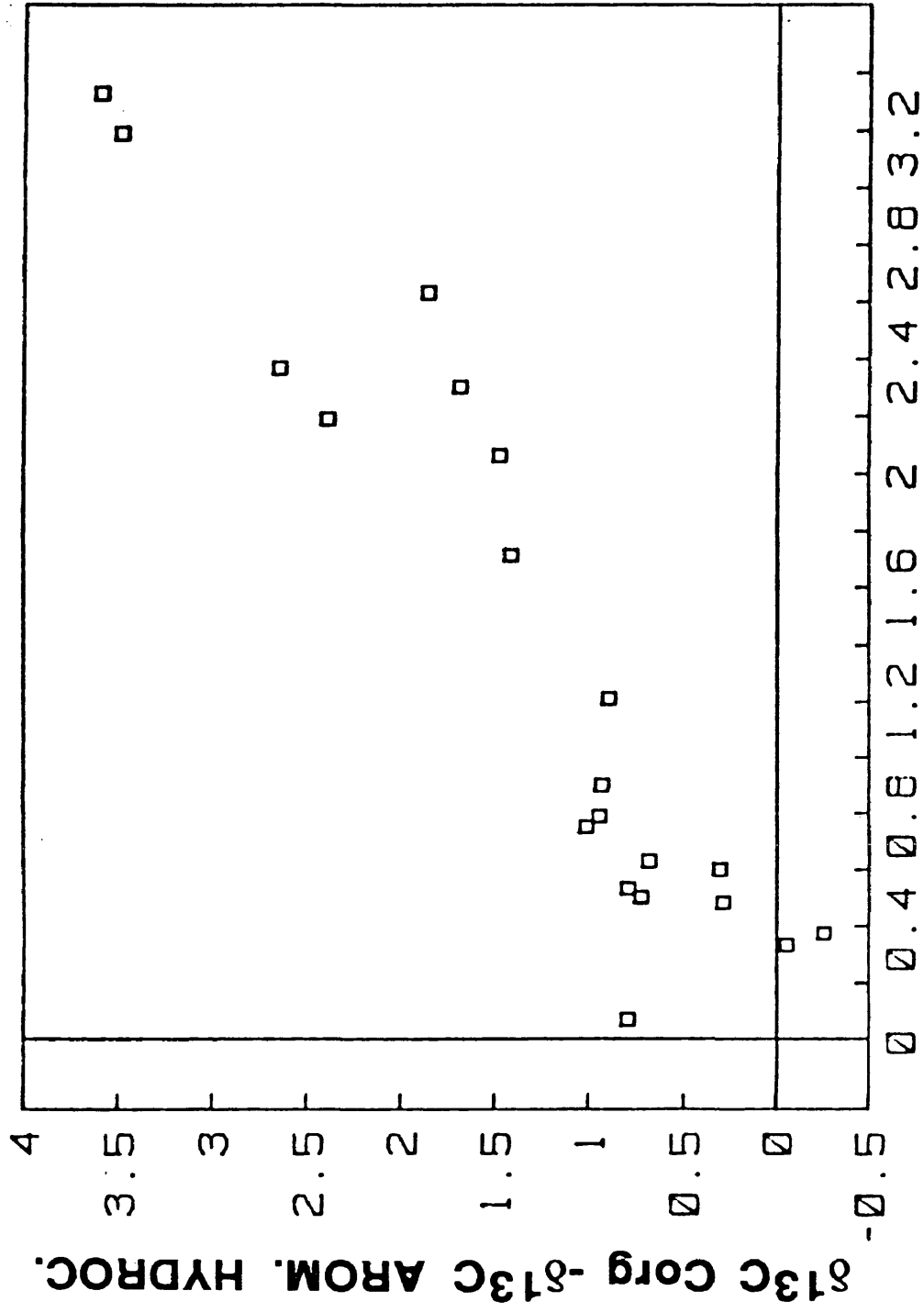


well as for oils in reservoirs, that hydrocarbons plotted in Figure 19 would be interpreted as marine in origin. This finding is consistent with the other geochemical data discussed previously that indicate a marine biological source for the *extractable organic matter*.

The difference in isotopic composition between the kerogen and extractable hydrocarbons varies from near zero to about 3.2 ‰ (Figure 20). With the exception of two samples, both the saturated and aromatic hydrocarbon fractions are relatively depleted in ^{13}C as compared to the kerogen. ^{13}C depletion of hydrocarbons relative to the associated kerogen is expected for two reasons.

First, lipids in living systems are depleted in ^{13}C by as much as about 15 ‰ as compared to carbohydrates, lignin, and proteins (Degens et al. 1968). Humic is generally regarded an important precursor to kerogen (Tissot and Welte, 1984), and humic is generally isotopically heavier (^{12}C -depleted) relative to other organic fractions (carbohydrates, lipids) in recent sediments (Spiker and Hatcher, 1984). Therefore, in thermally immature sediments (that is, prior to extensive thermal cleavage of kerogen bonds), the lipid fraction or, more particularly, the hydrocarbon fraction would be expected to have lower $\delta^{13}\text{C}$ values than the kerogen. Moreover, functional groups containing heteroatoms (carboxylic acids, esters, alcohols, and so forth) are generally isotopically heavier than nonheteroatomic moieties. Hydrocarbons, therefore, would be expected to be isotopically lightest of the lipid fraction. This expectation is

Figure 20. $\delta^{13}\text{C}$ (kerogen, or C_{org}) - $\delta^{13}\text{C}$ (saturates) versus $\delta^{13}\text{C}$ (kerogen, or C_{org}) - $\delta^{13}\text{C}$ (aromatics).



$\delta^{13}\text{C Corg} - \delta^{13}\text{C SAT. HYDROC.}$

supported by isotopic studies of various compound classes contained within the lipid fraction (saturates, aromatics, resins, asphaltenes) by Stahl (1977) and the data of the present study in which the saturated hydrocarbons are consistently lighter than the aromatic hydrocarbons (Figure 19).

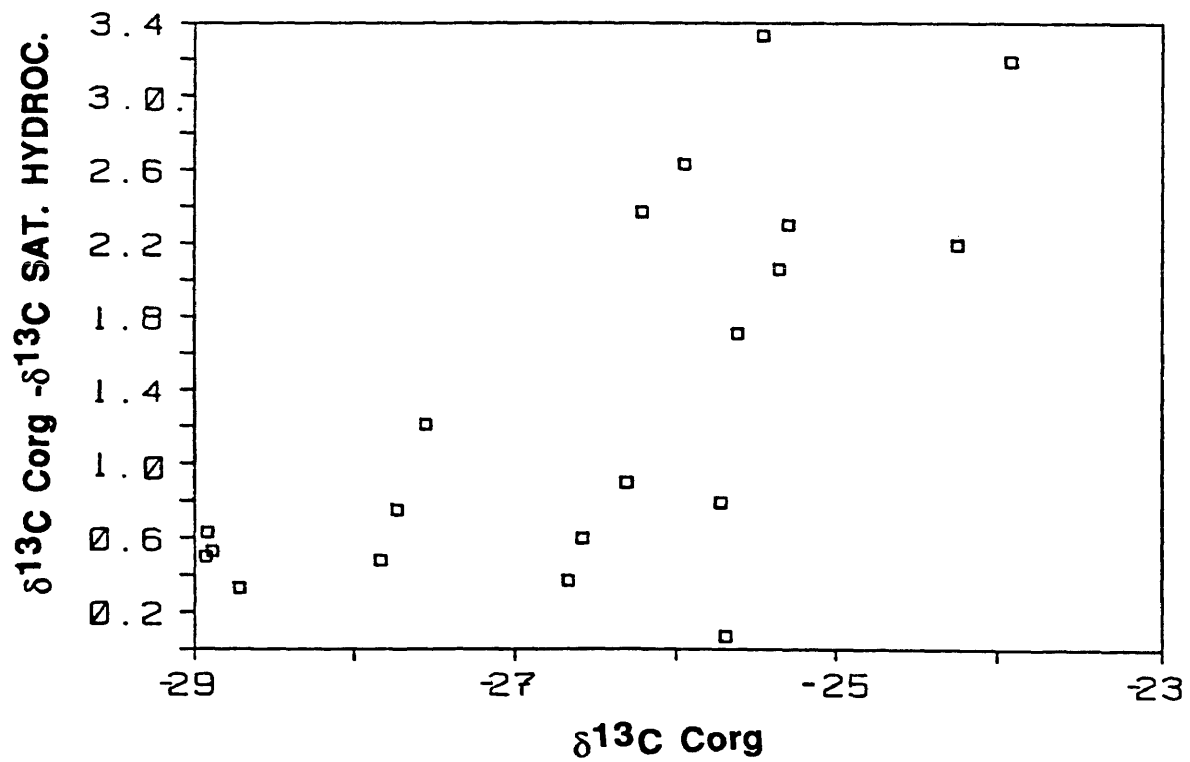
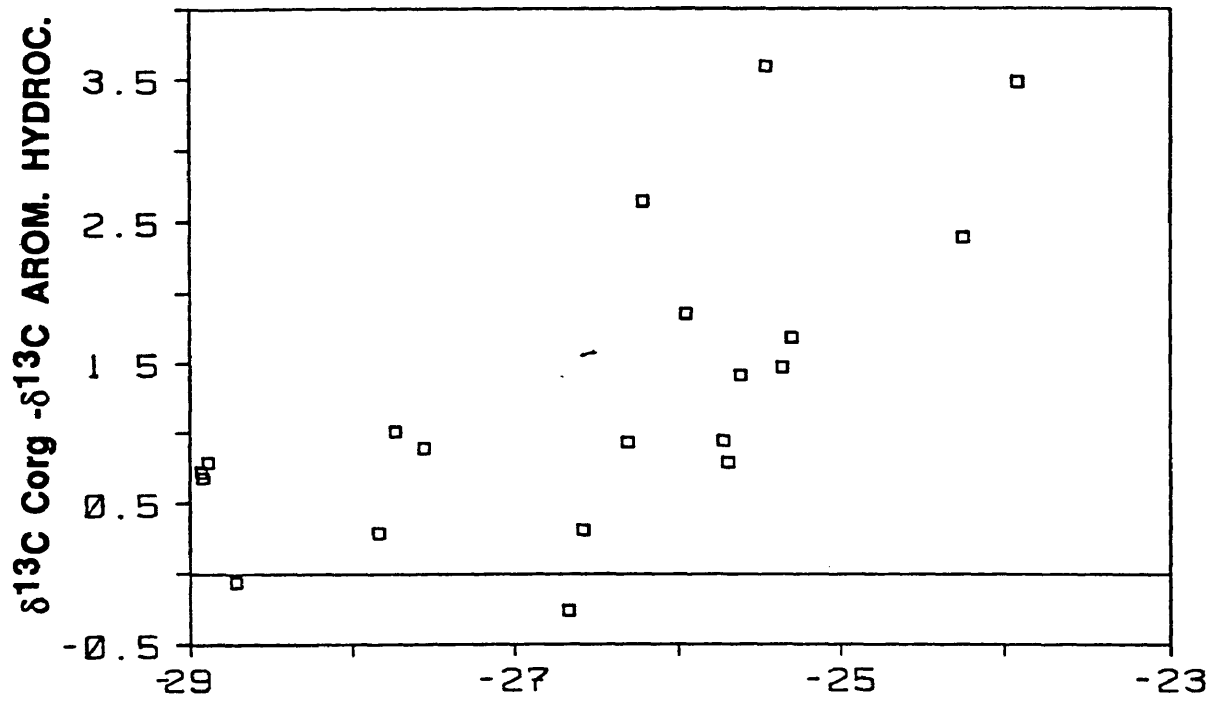
The second reason why kerogens tend to be isotopically heavier than associated bitumens or hydrocarbons is that thermal cleavage of carbon bonds is accompanied by an isotopic fractionation. Experimental work by Lewan (1983) on hydrous pyrolysis of shales shows that bitumens and hydrocarbons are isotopically lighter than the parent kerogen because of preferential cleavage of ^{12}C bonds. Because all of the samples of the present study are at low levels of thermal maturity (equivalent to vitrinite reflectance of about 0.6 percent), relatively little thermal generation of bitumen or hydrocarbons from kerogen has occurred. This conclusion is supported by the pyrolysis data, which indicate that the kerogens retain very high generation capacity. Therefore, kinetic effects associated with thermal generation of hydrocarbons are clearly of minor importance in explaining the isotopic compositions of hydrocarbons in the present study.

In a study of Mahakam Delta rocks, Schoell (1984) showed that the difference in ^{13}C values between extracts (resins) and kerogens is greatest (as much as about 2 ‰) at low thermal maturities. At higher maturities (vitrinite reflectance of approximately 0.7-1.0+ percent)

this difference decreases. It is interesting that in the present study the Δ values [$\delta^{13}\text{C}(\text{C}_{\text{org}}) - \delta^{13}\text{C}(\text{saturated or aromatic hydrocarbons})$] have a large range (Figure 20) despite their uniformly low thermal maturity. The large Δ values are consistent with the other data that indicate the presence of organic matter derived from multiple sources. If much of the soluble organic matter was derived from algal and bacterial sources, as is suggested by the GC analyses, porphyrin data, and biomarker distributions, and a significant component of the kerogen was derived from transported organic matter (terrestrial), then the $\Delta\delta^{13}\text{C}$ values would be expected to vary considerably. Furthermore, the magnitude of the Δ values depends on several factors discussed previously such as degree and path of early diagenesis, the exact source(s) of organic matter, and isotopic variability in the parent organic matter.

Figure 21 shows a positive correlation between $\delta^{13}\text{C}$ values of kerogen and Δ values. These data are consistent with the interpretations above that most of the soluble organic matter was derived from the water column and the kerogen contains variable proportions of allochthonous organic matter. The isotopically heaviest kerogens are interpreted to contain the greatest proportion of allochthonous (terrestrial derived) organic matter and, therefore, exhibit the largest Δ -values. On the other hand, decreasing $\delta^{13}\text{C}_{\text{org}}$ values are accompanied by decreasing Δ -values because more algal

Figure 21. Comparison of kerogen (C_{org}) $\delta^{13}C$ values and Δ values (difference in $\delta^{13}C$ values between C_{org} and hydrocarbon fractions).



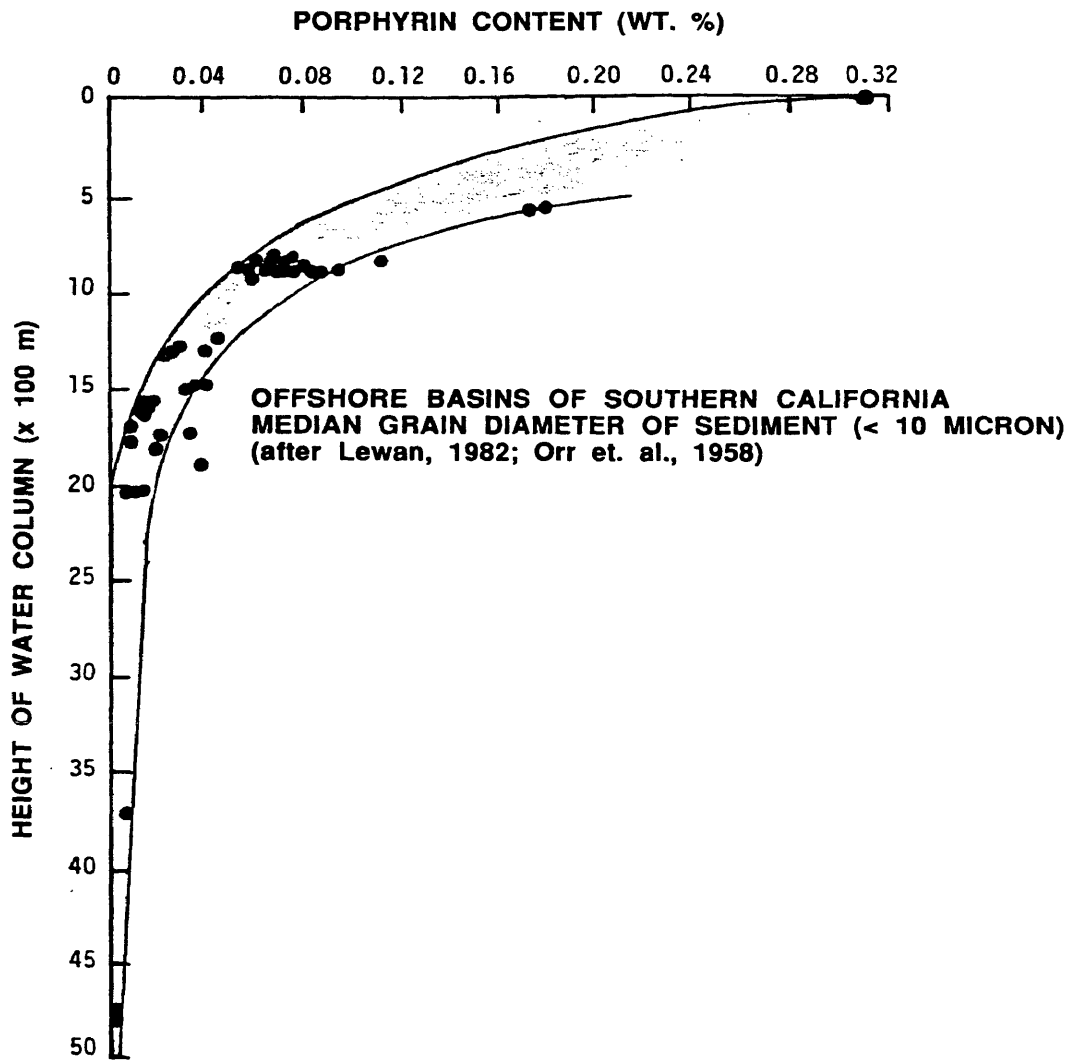
organic matter is present that is isotopically similar to the extractable hydrocarbon fraction.

ORGANIC-MATTER PRESERVATION

Controls on accumulation of high amounts of organic matter in sediments and sedimentary rocks are imperfectly understood and have been a subject of ongoing debate for many years (see, for example, Demaison and Moore, 1980; Parrish, 1982; Parrish and Curtis, 1982; Calvert, 1987; Pedersen and Calvert, 1990).

The tetrapyrrole content of sedimentary organic matter and crude oil depends on the interrelationship of several factors, such as organic productivity, sedimentation rate, thermal maturity, and redox conditions of the sedimentary environment (Orr et al., 1958; Lewan and Maynard, 1982; Baker and Louda, 1986; Baker et al., 1987). Long residence time in oxygenated water, either because of slow settling velocity or a long water column (Lewan and Maynard, 1982) (Figure 22), results in substantial degradation of tetrapyrroles. Pigments are among the most reactive compounds in marine organic matter (Henrichs and Doyle, 1986) and therefore are selectively degraded. For example, in a study of several lakes, Carpenter et al. (1986) reported loss of all pigments contained in detrital particles that remained in the epilimnion for periods longer than three days. Furlong and Carpenter (1988) found that less than one percent of the total pigment flux from the overlying water column was preserved in oxygenated marine sediments from Dabob Bay, Washington, and that

Figure 22. Concentration of tetrapyrroles (pheopigments) in organic matter from surface sediments in offshore California basins versus height of water column for the $\leq 10 \mu$ sediment particle size fraction. From Lewan et al. (1982) and Orr et al. (1958).



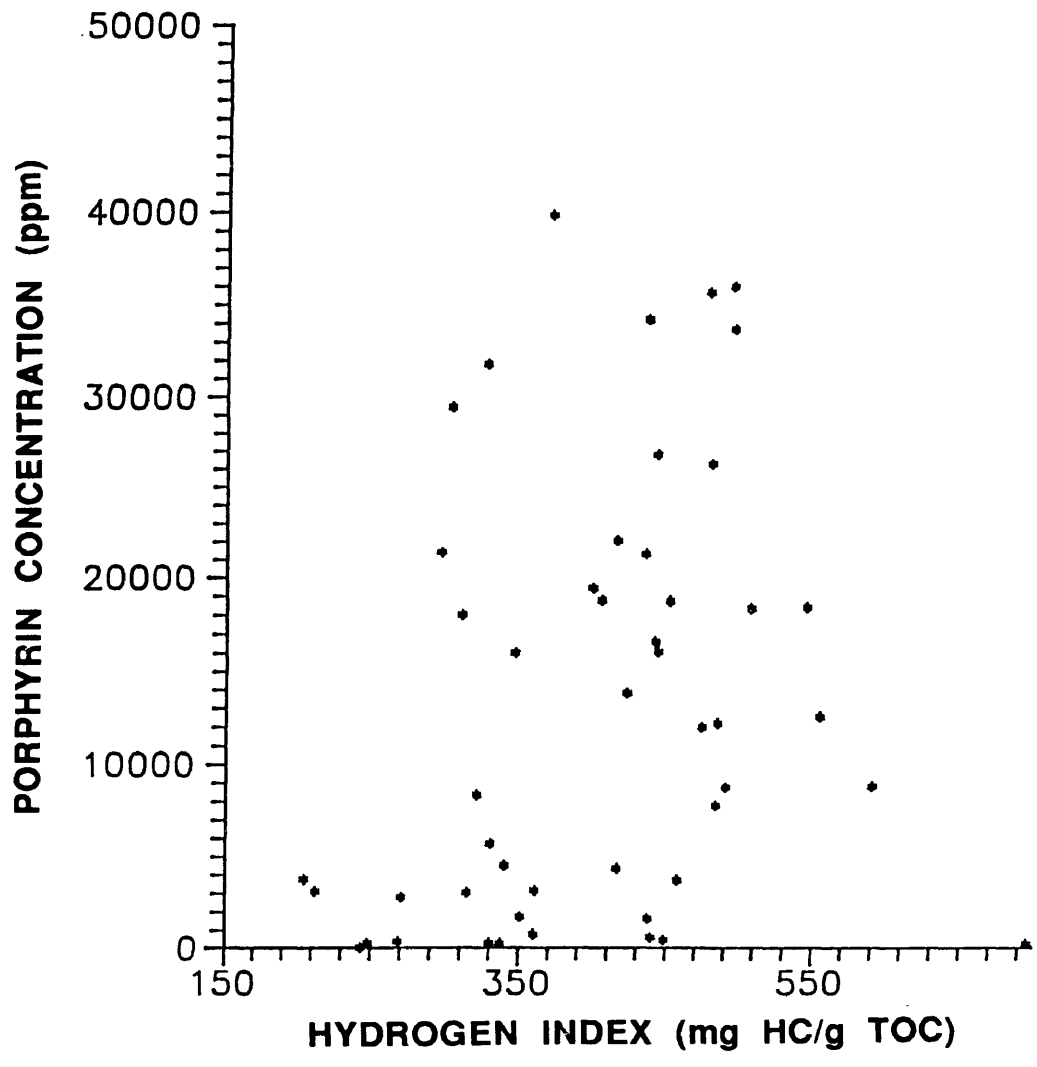
in marine waters pheopigment decomposed at rates of 5-20 times that of bulk organic carbon. They concluded, moreover, that pigments are significantly more reactive than the bulk lipid fraction of sedimentary organic matter. It is unlikely, therefore, that pigments could survive transport along with allochthonous organic matter. Accordingly, the ratio of porphyrins to either C_{Org} or bitumen provides a relative measure of preservation of primary (water-column photosynthate) organic matter and high concentration of porphyrins in type III organic matter would not be expected (Lewan and Maynard, 1982).

Mechanisms for decomposition of pigments include photochemical reactions and heterotrophic grazing (Moreth and Yentsch, 1970; Daley, 1973; Daley and Brown, 1973; SooHoo and Kiefer, 1982; Carpenter et al., 1986; Hurley and Armstrong, 1990); however, several studies have shown that planktonic grazing by zooplankton can enhance preservation of pheopigments through rapid settling of fecal particles (Downs and Lorenzen, 1985; Carpenter et al., 1986; Hurley and Armstrong, 1990). Carpenter et al. (1986) observed a relationship between body mass of zooplanktonic herbivores and pigment flux that suggests large zooplankters provide the most effective vectors of pigments (pheopigments) to sediments because of rapid sinking rates. Hurley and Armstrong (1990) suggested that direct sinking of phytoplankton can also be a major vertical transport mechanism. Interestingly, they concluded that anoxia is more important than

sedimentation rate in controlling preservation, although only a limited sedimentation rate range was considered ($1,200-889 \text{ g m}^{-2} \text{ yr}^{-1}$).

Samples of Desmoinesian and Missourian black shales from the restricted basin that have hydrogen indices as low as about $300 \text{ mg HC/g C}_{\text{Org}}$ have porphyrin concentrations as high as 29,000 ppm. At thermal maturities corresponding to vitrinite reflectance of 0.5-0.6 percent, these low hydrogen indices would be interpreted as transitional between type II-III or even type III organic matter (Espitalié and others, 1977; Tissot and Welte, 1984). This paradox between bulk organic-matter type and high porphyrin concentration can be explained by the model proposed above for contribution of type III organic matter during transgression of the sea (erosion) superimposed upon accumulation of primary organic matter from the overlying water column. Hydrogen index is plotted against porphyrin concentration (VOP-NiP) in Figure 23. Samples having hydrogen indices greater than $300 \text{ mg HC/g C}_{\text{Org}}$ have variable porphyrin concentrations, but samples having lower hydrogen indices ($190-300 \text{ mg HC/g C}_{\text{Org}}$) all have porphyrin concentrations less than 5,000 ppm. Only a few samples having the lower hydrogen indices were analyzed for porphyrins because these samples have light-colored extracted that obviously have low porphyrin concentrations. These low porphyrin contents are interpreted to indicate that low hydrogen indices are caused by poor preservation of primary organic matter

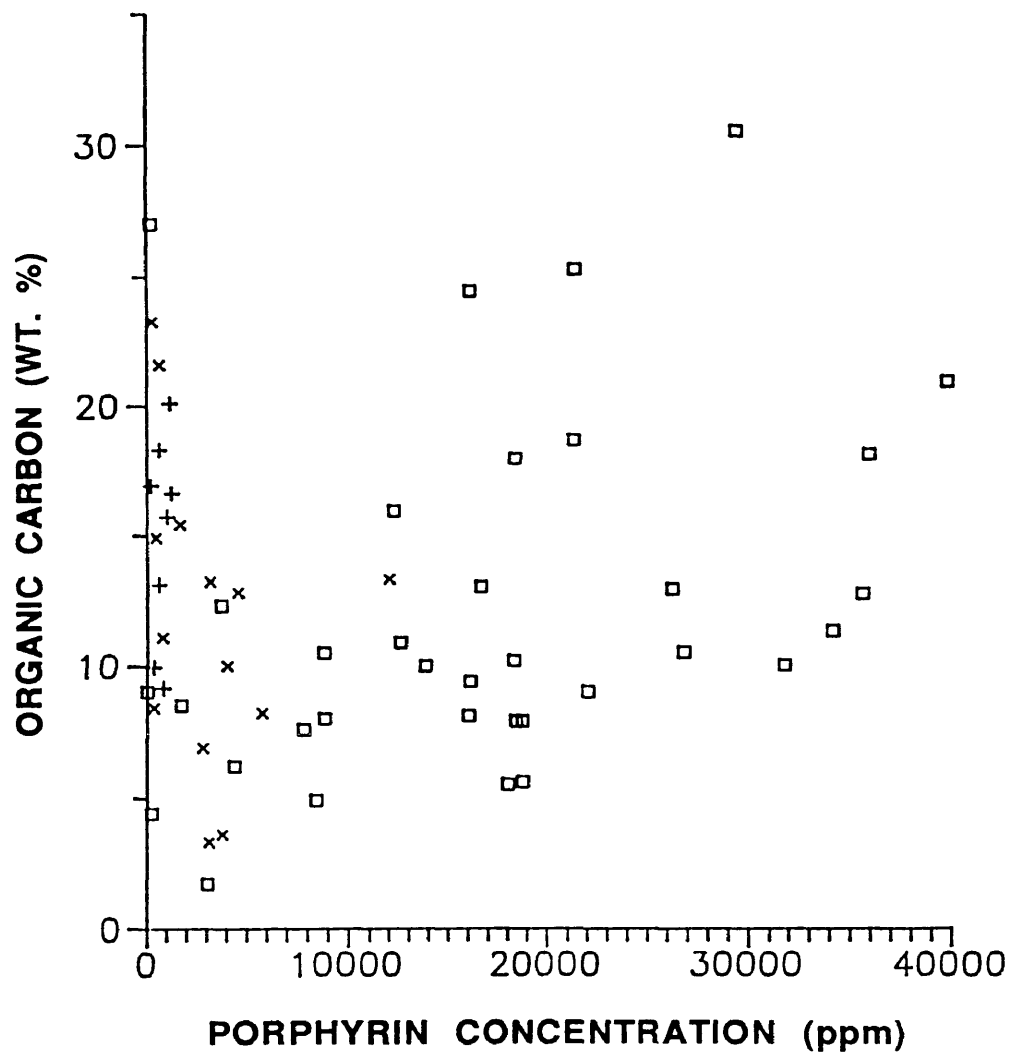
Figure 23. Hydrogen Index (mg hydrocarbons/g C_{Org}) for rock samples from Rock-Eval pyrolysis versus total porphyrin concentration (VOP + NiP) relative to bitumen (ppm).



combined with abundant allochthonous organic matter that results in high C_{Org} values. This situation would result in low porphyrin concentrations. Samples having higher hydrogen indices (300-600 mg HC/g C_{Org}) have variable porphyrin concentrations depending on the degree of preservation of primary organic matter and extent of dilution of the primary organic matter with allochthonous organic matter (including organic matter derived from erosion during advance of the sea). According to this reasoning, the hydrogen index would be largely independent of the porphyrin concentration for hydrogen indices above some minimum value associated with a threshold level of organic productivity and preservation. Assuming that porphyrins are more rapidly degraded than the bulk organic matter, the porphyrin to bitumen ratio could vary widely above this threshold value depending on various factors such as water-column height, bulk sedimentation rate, and water or sediment oxygen levels.

No systematic relationship exists between C_{Org} content and porphyrin concentration (Figure 24). In some cases, C_{Org} content of open marine samples is as high as about 24 weight percent and porphyrin concentration is very low. This suggests that even though large amounts of organic matter accumulated in the sediments, preservation of organic matter produced in the photic zone of the water column was relatively low compared to that for samples that have both high C_{Org} and high porphyrin concentrations (restricted basin samples). High C_{Org} values combined with low porphyrin

Figure 24. C_{Org} versus total porphyrin concentration (VOP + NiP) relative to bitumen (ppm). Squares indicate restricted basin samples, +'s indicate open marine samples from northeastern Colorado, x's indicate open-marine samples from Kansas and Oklahoma.



concentration could be caused by an overall longer water column and (or) absence of water-column stratification in the open-marine setting, and probably represents a combination of high production of organic matter in the water column and input of allochthonous organic matter as discussed above.

The major difficulty in attempting to interpret productivity or preservation of organic matter from these data is that two variables are involved (porphyrin and bitumen, or porphyrin and C_{Org}) that may vary independently. If most of the organic matter contained in a sediment is derived from the overlying water column, then because kerogen is more stable than bitumen, C_{Org} (approximately equal to kerogen content) would be the best choice for normalizing porphyrin data. In this case, porphyrin/ C_{Org} would provide a relative measure of preservation, with high ratios corresponding to greater preservation. On the other hand, high input of allochthonous organic matter as in the present study would cause independent variation in C_{Org} values. Therefore, because bitumen is less likely to survive degradation during long distance transport (terrestrial source), the ratio of porphyrin to bitumen would provide the best indication of preservation. This approach assumes, therefore, that the bitumen is mostly autochthonous.

Alternatively, the porphyrin data could be normalized to C_{Org} if an independent method would be available to assess the proportions of algal (autochthonous) and terrestrial (allochthonous) organic input

to the kerogen. As noted previously, comparison of carbon isotopic composition of kerogen and extractable hydrocarbons (Figure 21) can provide a qualitative assessment of allochthonous organic-matter input. The isotopically light C_{org} samples (ca -27 to -29 ‰) that have low Δ values (<1) are interpreted to contain both autochthonous hydrocarbons and the greatest relative proportion of autochthonous C_{org} .

The $\delta^{13}C_{org}$ data are compared with porphyrin concentration normalized to C_{org} and bitumen in Figure 25. According to the preceding reasoning, a positive correlation should exist between porphyrin/ C_{org} and $\delta^{13}C_{org}$. If increasing $\delta^{13}C_{org}$ values indicate greater mixing of terrestrial organic matter, then the porphyrin/ C_{org} ratio should decrease as more allochthonous C_{org} is added to the system as long as the indigenous production of porphyrins (water-column photosynthesis) remains relatively constant. Fluctuations in water column photosynthesis would introduce some scatter in the data, but a general trend should be nonetheless evident if this logic is correct. In that case, variation in porphyrin concentration would depend mostly on degree of mixing of organic matter from two sources. It is evident from Figure 25 that the normalized porphyrin content is highly variable for a given organic matter source as indicated by isotopic composition. Therefore, it is reasonable to conclude that the porphyrin content reflects mainly preservation rather than mixing of organic matter.

Figure 25. Comparison of $\delta^{13}\text{C}$ (C_{org}) and porphyrin concentration normalized to C_{org} and bitumen.

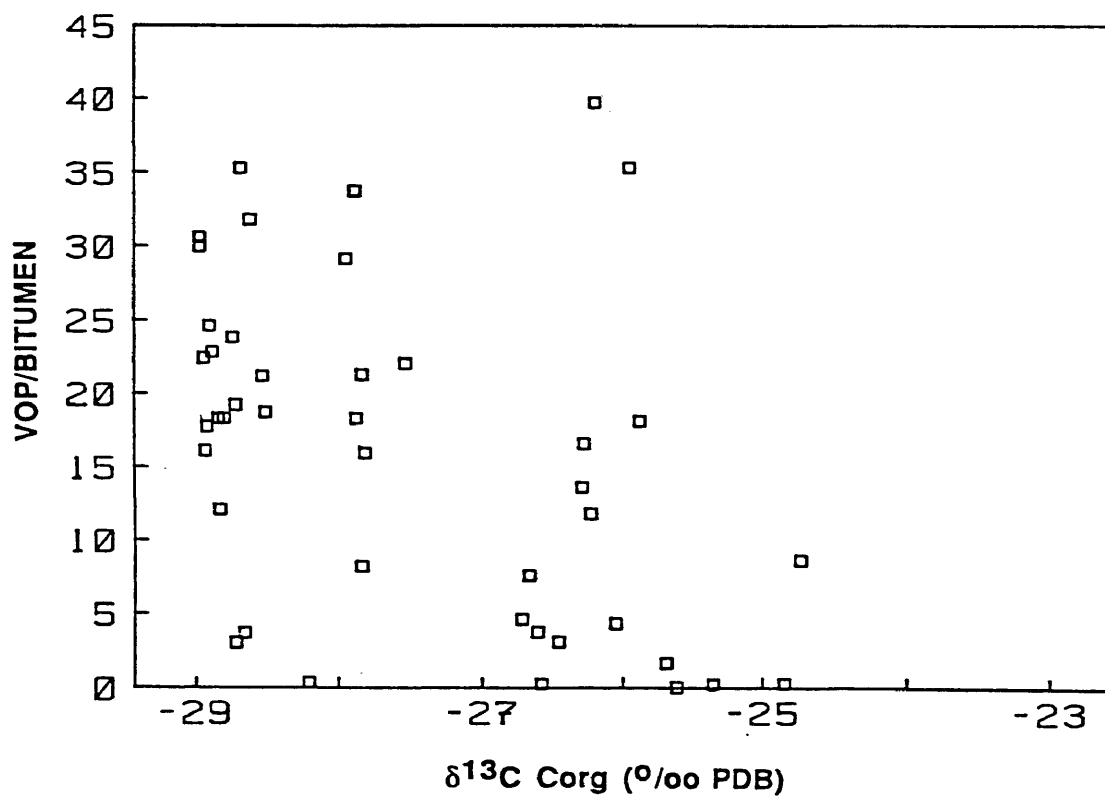
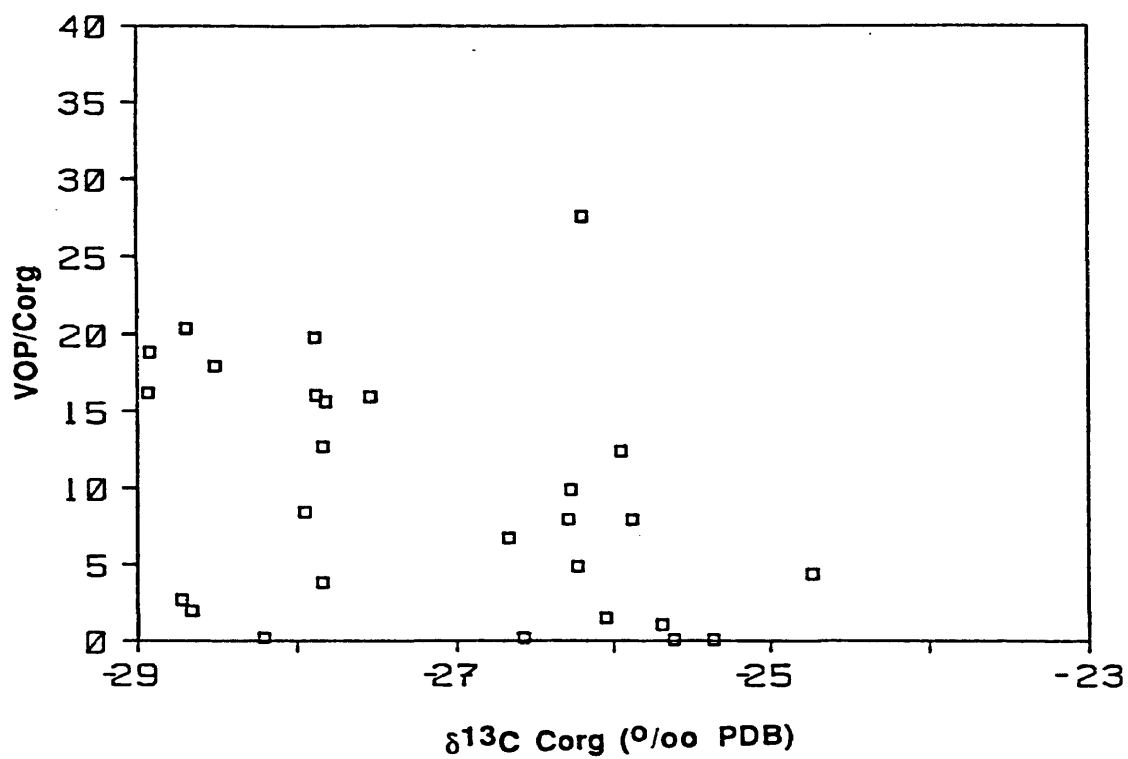
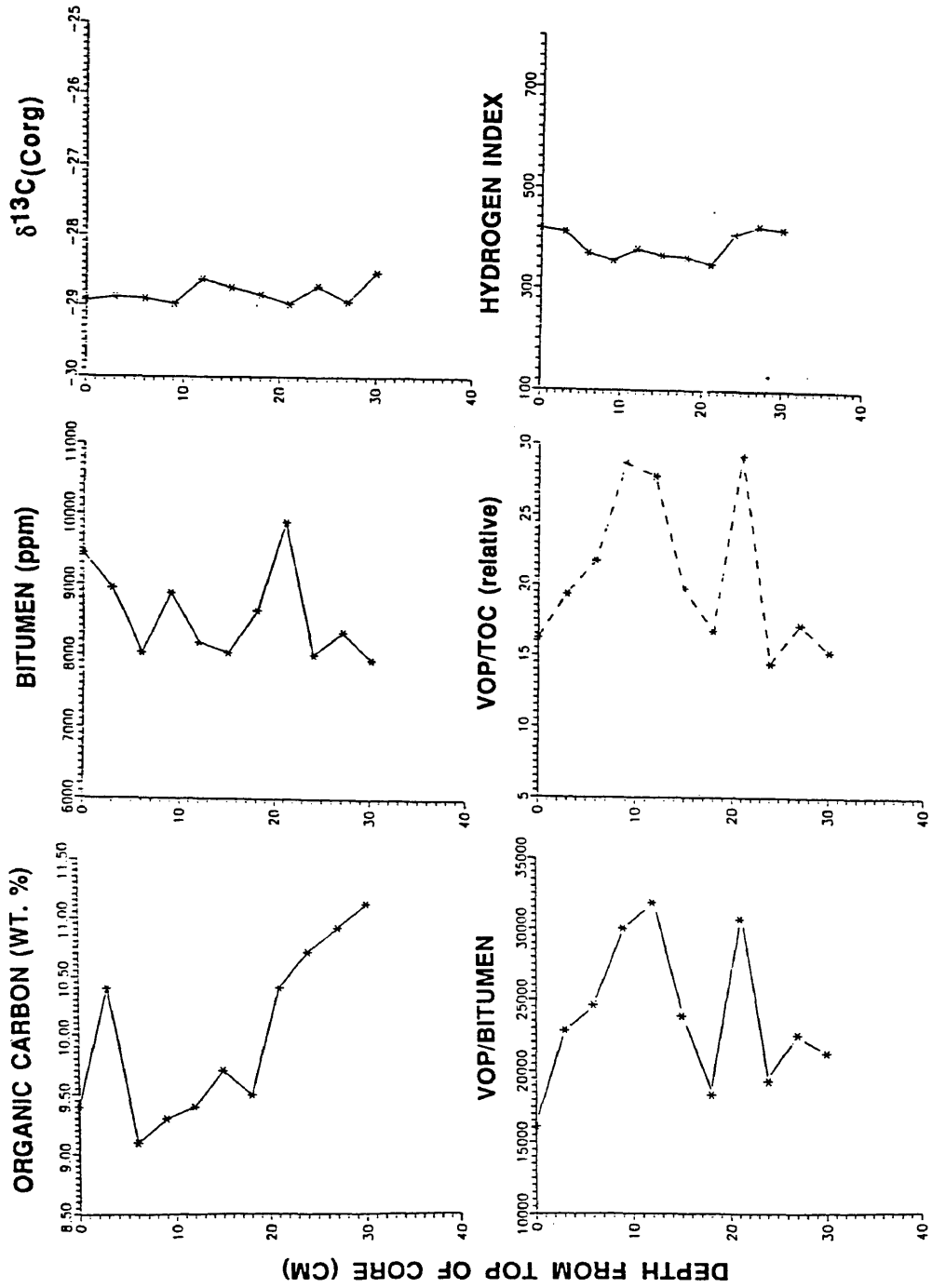


Figure 26 shows geochemical data for samples collected at approximately 1-cm intervals through a single black shale bed in the Mitchell 34-12 Seegrift well (samples 9-18, Table 1). The essentially constant $\delta^{13}\text{C}$ values of the kerogen (-28.53 to -28.97 ‰) indicate uniform organic-matter type throughout the entire interval. The hydrogen indices also varies little (Table 2), although C_{Org} decreases from bottom to top through most of the interval. The average bitumen content is 8,575 ppm and all but one sample (no. 15, Table 2) are within 10 percent of this value.

The purpose of analyzing this downhole set of samples is to test the applicability of porphyrin concentration as a relative measure of organic-matter preservation where other variables, such as mixing of organic matter from multiple sources or thermal effects, can be normalized. In this case, the carbon isotopic composition and hydrogen indices indicate that the organic-matter type is uniform. Interpretation of the specific biological source of the organic matter contained in the kerogen is less important in this case than the fact that no significant change in source occurs through the interval. Therefore, variation in the porphyrin concentration relative to bitumen or C_{Org} is interpreted to indicate relative preservation differences rather than variable degree of dilution by allochthonous organic matter.

Figure 26. Geochemical parameters of cores samples collected at approximately 1-cm intervals through a single black shale bed in the Mitchell 34-12 Seegrist well (samples 9-18, Table 2). Parameter abbreviations and units of measurement are described in Table 2.



Assuming that the organic-matter source does not change significantly through the interval, the change in both porphyrin and C_{Org} may represent variation in productivity *and* preservation. The decrease in C_{Org} suggests that productivity was at a maximum at the bottom of the interval and gradually decreased over time to near the top of the interval. In contrast, the normalized porphyrin content (relative to both C_{Org} and bitumen) exhibits wide variation over the same interval. This variation is interpreted to reflect variable preservation and no systematic relationship exists between productivity and preservation. Even though productivity decreases from bottom to top of the core according to C_{Org} data, the relative preservation does not show any systematic change. Interestingly, the VOP/ C_{Org} ratios of Figure 25 are similar to those reported by Downs and Lorenzen (1985) for carbon to pheopigment ratios in marine sediments (range 24-36 using the same relative scale as Figure 25).

All but one sample from the open-marine setting have relatively low porphyrin concentrations even though most C_{Org} values are quite high (Table 2). Considering the water depths of 50-100 m postulated for the epicontental sea (Heckel 1977, 1980, 1984), higher porphyrin concentrations might be expected if a significant thickness of anoxic water column were present. It is likely that most of the water column in the open-marine environment was oxygenated and that high amounts of organic matter accumulation were the result

primarily of high productivity combined with recycling of pre-existing organic matter. This model would explain not only the combination of high C_{org} values and low porphyrin contents, but also the relatively low sulfur content (high C/S ratio) and absence of biomarkers indicative of photosynthetic sulfur bacteria (aryl isoprenoids) in extracts from the open-marine environment. Relatively high *absolute* sulfur contents occur in the open-marine rocks suggesting that anoxic conditions may have existed in the sediments or in narrow water layer immediately overlying the sediments.

RECOGNITION OF HYPERSALINITY

An important research objective in molecular organic geochemistry is to determine diagnostic criteria for recognizing specific depositional environments for both sedimentary organic matter and oils. In the most general sense, criteria have been established for distinguishing marine and continental depositional environments. More recently, a number of workers have attempted to differentiate depositional regimes in more detail (for example, lacustrine freshwater, lacustrine saline water, marine or lacustrine hypersaline, marine carbonate, marine deltaic) (ten Haven et al., 1985, 1986, 1988; Sinnighe Damsté et al., 1986; Brassell et al., 1987, 1988; Mello et al., 1988; Jiang, 1988; Volkman, 1988). Although several of the earlier studies focused on geochemical criteria for recognition of "hypersaline" environments (ten Haven et al., 1985,

1988; Schwark and Pütt,am. 1990), the term "hypersaline" is somewhat ambiguous (Hite and Anders, 1991). According to Hite and Anders, hypersaline indicates all environments in which the salinity is greater than normal seawater (greater than 3.5 ‰), although the term is commonly used to indicate environments that are precipitating evaporitic salts.

According to the approach of these previous studies, the Desmoinesian and Missourian black shales (or marlstones) of the Minnelusa Formation would be classified as part of a marine evaporitic or hypersaline environment because the *overall* sequence is evaporitic and bedded anhydrites are present in each complete cyclothem. Similarly, in previous studies organic-rich rocks contained within an overall evaporitic sequence have sometimes been classified as hypersaline, but may represent a fairly broad range of salinity. For example, ten Haven et al. (1985) reported organic geochemical analyses of a marl as indicative of hypersaline conditions because the sequence studied contained evaporite deposits. The most organic rich rocks in ten Haven's study are the marls, deposited during times of maximum water depth, and the actual evaporite deposits (gypsum) have much lower organic matter contents and a different molecular distribution of organic compounds. According to Hite and Anders (1991), carbonate deposition may commence at a salinity of about 10 percent, whereas salinities of about 15 percent or more may be required for gypsum precipitation. Mello et al. (1988) distinguished

marine carbonate from marine evaporite deposits, but carbonates can precipitate in evaporitic environments and a continuum exists between carbonate and anhydrite deposition.

Therefore, as these examples illustrate, it is important to distinguish between the depositional conditions of the overall sequence and individual rock types contained within the sequence in order to avoid ambiguities in the application of geochemistry to paleoenvironmental assessment. Hite and Anders (1991) point out that organic productivity in the water column is commonly extremely high during highly saline conditions (10-15 percent), but that preservation in the underlying sediments is generally quite low. In contrast, although water-column productivity may be lower, preservation of organic matter commonly is often much greater during deposition of marlstones or carbonate rocks during moderately high salinity conditions in the evolution of an evaporitic basin.

In the present study, organic-matter content of the highly saline (approximately 15 percent) deposits such as anhydrite (gypsum) is very low. Only a few samples were analyzed, and they are not included in Table 2 because C_{Org} values are less than 0.2 weight percent. In terms of organic geochemical and economic significance (as petroleum source rocks), the most saline deposits (anhydrite, carbonate rocks excluding marlstone) are unimportant. In contrast, the organic-rich marlstones were deposited during periods of normal to possibly slightly greater than normal marine salinity but

probably less than about 10 percent (Hite and Anders, 1991). The geology of these rocks is consistent with that interpretation because the marlstones were deposited during maximum transgression and, therefore, greatest water depths. Therefore, the organic geochemical characteristics of the organic-rich marlstones in the present study can be considered indicative of a marine carbonate-evaporite environments characterized by normal or slightly elevated salinity, a density-stratified water column, and euxinic conditions in the lower water layer.

When water salinity increases the diversity of living organisms decreases, although the total biomass may be quite high (Hite and Anders, 1991). Research studies aimed at identification of specific biological marker compounds or assemblages of compounds as indicators of hypersaline depositional environments are based on the premise that unique biomarker patterns will occur when a decrease of overall diversity of organisms occurs coupled with the occurrence of specialized organisms adapted to live in extreme environments. Table 6 summarizes key geochemical parameters thought to be diagnostic of rocks and oils in hypersaline sequences. In addition to the features listed in Table 6, high nonhydrocarbon content (resins + asphaltenes) in rock extracts and oils is typical for hypersaline environments. In the present study, geochemical characteristics thought to indicate hypersalinity (Table 6) are generally absent except a slight even carbon predominance among *n*-alkanes in the

Table 6

Geochemical characteristics of rocks and oils in hypersaline sequences.
 [NA indicates not available; abd. abundant]

Reference	Pr/Ph	CPI	GI	%S	R22 Index	C35 Diasteranes	C25 Hopane	Isoprenoid	4-Me
1	<1.0	<1.0	NA	NA	NA	NA	NA	NA	NA
2	<1.0	NA	NA	NA	NA	NA	NA	Abundant	NA
3	0.3-1.2 ^b	<1.0	NA	NA	>1.0	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA	>C34	NA	NA
5,6 ^a	0.3	<1.0	11	3.6	NA	NA	NA	NA	Abundant
7	0.3-0.9	<1.0	NA	NA	>1.0	Low ^e	>C34	Absent	Abundant
8	<<1.0	<1.0	~40	NA	>1.0	Low	>C34	Abundant ^f	Abundant
9	NA	NA	NA	NA	>1.0	NA	NA	NA	Abundant
10	0.5-1.0	≥1.0	76-132	NA	>1.0	9-27% ^d	>C34	NA	NA
11	<<1.0	<1.0	~100	NA	>1.0	Low	>C34	Abundant	Abundant
12	0.1-0.5	≤1.0	35-216	High	NA	NA	>C34	NA	Abundant

Table 6. (continued)

	13	<1.0	≤1.0	70-120	0.3-2.5	~1.0	Low	>C34	Abundant	Abundant
	14	0.3	<1.0	~100	NA	>1.0	NA	NA	NA	NA
This study	0.7-1.4	≤1.0	<10-113 ^c	0.5-5.0	≥1.0	Low	<C34	Rare	NA	NA

- a) Both studies include same sample from evaporite sequence.
- b) 0.3 for anhydrite-rich sample; 1.2 for dolomite-rich sample.
- c) All samples except one have values less than about 40.
- d) Relative abundance in whole sterane fraction.
- e) Except one nodular anhydrite sample had high diasteranes.
- f) Only in marl sample, absent in gypsum.

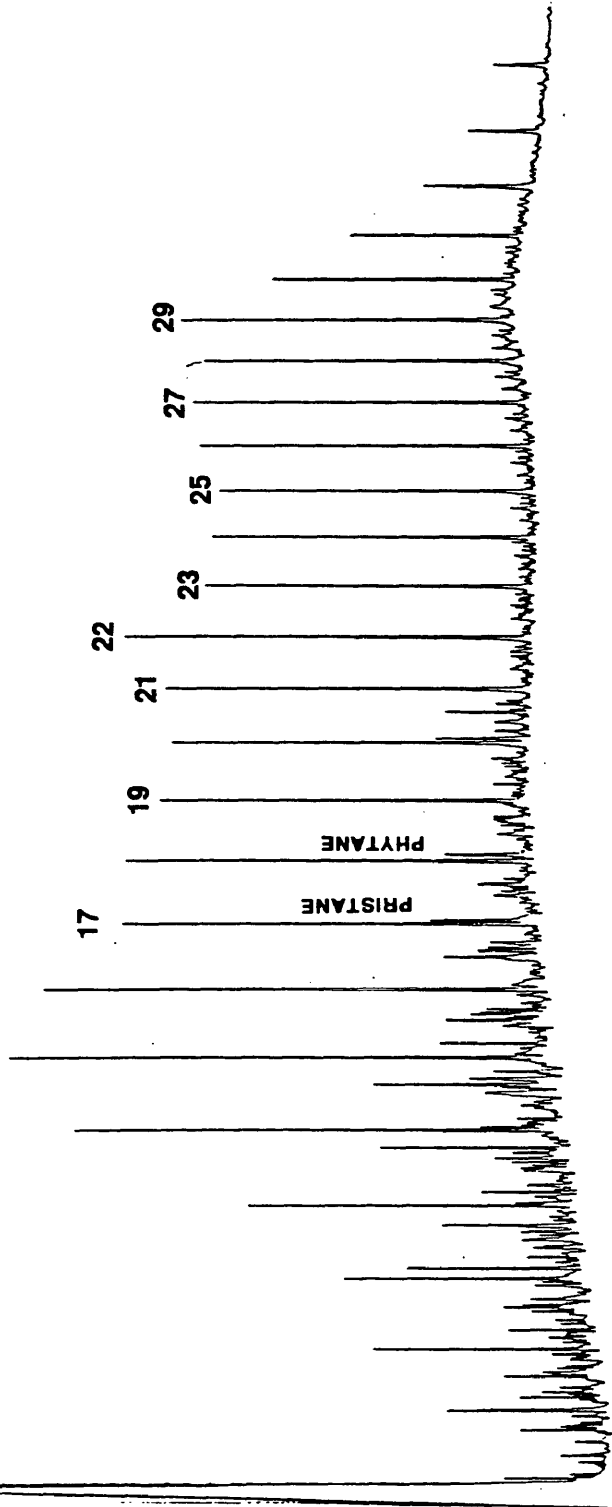
1. Welte and Waples (1973); 2. Waples et al. (1974) 3. Connan (1981); 4. McKirdy et al. (1983); 5. Seifert et al. (1984); 6. Moldovan et al. (1985); 7. Connan et al. (1986); 8. ten Haven et al. (1985); 9. de Leeuw et al. (1985); 10. Philp and Zhadan (1987); 11. ten Haven et al. (1988); 12. Fu Jiamo et al. (1986, 1988); 13. Mello et al. (1988); 14. Prinos Oil (Greece), J. Palacas and N. Rigakis (unpublished data).

C₂₅ region (Figure 11), low diasterane content (Figure 15), and high sulfur content (Table 2). Only three samples (nos. 59, 60, 61, Table 2) contain gammacerane in greater abundance than the C₃₁ hopane (homohopane). The only sample that has an R₂₂ index (ten Haven et al., 1988) greater than one is an organic-lean sample (Figure 27) and this sample has a CPI (C₂₅-C₃₂) greater than one (odd carbon predominance) and a pristane/phytane ratio of 1.3. These data suggest that indigenous organic matter from the hypersaline environment (R₂₂ index) is mixed with terrestrially derived organic matter (pristane/phytane ratio >1, odd carbon preference, abundant C₂₅+). Considering the relatively low organic carbon content, it is not surprising that the terrestrial organic components are so predominant.

A possible explanation for both the variability in geochemical data reported in the literature for hypersaline settings and the general lack of comparison with the present study is that a wide range of organic geochemical features is possible in hypersaline environments because hypersalinity includes a wide range of depositional conditions (35 to more than 350 ‰ salinity) and associated biological systems and diagenetic conditions. For example, ten Haven et al. (1985) studied both marl and gypsum samples from an evaporitic sequence of late Miocene age. The marl represents vitasaline conditions (25-142 ‰ salinity) and the gypsum represents penesaline to saline conditions (142-350 ‰ salinity) (Hite and Anders, 1991). ten Haven and others observed significant differences

Figure 27. GC of saturated hydrocarbon fraction of rock extract containing high amounts of the proposed hypersaline indicator *n*-C₂₂. The odd carbon preference and high pristane to phytane ratio are interpreted to indicate input of terrestrial organic matter.

CONOCO 23-1 PERKINS
2,460 M
CORG = 0.4%
(WELL NO. 8)



between the marl and gypsum samples. For example, the saturated hydrocarbons in the gypsum sample contained an even carbon preference in the C₂₅-C₃₀ region, whereas the marl sample contained an odd carbon predominance in the same fraction. This finding is noteworthy because Mello et al. (1988) listed odd/even preferences of one or less (that is, even carbon predominance) as a characteristic feature of marine evaporitic rocks. Several other workers have likewise concluded that even carbon predominances are characteristic of evaporitic sequences (Welte and Waples, 1973; Dembicki et al., 1976; Spiro and Aizenshtat, 1977; Tissot et al., 1977; Guoying et al., 1980). ten Haven et al., (1985) suggested that an input of "reworked" organic matter could obscure the even carbon predominance in the marl sample. Further, they found the C₂₅ isoprenoid compound only in the marl sample and concluded that the compound may be a marker only for certain organisms that live only in a restricted salinity range.

Recently, Summons and Powell (1986, 1987) and Schwark and Püttman (1990) presented evidence that high concentrations of aryl isoprenoids are indicative of hypersaline conditions. The data of the present study are consistent with these previous findings. Aryl isoprenoids in the C₁₃₊ range are abundant constituents of the black shales and marlstones from the restricted basin but are minor components or absent entirely in the open-marine samples. The presence of high amounts of aryl isoprenoids is strong evidence for a

stratified water column with euxinic conditions in the lower water layer, but it could be the result of either density or temperature stratification. The occurrence of evaporite deposits in the sequence and the overall salinity increase upward through each cyclothem (marlstone→carbonate→anhydrite) suggest, but do not prove, that density stratification (high salinity) occurred.

The preceding examples illustrate the difficulty in defining organic geochemical parameters that can be used as indicators of salinity conditions. The main problems are the salinity conditions are not always defined or even known and that multiple sources of organic matter are possible including allochthonous sources. An additional complication is that the salinity may be nonuniform through the water column. The model proposed herein for deposition of black shales include hypersaline water below a normal or near-normal salinity water layer above density stratification. Further, if the paleoclimatic model of Cecil (1990) is correct for deposition of cyclothems then high amounts of freshwater runoff could not only preclude development of high salinity in the upper water layer but would also carry nonindigenous organic matter to the depositional site and thus obscure the geochemical characteristics of the biological system in the water (hypersaline) and sediments.

CONCLUSIONS

This study illustrates the application of various organic geochemical parameters to interpretation of paleoenvironment during

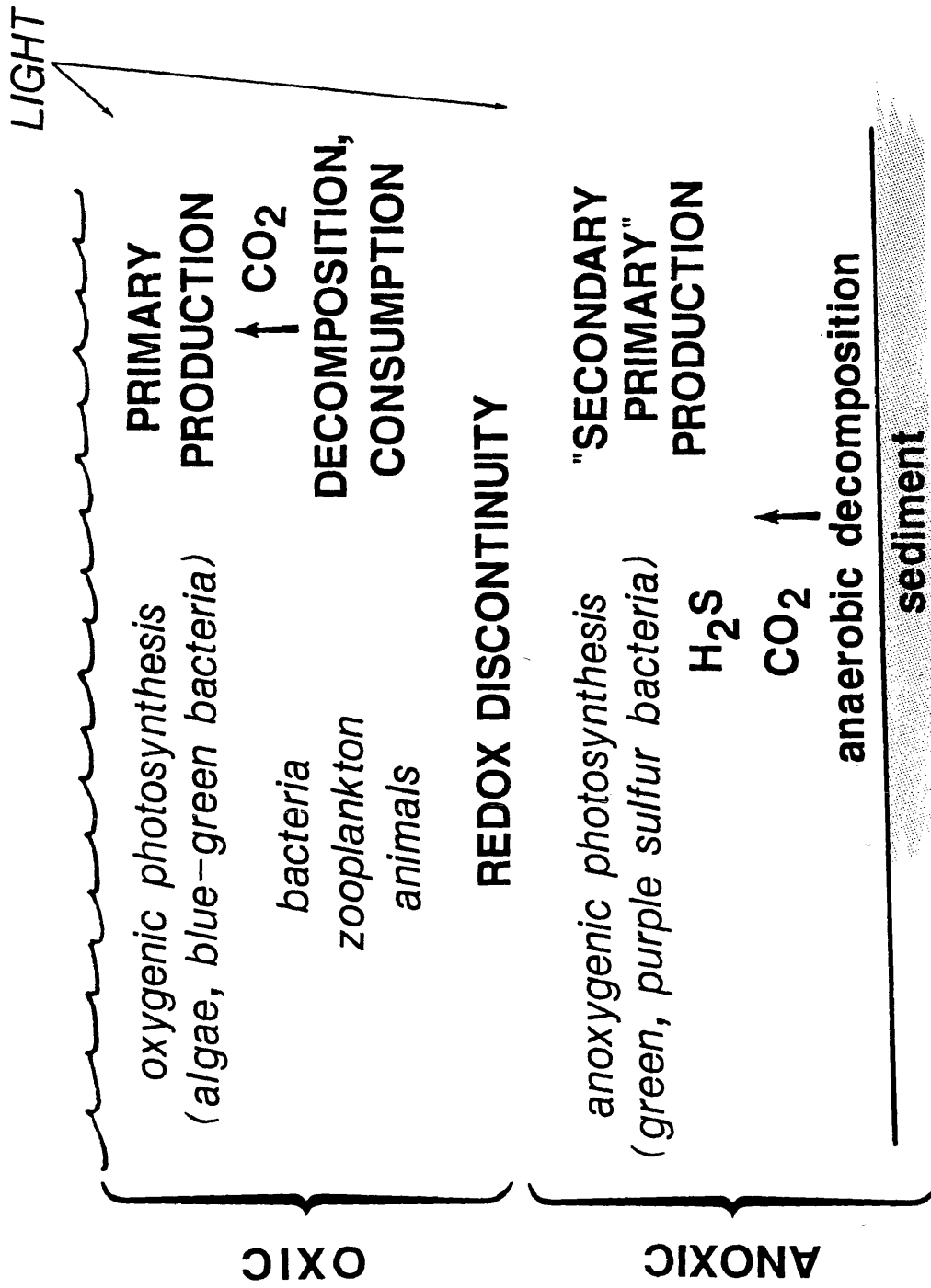
deposition of organic-rich black shales of Desmoinesian age of the western U.S. and to black shale deposition in general. The main points are summarized below.

Black organic-rich shales in the northern Denver basin and southeastern Powder River basin were deposited in a restricted basin containing a stratified water column. The lower water layer was probably euxinic. High porphyrin concentrations resulted from a combination of high organic productivity caused by abundant nutrients in a warm shallow sea and a short oxygenated water column. In the open-marine environment of eastern Colorado and adjacent areas of Kansas and Oklahoma, low porphyrin concentration, high C/S ratios, and absence of aryl isoprenoids indicates that a longer oxygenated water column was present even though the sediments themselves may have been strongly reducing at times as indicated by high V/Ni ratios in the porphyrin fractions.

High porphyrin concentration in mixed type II-III organic matter is unexpected but can be explained by a combination of high preservation of primary organic matter and an even greater input of recycled organic matter from erosion during sea-level rise (transgression) as black shale deposition commence. The result of these factors is accumulation of exceptionally organic rich shales that have high porphyrin to bitumen ratios but low porphyrin-to-C_{Org} ratios.

Concentration of porphyrins (versus C_{org} or bitumen) is useful for interpretation of relative degree of preservation of primary organic matter. In rocks of Desmoinesian age in the Minnelusa Formation in the Powder River basin and equivalent rocks of the northern Denver basin, preservation of organic matter was quite high in the organic-rich rocks. Preservation was enhanced by water-column stratification and anoxic or euxinic conditions in the lower water layer (Fig. 28).

Figure 28. Summary of interpreted water column conditions in the "restricted basin" part of the study area in Nebraska during deposition of organic-rich rocks. The upper water column contained oxygen in sufficient amounts to support aerobic photosynthesis, but was possibly thinner than the lower anoxic water layer in which sulfate reduction and anoxygenic photosynthesis were taking place.



MODIFIED FROM PFENNING (1978)

REFERENCES CITED

- Agatston, R.S., 1954, Pennsylvanian and Lower Permian of Northern and Eastern Wyoming: American Association of Petroleum Geologists Bulletin, v. 38, p. 508-583.
- Arthur, M.A., Dean, W.E., and Claypool, G.E., 1985, Anomalous ^{13}C enrichment in modern marine organic carbon: Nature, v. 315, p. 216-218.
- Baker, E.W., and Louda, J.W., 1986, Porphyrins in the geological record, in Johns, R.B., ed., Biological markers in the sedimentary record: Elsevier, Oxford, p. 125-225.
- Baker, E.W., Louda, J.W., and Orr, W.L., 1987, Application of metalloporphyrin biomarkers as petroleum maturity indicators-The importance of quantitation: Organic Geochemistry, v. 11, p. 303-310.
- Bates, R.L., 1955, Permo-Pennsylvanian formations between Laramie Mountains, Wyoming and Black Hills, South Dakota: American Association of Petroleum Geologists Bulletin, v. 39, p. 1979-2002.
- Berner, R.A., 1970, Sedimentary pyrite formation: American Journal of Science, v. 268, p. 1-23.
- Boreham, C.J., and Powell, T.G., 1987, Sources and preservation of organic matter in the Cretaceous Toolebuc Formation, eastern Australia: Organic Geochemistry, v. 11, p. 433-499.

- Brassell, S. Eglinton, G., and Howell, V. J., 1987 Palaeoenvironmental assessment of marine organic-rich sediments using molecular organic geochemistry, in Brooks, J., and Fleet, A.J., eds., Marine petroleum source rocks: Geological Society Special Publication 26, p. 79-98.
- Brassell, S.C., Sheng Guoying, Fu Jiamo and Eglinton, G., 1988, Biological markers in lacustrine Chinese oil shales, in Fleet, A.J., Kelts, K., and Talbot, M.R., eds., Lacustrine petroleum source rocks: Geological Society Special Publication 40, Oxford, P. 299-308.
- Brooks, J., Cornford, C., and Archer, R., 1987, The role of hydrocarbon source rocks in petroleum exploration, in Brooks, J. and Fleet, A.J., eds., Marine source rocks: Boston, Blackwell Scientific Publications, p. 17-46.
- Calder, J.A., and Parker, P.L., 1973, Geochemical implications of induced changes in ^{13}C fractionation by blue-green algae: *Geochimica et Cosmochimica Acta*, v. 37, p. 133-140.
- Calvert, S.E., 1987, Oceanographic controls on the accumulation of organic matter in marine sediments, in Brooks, J., and Fleet, A.J., eds., Marine petroleum source rocks, Geological Society Special Publication 26, p. 137-151.
- Cardinal, D.F. and Holmes, K.H., 1984, Lower Permian and Pennsylvanian stratigraphy and structure of the tri-state area, southeastern Wyoming, western Nebraska, and southwestern

- South Dakota, in Goolsby, J. and Morton, D., eds., *The Permian and Pennsylvanian Geology of Wyoming: Wyoming Geological Association Annual Field Conference, 35th, Guidebook,*, p. 333-340.
- Carpenter, S.R., Elser, M.M., and Elser, J.J., 1986, Chlorophyll production, degradation, and sedimentation: Implications for paleolimnology: *Limnology and Oceanography*, v. 31, no. 1, p. 112-123.
- Cecil, C.B., 1990, Paleoclimate controls on stratigraphic repetition of chemical and siliclastic rocks: *Geology*, v. 18, p. 533-536.
- Clarke, F.W., 1915, *Analyses of rocks and minerals from the laboratory of the U.S. Geological Survey, 1880-1914: U.S. Geological Survey Bulletin 591, 376p.*
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H, and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: *Chemical Geology*, v. 28, p. 199-260.
- Clayton, J.L., 1989, Geochemical evidence for Paleozoic oil in Lower Cretaceous O sandstone, northern Denver basin: *American Association of Petroleum Geologists Bulletin*, v. 73, p. 977-988.
- Clayton, J.L., and Ryder, R.T., 1984, Organic geochemistry of black shales and oils in the Minnelusa Formation (Permian and Pennsylvanian), Powder River basin, Wyoming, in Woodward, J., Meissner, F.F. and Clayton, J.L., eds., *Hydrocarbon source rocks*

- of the greater Rocky Mountain region: Denver Rocky Mountain Association of Geologists, p. 231-253.
- Coffin R.B., Fry, B., Peterson, R.J., and Wright, R.T., 1989, Carbon isotopic compositions of estuarine bacteria: *Limnology and Oceanography*, v. 34, no. 7, p. 1305-1310.
- Connan, J., 1981, Biological markers in crude oils, in Mason, J.F., ed., *Petroleum Geology in China: Pennwell Books*, p. 49-70.
- Conna, J., Bouroulee, J., Dessort, D., and Albrecht, P., 1986, The microbial input in carbonate-anhydrite facies of a sabkha paleoenvironment from Guatemala: A molecular approach, in Leythaeuser, D., and Rullkötter, J., eds., *Advances in organic geochemistry 1985: Organic Geochemistry*, v. 10, p. 29-50.
- Craig, H., 1953, The geochemistry of the stable carbon isotopes: *Geochimica et Cosmochimica Acta*, v. 3, p. 53.
- Daley, R.J., 1973, Experimental characterization of lacustrine chlorophyll diagenesis, 2, Bacterial, viral and herbivore grazing effects: *Arch. Hydrobiology*, v. 72, p. 409-439.
- Daley, R.J., and Brown, S.R., 1973, Experimental characterization of lacustrine chlorophyll diagenesis: I, Physiological and environmental effects. *Arch. Hydrobiology*, v. 72, p.277-304.
- Sinnighe Damsté, J.S., and de Leeuw, J.W., 1986, The origin and fate of isoprenoid C₂₀ and C₁₅ sulphur compounds in sediments and oils: *International Journal of Environmental Analytical Chemistry*, v. 49, p. 1-19.

- Dean, W.E., Arthur, M.A., and Claypool, G.E., 1986, Depletion of ^{13}C in Cretaceous marine organic matter--Source, diagenetic, or environmental signal?; *Marine Geology*, v. 70, p. 119-157.
- Dean, W.E., and Anders, D.E., in prep, Effects of source, depositional environment, and diagenesis on characteristics of organic matter in oil shale from the Green River Formation, Wyoming, Utah, and Colorado: U.S. Geological Survey Bulletin.
- Degens, E.T., Guillard, R.R.L., Sackett, W.M., and Hellebust, J.A., 1968, Metabolic fractionation of carbon isotopes in marine plankton, I. Temperature and respiration experiments: *Deep Sea Resources*, v. 15, p. 1-9.
- Demaison, G.J., and Moore, G.T., 1980, Anoxic environments and oil source bed genesis: *American Association of Petroleum Geologists Bulletin*, v. 64, p. 1179-1209.
- Dembicki, H., Meinschein, W.G., and Hattin, D.E., 1976, Possible ecological and environmental significance of the predominance of even-carbon number $\text{C}_{20}\text{-C}_{30}$ *n*-alkanes: *Geochimica et Cosmochimica Acta*, v. 40, p. 203-208.
- Desmond, R.J., Steidtmann, J.R., and Cardinal, D.F., 1984, Stratigraphy and depositional environments of the Middle Member of the Minnelusa Formation central Powder River basin, Wyoming: in Goolsby, J. and Morton, D., eds., *The Permian and Pennsylvanian Geology of Wyoming*, Wyoming Geological Association 35th Annual Field Conference Guidebook, p. 213-239.

- Deuser, W.G., Degens, E.,T, and Guillard, R.R.L., 1968, Carbon isotope relationships between plankton and sea water: *Geochimica et Cosmochimica Acta*, v. 32, p. 657-660.
- Didyk, B.M., Alturki, Y.I.A., Pillinger, C.T., and Eglinton, G., 1974, Petroporphyrins as indicators of geothermal maturation: *Nature*, v. 256, p. 563-565.
- Downs, J.N., and Lorenzen, C.J., 1985, Carbon:pheopigment ratios of zooplankton fecal pellets as an index of herbivorous feeding: *Limnology and Oceanography*, v. 30, no. 5, p. 1024- 1036.
- Doyle, J.D., 1987, Depositional environments of the Pennsylvanian and Lower Permian of the Hartville Uplift and adjacent areas in eastern Wyoming, western Nebraska, and southwest South Dakota: Colorado School of Mines, Golden, Ph.D. Thesis, 309 p.
- Eckardt, C.B ., Wolf, M. and Maxwell, J.R., 1989, Iron porphyrins in the Permian Kupferschiefer of the Lower Rhine Basin, N.W. Germany: *Organic Geochemistry*, v. 14, p. 659-666.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977, Méthode rapide de caractérisation des roches mères, de leur potential pétrolier et de leur degré d'évolution: *Revue de L'Institute Francias du Pétrole*, v. 32, p. 23-42.
- Filby, R.H. and Van Berkel, G.J., 1987, *Geochemistry of Metal Complexes in Petroleum. Source Rocks, and Coals: An Overview:* in Filby, R.H., and Branthaver, J.F., eds., *Metal Complexes in*

- Fossil Fuels, American Chemical Society Series 344, Washington, p. 2-39.
- Fontugne, M.R., and Duplessy, J.C., 1981, Organic carbon isotopic fractionation by marine plankton in the temperature range -1 to 31 °C: *Oceanography Acta*, v. 32, p. 657-660.
- Foster, D.I., 1958, Summary of the stratigraphy of the Minnelusa Formation, Powder River basin, Wyoming, in *Powder River Basin Guidebook: Wyoming Geological Association*, p. 39-44.
- Freeman, D.H., Angeles, R.M., Freeman, K.H., Hoering, T.C., Flynn, J.S., Lango, T.A., and Homonay-Preyer, T.A., 1987, Group isolation of nickel and vanadyl porphyrins from crude oils using macroporous silica gel, in Filby, R.H. and Branthaver, J.F., eds., *Metal complexes in fossil fuels: American Chemical Society Symposium Series 344*, p. 402-422.
- Freeman, K.H., Hayes, J.M., Trendel, J.M., and Albrecht, P., 1990, Evidence from GC-MS carbon-isotopic measurements for diverse origins of sedimentary hydrocarbons: *Nature*, v. 353, p. 254-256.
- Fuex, A.N., 1977, The use of stable carbon isotopes in hydrocarbon exploration: *Journal of Geochemical Exploration*, v. 7, p. 155-188.
- Fu Jiamo, Sheng Guoying, and Liu, Dehan, 1988, Organic geochemical characteristics of major types of terrestrial petroleum source rocks in China, in Fleet, A.J., Kelts, K., and Talbot, M.R., eds.,

- Lacustrine petroleum source rocks: Geological Society Special Publication 40, p. 279-289.
- Fu Jiamo, Sheng Guoying, Peng Pingan, Brassell, S.C., Eglinton, G., and Jiang, Jigang, 1986, Peculiarities of salt lake sediments as potential source rocks in China, in Leythaeuser, D., and Rüllkötter, J., eds., *Advances in Organic Geochemistry 1985: Organic Geochemistry*, v. 10, p. 119-126.
- Furlong, E.T., and Carpenter, R., 1988, Pigment preservation and remineralization in oxic coastal marine sediments: *Geochimica et Cosmochimica Acta*, v. 52, p. 897-99,.
- Galimov, E.M., 1974, Organic geochemistry of carbon isotopes, in Tissot, B., and Bienner, F., eds.: *Advances in organic geochemistry 1973*: Paris, Editions Technip, pp. 439-452.
- Galimov, E.M., 1980, $^{13}\text{C}/^{12}\text{C}$ in kerogen, in Durand, B., ed., *Kerogen*: Paris, Editions Technip, pp. 271-299.
- Gearing, J.N., Gering, P.J., Rudnick, D.T., Requejo, A.G., and Hutchins, M.J., 1984, Isotopic variability of organic carbon in a phytoplankton-based, temperature estuary: *Geochimica et Cosmochimica Acta*, v. 48, p. 1089-1098.
- Goldhaber, M.B., and Kaplan, I.R., 1974, The sulfur cycle, in *The sea*, v. 5: New York, Wiley, p. 569-655.
- Guerrero, R., Montesinos, E., Pédro-Akió, C., Esteve, I., Mas, J., van Gemerden, H., Hofman, P.A.G., and Bakker, J.E. , 1985, Phototrophic sulfur bacteria in two Spanish lakes: Vertical

- distribution and limiting factors: *Limnology and Oceanography*, v. 30, p. 919-931.
- Guoying, S., Shanfa, F., Dehan, L., Nengxian, S., and Hongming, Z., 1980, The geochemistry of *n*-alkanes with an even-odd predominance in the Tertiary Shahejie Formation of northern China, in Douglas, A.G., and Maxwell, J.R., eds.: *Advances in organic geochemistry 1979*, Pergamon Press, p. 115-121.
- ten Haven, H.L., de Leeuw, J.W., and Schenck, P.A., 1985, Organic geochemical studies of a Messinian evaporitic basin, northern Apennines (Italy) I-Hydrocarbon biological markers for a hypersaline environment: *Geochimica et Cosmochimica Acta*, v. 49, p. 2181-2191.
- ten Haven, H.L., de Leeuw, J.W., and Schenck, P.A., 1986, Organic geochemical studies of a Messinian evaporitic basin, northern Apennines (Italy) II--Isoprenoid and *n*-alkyl thiophenes and thiolanes, in Leythaeuser, D., and Rullkötter, J., eds., *Advances in organic geochemistry 1985: Organic Geochemistry*, v. 10, p. 791-805.
- ten Haven, H.L., de Leeuw, J.W., Sinnighe Damsté, J., Schenck, P.A., Palmer, S.E., and Zumberge, J., 1988, Application of biological markers in the recognition of palaeo-hypersaline environments, in Fleet, A.J., Kelts, K., and Talbot, M.R., eds., *Lacustrine petroleum source rocks: Geological Society Special Publication* 40, p. 123-130.

- Hayes, J.M., Freeman, K.H., Popp, B.N., and Hoham, C.H., 1990, Compound-specific isotopic analyses--A novel tool for reconstruction of ancient biogeochemical processes, in Durand, B., and Behar, F., eds., *Advances in organic geochemistry 1989: Organic Geochemistry*, v. 16, p. 1115-1128.
- Hayes, J.M., Popp, B.N., Takigiku, R., and Johnson, M.W., 1989, An isotopic study of biogeochemical relationships between carbonates and organic carbon in the Greenhorn Formation: *Geochimica et Cosmochimica Acta*, v. 53, p. 2961-2972.
- Heckel, P.H., 1977, Origin of phosphatic black shale facies in Pennsylvanian cyclothems of Midcontinent North America: *American Association of Petroleum Geologists Bulletin*, v. 61, p. 1045-1068.
- Heckel, P.H., 1984, Factors in mid-continent Pennsylvanian limestone deposition, in Hyne, N.J., ed., *Limestones of the Midcontinent: Tulsa Geological Society*, p. 25-50.
- Henrichs, J.I., and Doyle, A.P., 1986, Decomposition of ¹⁴C-labeled organic substrates in marine sediments: *Limnology and Oceanography*, v. 31, p. 765-778.
- Hite, R.J., and Anders, D.E., 1991, Petroleum and evaporites, in J.L. Melvin, ed., *Evaporites, Petroleum and Mineral Resources Elsevier, New York*, p. 349-411.
- Holzer, G., Oró, J., and Tornabene, T.G., 1979, GAs chromatographic-mass spectrometric analysis of neutral lipids from

- methanogenic and thermoacidophilic bacteria: *Journal of Chromatography*, v. 186, p. 795-809.
- Hoyt, J.H., 1962, Pennsylvanian and Lower Permian of northern Denver basin, Colorado, Wyoming and Nebraska: *American Association of Petroleum Geologists Bulletin*, v. 46, p. 46-59.
- _____, 1963, Permo-Pennsylvanian and lower Permian of the northern Denver basin, in Bolyard, D.W. and Katich, P.J., eds., *Geology of the northern Denver basin: Rocky Mountain Association of Geologists 14th Annual Field Conference Guidebook*, p. 68-83.
- Huang, W.Y., and Meinschein, W.G., 1979, Sterols as ecological indicators: *Geochimica et Cosmochimica Acta*, v. 43, p. 739-745.
- Hurley, J.P., and Armstrong, D.E., 1990, Fluxes and transformations of aquatic pigments in Lake Mendota, Wisconsin: *Limnology and Oceanography*, v. 35, no. 2, p. 384-398.
- Jenden, P.D., Newell, K.D., Kaplan, I.R., and Watney, W.L., 1988, Composition and stable-isotope geochemistry of natural gases from Kansas, Midcontinent, U.S.A.: *Chemical Geology*, v. 71, p. 117-147.
- Jiang, De-xin, 1988, Spores and pollen in oils as indicators of lacustrine source rocks, in Fleet, A.J., Kelts, K., and Talbot, M.R., eds., *Lacustrine petroleum source rocks: Geological Society Special Publication 40*, p. 159-169.
- Jorgensen, B .B., 1982, Ecology of the bacteria of the sulphur cycle with special reference to anoxic-oxic interface environments:

- Philosophical Transactions Royal Society of London B., v. 298, p. 543-561.
- Kepkay, P.E., Cooke, R.C., and Novitsky, J.A., 1979, Microbial autotrophy--A primary source of organic carbon in marine sediments: *Science*, v. 204, p. 68-69.
- Lang, W.B., 1937, The Permian Formation of the Pecos Valley of New Mexico and Texas: *American Association of Petroleum Geologists Bulletin*, v. 21, p. 833-898.
- de Leeuw, J.W., Sinnighe Damsté, J.S., Klok, J., Schenck, P.A., and Boon, J.J., 1985, Biochemistry of Gavish Sabkha sediments I., Studies on neutral reducing sugars and lipid moieties by gas chromatography-mass spectrometry, in Friedman, M., and Krumbein, W.E., eds., *Hypersaline ecosystems--The Gavish sabkha: Ecological Studies*, v. 53, p.3 50-367.
- Leventhal, J.S., 1983, An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition: *Geochimica et Cosmochimica Acta*, v. 47, p. 133-137.
- Lewan, M.D., 1983, Effects of thermal maturation on stable organic carbon isotopes as determined by hydrous pyrolysis of Woodford Shale: *Geochimica et Cosmochimica Acta*, v. 47, p. 1471-1479.

- Lewan, M.D., 1984, Factors controlling the proportionality of vanadium to nickel in crude oils: *Geochimica et Cosmochimica Acta*, v. 48, p. 2231-2238.
- Lewan, M.D., 1986, Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks: *Geochimica et Cosmochimica Acta*, v. 50, p. 1583-1591.
- Lewan, M.D., and Maynard, J.B., 1982, Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks: *Geochimica et Cosmochimica Acta*, v. 46, p. 2547-2560.
- MacLachlan, J. and Bieber, A., 1963, Permian and Pennsylvanian geology of the Hartville uplift-Alliance basin-Chadron Arch area: in Bolyard, D.W. and Katich, P.J., eds., *Geology of the northern Denver basin and adjacent uplifts*, Rocky Mountain Association of Geologists 14th Annual Field Conference Guidebook, p. 84-94.
- Mallory, W.W., 1958, Pennsylvanian coarse arkosic red beds and associated mountains in Colorado: in *Symposium on Pennsylvanian rocks of Colorado and adjacent areas*, Rocky Mountain Association of Geologists 14th Annual Field Conference Guidebook, p. 17-70.
- _____, 1960, Outline of Pennsylvanian stratigraphy of Colorado: in Weimer, R.J., and Haun, J.D., eds., *Guide to the geology of Colorado*: Rocky Mountain Association of Geologists, p. 23-33.

- _____. 1967, Pennsylvanian and associated rocks in Wyoming: U.S. Geological Survey Professional Paper 554-G, 31p.
- _____. 1972, Pennsylvanian arkose and the ancestral Rocky Mountains: in Mallory, W.W., ed., Geologic Atlas of the Rocky Mountain region: Rocky Mountain Association of Geologists, p. 131-132.
- Mason, B., 1965, Principles of Geochemistry: New York, John Wiley & Sons, Inc.
- Maughan, E.K., 1978, Pennsylvanian (Upper Carboniferous) System of Wyoming: U.S. Geological Survey Open-File Report 78-377. 32p.
- McKenzie, J.A., 1982, Carbon-13 cycle in Lake Greifen--A model for restricted ocean basin, in Schlanger, S.O., and Cita, M.B., eds., Nature and origin of Cretaceous carbon-rich facies: London, Academic Press, p. 145-175.
- McKirdy, D.M., Aldridge, A.K., and Ympa, P.J.M., 1983, A geochemical comparison of some crude oils from pre-Ordovician carbonate rocks, in Advances in organic geochemistry 1981: Chichester, John Wiley & Sons Ltd., p. 99-107.
- Meissner, F.F., Woodward, J., and Clayton, J.L., 1984, Stratigraphic relationships and distribution of source rocks in the greater Rocky Mountain Region, in Woodward, J., Meissner, F.F., Clayton, J. L., eds., Hydrocarbon source rocks of the greater Rocky Mountain region: Denver Rocky Mountain Association of Geologists, p. 1-34.

Mello, M.R., Telnaes, N., Gaglianone, P.C., Chicarelli, M.I., Brassell, S.C., and Maxwell, J.R., 1988, Organic geochemical characterisation of depositional palaeoenvironments of source rocks and oils in Brazilian marginal basins, in Mattavelli, L., and Novelli, L., eds., *Advances in organic geochemistry 1987: Organic Geochemistry*, v. 13, p. 31-45.

Michaelis, B., and Albrecht, P., 1979, Molecular fossils of archaeobacteria in kerogen. *Naturwissenschaften* 66, p. 420-422.

Moldowan, J.M., Seifert, W.K., and Gallegos, E.J., 1985, Relationship between petroleum composition and depositional environment of petroleum source rocks: *American Association of Petroleum Geologists Bulletin*, v. 69, p. 1255-1268.

Moldowan, J.M., Sundararaman, P., and Schoell, M., 1986, Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany, in Leythaeuser, D., and Rullkötter, J., eds., *Advances in organic geochemistry 1985: Organic Geochemistry*, v. 10, p. 915-926.

Momper, J.A., 1963, Nomenclature, lithofacies and genesis of Permian-Pennsylvanian rocks--northern Denver Basin, in Bolyard, D.W., and Katich, P.J., eds., *Geology of the northern Denver basin, Rocky Mountain Association of Geologists 14th Annual Field Conference Guidebook*, p. 41-67.

_____, 1966, Stratigraphic principles applied to the study of the Permian and Pennsylvanian systems in the Denver Basin:

Wyoming Geological Association 20th Annual Conference
Guidebook, p. 876-90.

- ____ 1978, Oil migration limitations suggested by geological and geochemical considerations, in Roberts, W.H., III, and Cordell, R.J., organizers, Physical and chemical constraints on petroleum migration: American Association of Petroleum Geologists Continuing Education Course Notes Series 8, p. B-1 to B-60.
- Momper, J.A., and Williams, J.A., 1979, Geochemical exploration in the Powder River Basin: Oil and Gas Journal, v. 77, p. 129-134.
- Moreth, C.M., and Yentsch, C.S., 1970, The role of chlorophyllase and light in the decomposition of chlorophyll from marine phytoplankton: Journal of Experimental Marine Biology and Ecology, v. 4, p. 2138-2149.
- Oana, S., and Deevey, E.S., 1960, Carbon-13 in lake waters and its possible bearing on paleolimnology: American Journal of Science, v. 258-A, p. 253-272.
- Orr, W.L., Emery, K.O., and Grady, J.R., 1958, Preservation of chlorophyll derivatives in sediments off southern California: American Association of Petroleum Geologists Bulletin, v. 42, p. 925-962.
- Orr, W.L., 1974, Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation--study of Big Horn Basin Paleozoic oils: American Association of Petroleum Geologists Bulletin, v. 58, p. 2295-2318.

- Park, R., and Epstein, S., 1960, Carbon isotope fractionation during photosynthesis: *Geochimica et Cosmochimica Acta*, v. 21, p. 110-126.
- Parrish, J.T., 1982, Upwelling and petroleum source beds, with reference to Paleozoic: *American Association of Petroleum Geologists Bulletin*, 66, p. 750-774.
- Parrish, J.T., and Curtis, R.L., 1982, Atmospheric circulation, upwelling, and organic-rich rocks in the Mesozoic and Cenozoic eras: *Palaeogeography Palaeoclimate Palaeoecology*, v. 40, p. 31-66.
- Pedersen, T.F., and Calvert, S.E., 1990, Anoxia vs. productivity--What controls the formation of organic-carbon-rich sediments and sedimentary rocks: *American Association of Petroleum Geologists Bulletin*, v. 74, p. 454-466.
- Pfenning, N., 1978, General physiology and ecology of photosynthetic bacteria, in R.K. Clayton and W.R. Sistrom, eds., *The photosynthetic bacteria*, p. 3-18, Plenum, New York.
- Philp, R.P., and Zhaoan, Fan, 1987, Geochemical investigation of oils and source rocks from Qianjiang Depression of Jiangnan Basin, a terrigenous saline basin, China: *Organic Geochemistry*, v. 11, p. 549-562.
- Rascoe, B., and Baars, D.L., 1972, Permian System: in Mallory, W.W., ed., *Geologic atlas of the Rocky Mountain region*, Rocky Mountain Association of Geologists, p. 143-165.

- Sackett, W.M., Eckelmann, W.R., Bender, M.L., and Be, A.W.H., 1965, Temperature dependence of carbon isotope composition in marine plankton and sediments: *Science*, v. 148, p. 235-237.
- Schoell, M., 1984, Stable isotopes in petroleum research, in Brooks, J., and Welte, D., eds.: *Advances in Petroleum Geochemistry 1*: London, Academic Press, p. 215-245.
- Schwark, L., and Püttman, W., 1990, Aromatic hydrocarbon composition of the Permian Kupferschiefer in the Lower Rhine Basin, NW Germany, in Durand, B., and Behar, F., eds., *Advances in organic geochemistry 1989: Organic Geochemistry*, v. 16, p. 749-761.
- Seifert, W.K., Moldowan, J.M., and Demaison, G.J., 1984, Source correlation of biodegraded oils, in Schenck, P.A., de Leuw, J.W., and Lijmbach, G.W.M., eds., *Advances in organic geochemistry 1983: Organic Geochemistry*, v. 6, p. 633-643.
- Sofer, A., 1987, Stable carbon isotope compositions of crude oils: application to source depositional environments and petroleum alteration: *American Association of Petroleum Geologists Bulletin*, v. 58, p. 1-49.
- SooHoo, J.B., and Kiefer, D.A., 1982, Vertical distribution of phaeopigments-I-A simple grazing and photooxidative scheme for small particles: *Deep Sea Research*, v. 29, p. 1539-1551.

- Spiker, E.C., and Hatcher, P.G., 1984, Carbon isotopic fractionation of sapropelic organic matter during early diagenesis: *Organic Geochemistry*, v. 5, p. 283-290.
- Spiro, B., and Aizenshtat, Z., 1977, Bacterial sulphate reduction and calcite precipitation in hypersaline deposition of bituminous shales: *Nature*, v. 269, p. 235-237.
- Stahl, W.J., 1977, Carbon and nitrogen isotopes in hydrocarbon research and exploration: *Chemical Geology*, v. 20, p. 121-149.
- Summons, R.E., and Powell, T.G., 1986, *Chlorobiaceae* in Paleozoic seas revealed by biological markers, isotopes and geology: *Nature*, v. 319, p. 763-765.
- Summons, R.E., and Powell, T.G., 1987, Identification of aryl isoprenoids in source rocks and crude oils -- Biological markers for the green sulfur bacteria: *Geochimica et Cosmochimica Acta*, v. 52, p. 557-566.
- Sweeney, R.E., 1972, Pyritization during diagenesis of marine sediments: Ph.D. thesis, University of California at Los Angeles, 184 pp.
- Takahashi, M., and Ichimura, S., 1968, Vertical distribution and organic matter production of photosynthetic sulfur bacteria in Japanese lakes: *Limnology and Oceanography*, v. 13, p. 644-655.
- Tissot, B., Durand, B., Espitalié, J., and Combaz, A., 1974, Influence of nature and diagenesis of organic matter in formation of

- petroleum: American Association of Petroleum Geologists Bulletin, v. 58, p. 499-506.
- Tissot, B., Pelet, R., Roucahe, J., and Combaz, A., 1977, Utilisation des alcanes comme fossiles géochimiques indicateurs des environnements géologiques, in Campos, R., and Goni, J., eds.: Advances in Organic Geochemistry 1975, Enadimsa, p. 117-154.
- Tissot, B.H., and Welte, D.H., 1984, Petroleum formation and occurrence. New York, Springer-Verlag, 699p.
- Tornabene, T.G., Langworthy, T.A., Holzer, G., and Oró, J., 1979, Squalenes, phytanes and other isoprenoids as major neutral lipids of methanogenic and thermoacidophilic 'Archaeobacteria': Journal of Molecular Evolution, v. 13, p. 73-83.
- Tornabene, T.G., Lloyd, R.E., Holzer, G., and Oró, J., 1980, Lipids as a principle for the identification of Archaeobacteria, in Holmquist, R., ed., GOSPAR, Life Sciences and Space Research, v. VIII: Oxford, Pergamon Press, p. 109-121.
- Tornabene, T.G., Wolfe, R.S., Balch, W.E., Holzer, G., Fox, G.E., and Oró, J., 1978, Phytanyl-glycerol ethers and squalenes in the Archaeobacterium Methanobacterium thermoautotrophicum: Journal of Molecular Evolution, v. 13, p. 73-83.
- Tourtelot, H.A., 1963, Preliminary investigation of the geologic setting and chemical composition of the Pierre Shale, Great Plains Region, U.S. Geological Survey Professional Paper 390, 74p.

- Tranter, C.E., and Petter, C.K., 1963, Lower Permian and Pennsylvanian stratigraphy of the Northern Rocky Mountains: Wyoming Geological Association-Billings Geological Society Joint Field Conference Guidebook, p. 45-53.
- Tromp, P.L., 1981, Stratigraphy and depositional environments of the "Leo Sands" of the Minnelusa Formation, Wyoming and South Dakota: Laramie, University of Wyoming, M.S. thesis, p.
- Tromp, P.L., Cardinal, D.F., and Steidtmann, J.R., 1981, Stratigraphy and depositional environments of the "Leo Sands" in the Minnelusa Formation, Wyoming and South Dakota: in Wyoming Geological Association Guidebook, 32nd Annual Field Conference, p. 11-21.
- Tuttle, M., Goldhaber, M.B., and Williamson, D.L., 1986, An analytical scheme for determining forms of sulphur in oil shales and associated rocks: *Talanta*, v. 33, p. 953-961.
- Van Berkel, G.J., Quirke, J.M.E.R., and Filby, R.H., 1989, The Henryville Bed of the New Albany shale--I, Preliminary characterization of the nickel and vanadyl porphyrins in the bitumen: *Organic Geochemistry*, v. 14, p. 119-128.
- Volkman, J.K., 1988, Biological marker compounds as indicators of the depositional environments of petroleum source rocks, in Fleet, A.J., Kelts, K., and Talbot, M.R., eds., *Lacustrine petroleum source rocks: Geological Society Special Publication 40*, p. 103-122.

- Waples, D. W., Haug, P., and Welte, D.H., 1974, Occurrence of a regular C_{25} isoprenoid hydrocarbon in Tertiary sediments representing a lagoonal, saline environment. *Geochimica et Cosmochimica Acta*, v. 38, p. 381-387.
- Weimer, R.J., 1978, Influence of transcontinental arch on Cretaceous marine sedimentation: a preliminary report: in Pruit, J.D., and Coffin, P.E., eds., *Energy Resources of the Denver Basin*, Rocky Mountain Association of Geologists, p. 211-222.
- Welte, D.H., and Waples, D.W., 1973, Über die Bevorzugung geradzahliger *n*-alkane in Sedimentgesteinen: *Naturwissenschaften*, v. 60, p. 516-5178.
- Wenger, L.M., and Baker, D.R., 1986, Variations in organic geochemistry of anoxic-oxic black shales-carbonate sequences in the Pennsylvanian of the Midcontinent, U.S.A., in Leythaeuser, D., and Rullkötter, eds., *Advances in organic geochemistry 1985: Organic Geochemistry*, v. 10, p. 85-92.
- Wenger, L.M., Baker, D.R., Chung, H.M., and McCulloh, T.H., 1988, Environmental control of carbon isotope variations in Pennsylvanian black shale sequences, Midcontinent, U.S.A., in Mattavelli, L., and Novelli, L., eds., *Advances in organic geochemistry 1987: Organic Geochemistry*, v. 13, p. 765-771.
- Wilson, J.M., 1978, Permo-Pennsylvanian of the west-central Nebraska panhandle, in Pruit, J.D., and Coffin, P.E., eds., *Energy*

resources of the Denver Basin: Denver Rocky Mountain
Association of Geologists, p. 129-140.

Wong, W.W., and Sackett, W.M., 1978, Fractionation of stable carbon
isotopes by marine phytoplankton: *Geochimica et
Cosmochimica Acta*, v. 42, p. 1809-1815.