Organic Geochemistry of Black Shales, Marlstones, and Oils of Middle Pennsylvanian Rocks from the Northern Denver and Southeastern Powder River Basins, Wyoming, Nebraska, and Colorado

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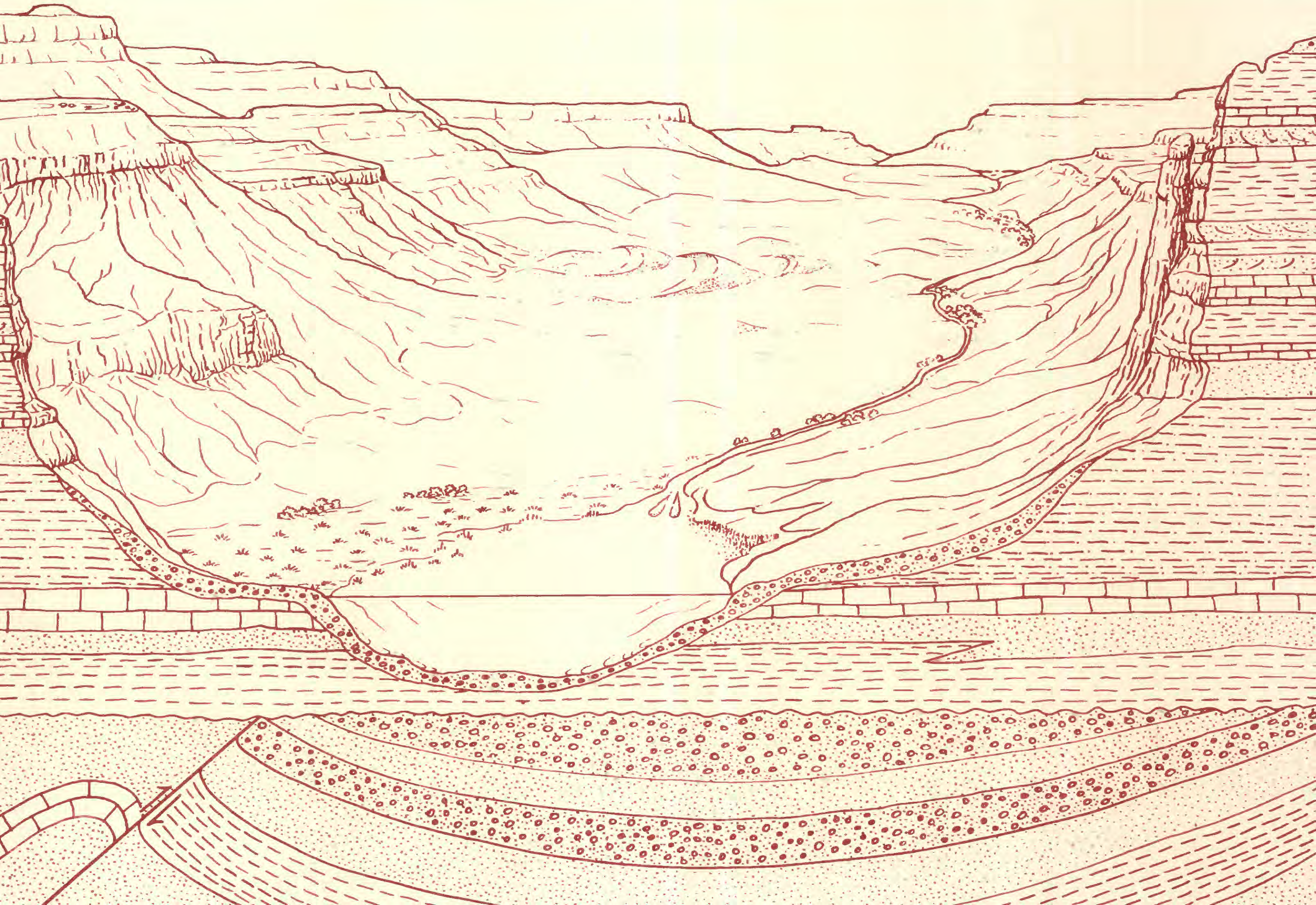

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Chapter K

Organic Geochemistry of Black Shales, Marlstones, and Oils of Middle Pennsylvanian Rocks from the Northern Denver and Southeastern Powder River Basins, Wyoming, Nebraska, and Colorado

By J.L. CLAYTON, A. WARDEN, T.A. DAWS, P.G. LILLIS,
G.E. MICHAEL, and M. DAWSON

A multidisciplinary approach to research studies of sedimentary
rocks and their constituents and the evolution of
sedimentary basins, both ancient and modern

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Organic Geochemistry of Black Shales, Marlstones, and Oils of Middle Pennsylvanian Rocks from the Northern Denver and Southeastern Powder River Basins, Wyoming, Nebraska, and Colorado

By J.L. Clayton, A. Warden, T.A. Daws, P.G. Lillis, G.E. Michael, *and* M. Dawson

Abstract

Organic-rich (C_{org}≤30 weight percent) black shales of Middle Pennsylvanian age (Desmoinesian and Missourian) are present in much of the west-central United States. Black shales (or marlstones) in the northern Denver and southeastern Powder River Basins of western Nebraska, northeastern Colorado, and eastern Wyoming were deposited in an embayment of the Midcontinent Pennsylvanian sea in which water salinity was possibly slightly above normal marine. In the epicontinental sea to the south, in Colorado, Kansas, and Oklahoma, shales were deposited under conditions of normal marine salinity.

On the basis of Rock-Eval pyrolysis, the bulk organic matter is type II–III. High porphyrin (as much as 40,000 ppm relative to bitumen), total sulfur (as much as 5 weight percent), farnesane, and aryl isoprenoid contents are characteristic of shales and marlstones deposited in the embayment. In the open-marine samples values for all of these parameters are lower. Stable carbon isotope ratios of saturated and aromatic hydrocarbons suggest a marine organic-matter source for the soluble organic matter in both areas. The isotopic composition of kerogen (C_{org}) in the rocks of about –24‰ to –29‰ indicates mixed sources of organic matter for the insoluble organic fraction. These geochemical features suggest that black shales of the southeastern Powder River and northern Denver Basins were deposited in a stratified water column caused by possibly 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 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 are also evident (low gammacerane contents and pristane to phytane ratios greater than 1.0). These data are interpreted to indicate that the organic geochemistry of rocks deposited in evaporite sequences is somewhat variable depending on the exact salinity conditions and the source of organic matter, particularly if allochthonous organic matter is present. The black shales and marlstones are part of an evaporite sequence, but the water salinity at the time of deposition may have been quite variable; it may have been normal marine at times. 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.

Oils produced from rocks of Pennsylvanian and Permian age (Minnelusa Formation) in the southeastern Powder River Basin contain very high porphyrin (as much as 489 ppm) and generally high sulfur (0.5–4.1 weight percent) contents. The highest porphyrin contents are in oils produced from the middle member of the Minnelusa Formation, although oils produced from the upper member also have high porphyrin contents compared to oils in general. Although no systematic relationship exists between porphyrin content and API gravity, sulfur content correlates directly with porphyrin content. The high porphyrin content of these oils suggests that the source rocks are the Desmoinesian- and Missourian-age (middle member of the Minnelusa Formation in the Powder River Basin) black shales and marlstones. Extracts of whole-core (uncrushed) samples of the organic-rich black shales and marlstones consist mostly of oil, rather than bitumen, that is distributed along primary migration routes (microfractures and bedding-plane partings) in the source rock. The bulk composition of these extracts is similar to that of oils produced from reservoirs, whereas the composition of bitumen obtained by extracting powdered source-rock samples is not.

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INTRODUCTION

Recently, considerable research has been directed toward improved applications of organic geochemistry in assessment of paleoenvironment (Brassell and others, 1987). Various multiparameter approaches have been used to interpret paleoenvironments based on analysis of rocks and crude oils (Moldowan and others, 1986; Brassell and others, 1987; Mello and others, 1988). Successful paleoenvironmental assessment of ancient rocks or crude oils requires an understanding of the link between the organic components of recent sediments and their diagenetic or catagenetic products in ancient sediments (Brassell and others, 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 was 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 approximately 0.4–0.6 percent). The strategy was to select a study area where the paleogeography is reasonably well known from geological and paleontological studies and to integrate paleogeography and organic geochemical and geological data. The primary objective of this study was to test the use of organic geochemical techniques for interpreting paleoenvironment during deposition of organic-rich rocks in a stratigraphically narrow interval (about 30–100 m thick) of Middle Pennsylvanian (Desmoinesian) 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 may have existed at times in the water column. For comparative purposes, a few samples of Desmoinesian-age organic-rich rocks from Kansas, Missouri, and Oklahoma were included in the study.

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

The second major objective of this study was to determine porphyrin contents of oils produced from Pennsylvanian- and Permian-age rocks (Minnelusa Formation and stratigraphic equivalents) in the northern Denver and southeastern Powder River Basins. Further, because previous extraction of powdered samples of potential source rocks (Desmoinesian and Missourian) has yielded inconclusive correlations with the oils (Clayton and Ryder, 1984), we used a new technique of extracting whole-core (uncrushed) rock samples in an attempt to extract the oil phase that is actually undergoing primary migration and is a separate phase from the bitumen, which is associated mainly with kerogen in the rock.

Acknowledgments.—Bird Oil Corporation, Conoco Inc., Hunt Oil, and Mitchell Energy provided samples. Analytical work by P.H. Briggs and J.D. King is gratefully acknowledged. The paper was significantly improved by reviews by D. Anders, M. Lewan, and J. Palacas and discussions with F.F. Meissner.

GEOLOGIC SETTING

During Middle Pennsylvanian time (Desmoinesian) (about 310 Ma), the area of the present-day northern Denver Basin and southeastern Powder River Basin (fig. 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 was 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 reports discuss the Pennsylvanian stratigraphy and tectonics of the northern Denver Basin and southeastern Powder River Basin in detail (Agatston, 1954; Bates, 1955; Foster, 1958; Mallory, 1958, 1960, 1967, 1972; Hoyt, 1962, 1963; MacLachlan and Bieber, 1963; Momper, 1963; Tranter and Petter, 1963; Rascoe and Baars, 1972; Wilson, 1978; Tromp, 1981; Tromp and others, 1981; Cardinal and Holmes, 1984; Desmond and others, 1984), and only a brief summary is given here.

The stratigraphy of Mississippian through Permian rocks in the northern Denver Basin and southeastern Powder River Basin is given in figure 2*A*. The top of the Pennsylvanian is at the Red shale marker (Foster, 1958; Mallory, 1967; Maughan, 1978; Cardinal and Holmes, 1984), a distinctive red Shale and mudstone unit. Rocks of Atokan through Missourian age consist predominantly of shallow-marine carbonate rocks, anhydrite, chert, sandstone, shale, and marlstone (Cardinal and Holmes, 1984).

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 Basin and southeastern Powder River Basin. Tromp (1981) reported that these rocks contain 40–60 percent quartz, a few to 50 percent dolomite, generally less than 10 percent illite, and as much as 10 percent 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 our study. The high magnesium values

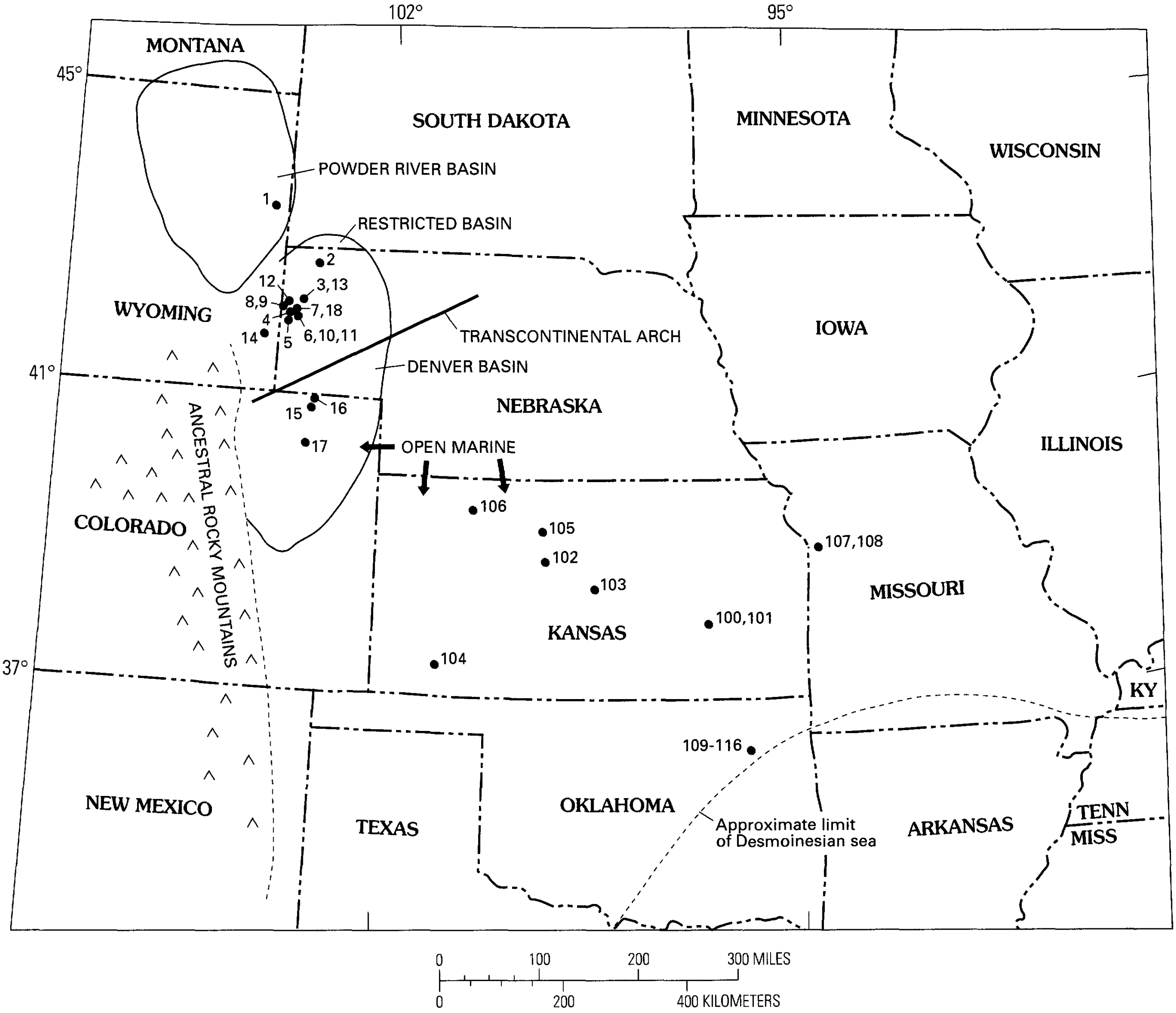


Figure 1. Paleogeography of west-central United States during deposition of Desmoinesian cyclothems during regressive episode. Numbers refer to well (1–17) and sample (100–116) locations in table 2.

suggest that dolomite is an important constituent of the carbonate mineral fraction. We determined total carbonate carbon separately for five samples (samples 60, 61, 63–65, table 1), then calculated the amount of CaO and MgO required to account for the measured carbonate carbon. Except for one sample (sample 65), the carbonate carbon values determined directly are very similar to the calculated values. In other words, essentially all of the MgO and CaO must be present as carbonate minerals. We then determined carbonate content for all of the other samples, assuming that all of the CaO and MgO is present as carbonate minerals (last column of table 1). We did not consider the possibility of siderite as a significant constituent because the generally high sulfur values suggest that most of the iron is present as iron sulfide minerals. In many cases, the amount of sulfur in these rocks is close to or in excess of the stoichiometric requirement for FeS_2 or FeS, and therefore very little iron was 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 are 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 Basin and southeastern Powder River Basin are incomplete and in some cases are apparently separated by periods of erosion or nondeposition (Momper, 1966; Cardinal and Holmes, 1984).

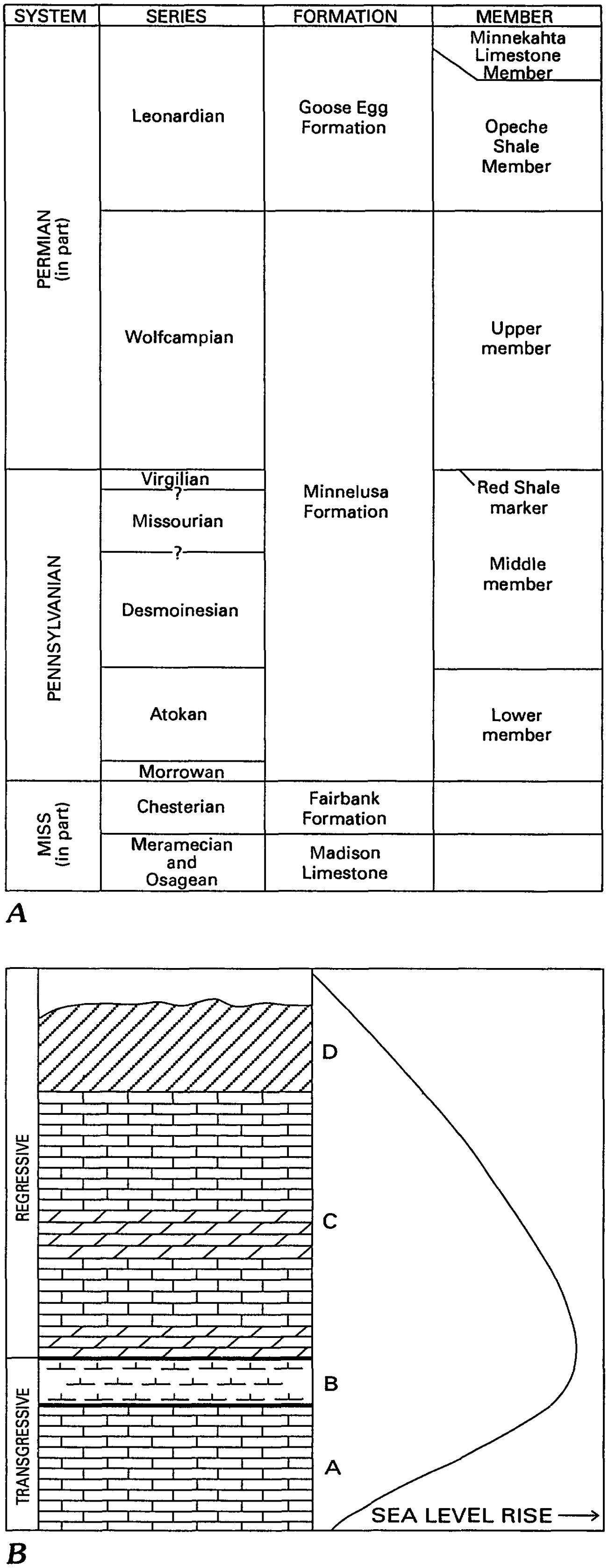


Figure 2 (facing column). *A*, Stratigraphy of late Paleozoic rocks in the northern Denver Basin and southeastern Powder River Basin. *B*, Generalized sequence of rock types in a typical cyclothem sequence in the northern Denver Basin (western Nebraska) and relation to sea level. A, subtidal marine limestone; B, subtidal and intertidal black shale and marlstone; C, limestone, dolomite, and anhydrite; D, anhydrite. Modified from Doyle (1987).

The total thickness of Desmoinesian rocks in this area is about 30–100 m (Wilson, 1978; Doyle, 1987). In a typical idealized cycle of Desmoinesian or Missourian rocks of the Nebraska Panhandle (fig. 2*B*), organic-rich black shales and marlstones are overlain by a regressive series of carbonate rock types and anhydrite is at the top of the cycle. As many as nine cyclothems containing organic-rich black shales or marlstones have been identified in the study area.

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 Paleozoic time (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 (Hoyt, 1963; Momper, 1963; Weimer, 1978; Wilson, 1978; Cardinal and Holmes, 1984) and may have affected Mesozoic sedimentation (Weimer, 1978). Cardinal and Holmes (1984) suggested that the Transcontinental Arch caused nondeposition and erosion over a large part 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.

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

Nevertheless, the presence of evaporite rocks (carbonate-anhydrite sequences) indicates that oceanic circulation was restricted during Desmoinesian and Missourian time. According to Doyle (1987) and Desmond and others (1984), most of the black shales or marlstones in western Nebraska and eastern Wyoming are subtidal deposits; supratidal, sabkha, and eolian deposits are along the margins

Table 1. Elemental analysis of selected black shale and marlstone samples of Desmoinesian and Missourian age, northern Denver Basin and southeastern Powder River Basin

[Values are in weight percent of the whole rock. Locations of wells shown by numbers in figure 1. Leader (–), not determined]

Sample	SiO_2[1]	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	S[2]	OM[3]	Carbonate[4]
2. Mitchell 34–12 Seegrist, sec. 12, T. 33 N., R. 52 W., Dawes County, Nebraska												
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. 27 N., R. 54 W., Sioux County, Nebraska												
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	0.54	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. 24 N., R. 56 W., Sioux County, Nebraska												
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. 25 N., R. 56 W., Sioux County, Nebraska												
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
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	–	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	–	1.7	54
9. Conoco 35–1 Duncan, sec. 35, T. 25 N., R. 57 W., Sioux County, Nebraska												
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	–	20.2	28 (36)
15. Sun M. Segelke 1, sec. 26, T. 11 N., R. 53 W., Logan County, Colorado												
91	47.4	8.5	4.0	6.5	8.1	0.42	3.5	0.32	0.43	2.2	9.2	26
17. Hunt 1–33 Brunkhardt, sec. 33, T. 5 N., R. 54 W., Washington County, Colorado												
93	41.0	11.5	3.5	3.7	12.5	0.61	3.5	0.38	0.70	1.5	9.3	31
Average shale[5]		15.5	2.5	2.5	3.1	1.3	3.3	0.65	0.17	0.82	–	–
Average shale[6]		15.4	2.5	2.4	3.1	1.3	3.2	0.65	0.17	–	–	–
Average limestone[6]		0.81	–	7.9	42.6	0.05	0.33	0.06	0.04	–	–	–
Example marlstone[7]		9.8	–	2.0	21.7	0.64	2.2	0.37	0.23	0.19	<0.5	–

[1] SiO_2 determined by difference; not available for last four samples.

[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. Value in parentheses is separate carbonate determination based on carbonate carbon content determined by acid digestion of the rock.

[5] Clarke (1915).

[6] Mason (1965).

[7] Of Cretaceous age (Pierre Shale) (Tourtelot, 1962).

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 deposition of black shales in the Nebraska Panhandle during Desmoinesian time (Doyle, 1987).

The high carbonate content of these black shales and marlstones and the absence of fossils (Desmond and others, 1984) are consistent with, but do not prove, that salinities were above normal during deposition. Anhydrite nodules common in many of the shale and marlstone beds are probably mostly secondary in origin, although petrographic work by D. Masse (oral commun., 1991) indicates that some primary anhydrite is present. The geological and geochemical data presently available are insufficient to derive any unequivocal conclusions about water salinities during the deposition of organic-rich black shales and marlstones. We believe that salinities probably were greater than 35‰ (normal marine) at times, especially during deposition of the upper part of individual marlstone beds that are overlain by evaporite lithologies. This hypothesis is supported by the limited occurrence of primary anhydrite in the marlstones as noted above. Accordingly, the organic geochemical data obtained from analysis of the organic-rich black shales and marlstones are interpreted in subsequent sections of this report in the context of an evaporite *sequence*, although individual shale or marlstone beds may have been deposited under a wide range of water salinities, including normal marine at times.

In contrast, black shales in northeastern Colorado and the Midcontinent region were probably deposited in a shallow-marine environment with normal marine salinities (Heckel, 1977). Heckel (1977, 1980, 1984) concluded that the black shales of the Midcontinent cyclothems 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 at water depths of about 50–100 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 as a "restricted-basin." The term "restricted basin" is meant to imply that water circulation was restricted on the shelf area (Lusk Embayment), but it does not necessarily require a topographic barrier, or sill, as the restricting mechanism, as discussed above.

An alternative model for cyclothemic deposits was recently 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 during periods of greater rainfall. During times of continually wet conditions, chemically precipitated rocks likely include 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. This model of paleoclimatic control has not yet been tested for cyclothems of the western United States.

SAMPLING AND ANALYTICAL METHODS

The locations of wells from which samples were used in this study are shown in figure 1. Only subsurface core samples were used except for the Hunt 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 or marlstone beds. In the present paper, rocks in the restricted-basin setting and adjacent open-marine setting in northeastern Colorado are the main focus. Samples of rocks of equivalent age were collected from the open-marine environment of Kansas Missouri, and Oklahoma for comparison of certain geochemical parameters (table 2). Samples 100–108 were analyzed by Hatch and others (1989) and G.A. Desborough, J.R. Hatch, and J.S. Leventhal (U.S. Geological Survey, unpub. data, 1991); samples 109–116 were analyzed by Wenger and Baker (1986).

The thermal maturity of the Desmoinesian and Missourian interval is about the same throughout the study area. Vitrinite reflectance (percent R_o), 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, and 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). Geochemical differences between samples primarily reflect variations 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 sulfur. C_{org} contents were determined for 101 samples using a Delsi Model II Rock-Eval instrument equipped with a C_{org} module. Sulfur contents were determined for selected samples using a Leco sulfur analyzer.

Sulfur content of oils was determined by combustion of the oil in a Parr bomb followed by precipitation of the sulfur as $BaSO_4$. The $BaSO_4$ precipitates were washed, filtered, and dried before gravimetric determination of the amount of $BaSO_4$. The sulfur values obtained using this method are reported to three significant figures, whereas values obtained using the Leco combustion technique are less precise and are reported only to two significant figures.

Based on the pyrolysis assay, 59 samples were selected for extraction. Bitumen was obtained by extraction for 24 hr 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 (the bitumen remaining after removal of asphaltenes) was taken to dryness using a rotary evaporator. Nickel porphyrins (NiP) and vanadyl porphyrins (VOP) were isolated using column chromatography (250-µm macroporous silica gel) by successive elution with 0.35 percent ethyl acetate in cyclohexane and 8.0 percent ethyl acetate in cyclohexane (Freeman and others, 1987). Quantitation of the porphyrin fractions was accomplished using an HP8542 ultraviolet/visible diode array. Porphyrin analysis of oils was accomplished by weighing approximately 100 mg of oil and removing saturated and aromatic hydrocarbons by

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. Leader (–), not determined; slash (/), duplicate analysis]

Sample number	Sample depth	C_{org}[1]	EOM[2]	SAT. HC[3]	S/A[4]	Pr/Ph[5]	Pr/nC_{17}	NiP[6]	VOP[7]	V/V+Ni[8]	S_T[9]	C_{org}/S_T	S_1[10]	S_2[11]	HI[12]	T_{max}
RESTRICTED-BASIN SAMPLES																
1. Shell 31–16, sec. 16, T. 42 N., R. 62 W., Westin County, 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	427
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	591	435
2. Mitchell 34–12 Seegrist, sec. 12, T. 33 N., R. 52 W., Dawes County, Nebraska																
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	1,394.72	10.4	9,893	–	–	–	–	293	30,620	0.99	–	–	3.1	36.4	349	435
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	1.05	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. 27 N., R. 54 W., Sioux County, Nebraska																
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. 18, T. 24 N., R. 56 W., Sioux County, Nebraska																
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	2.9	2.6	2.4	36.5	484	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	–

Table 2. Organic geochemical data for rocks, northern Denver Basin and southeastern Powder River Basin—Continued

Sample number	Sample depth	C_{org}[1]	EOM[2]	SAT. HC[3]	S/A[4]	Pr/Ph[5]	Pr/nC$_{17}$	NiP[6]	VOP[7]	V/V+Ni[8]	S_T[9]	C_{org}/S_T	S_1[10]	S_2[11]	HI[12]	T_{max}
5. Bird 2–3 Laucomer, sec. 5, T. 24 N., R. 55 W., Sioux County, Nebraska																
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	2,260	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
35	2,271	8.1	7,925	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. 25 N., R. 55 W., Sioux County, Nebraska																
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
7. Bird 11–16 Corman, sec. 11, T. 25 N., R. 56 W., Sioux County, Nebraska																
47	2,350.9	6.7	–	–	–	–	–	–		0.99	2.3	2.9	1.1	29.5	441	438
48	2,351.2	10.2	–	–	–	–	–	T	18,309	1.00	2.3	4.4	2.1	52.1	508	433
49	2,351.5	5.6	5,364	825	0.4	1.26	0.68	50	18,723	1.00	1.4	4.0	1.8	22.7	405	437
50	2,351.8	5.6	4,645	360	0.2	1.16	0.61	–	–	–	2.2	2.5	1.8	38.3	690	435
51	2,364.0	30.4	8,783	1,123	0.2	1.25	0.29	259	29,147	0.99	2.5	12.2	5.2	92.3	303	431
52	2,364.3	17.9	–	–	–	–	–	–	–	–	–	–	4.8	87.9	492	431
53	2,367	12.7	4,445	387	0.2	1.17	0.37	270	35,327	0.99	3.8	3.3	2.3	60.7	479	433
54	2,376.5	10.0	–	–		–	–	–	–	–	–	–	2.2	34.8	348	432
55	2,376.8	18.6	11,084	1,206	0.2	–	–	9	21,267	1.00	4.1	4.5	4.8	80.9	435	428
56	2,385.4	11.3	6,622	305	0.1	1.00	0.80	409	33,737	0.99	3.0	3.8	2.4	49.3	437	432
57	2,385.6	1.5	–	–	–	–	–	–	–	–	–	–	1.9	2.5	169	437
8. Conoco 23–1 Perkins, sec. 23, T. 25 N., R. 57 W., Sioux County, Nebraska																
58	2,461	6.2	2,100	400	0.6	–	–	T	4,364	1.00	3.1	2.0	1.1	26.0	416	446
59	2,462	0.8	1,200	700	2.3	–	–	–	–	–	–	–	0.8	0.6	82	430
9. Conoco 35–1 Duncan, sec. 35, T. 25 N., R. 57 W.), Sioux County, Nebraska																
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. 25 N., R. 55 W., Sioux County, Nebraska																
66	2,129	10.3	–	–	–	–	–	–	–	–	–	–	1.4	62.2	605	436
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. 26 N., R. 56 W., Sioux County, Nebraska																
72	2,378	10.0	10,700	–	–	–	–	442	31,326	0.99	3.1	3.2	1.8	32.8	328	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. 27 N., R. 54 W., Sioux County, Nebraska																
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. 25 N., R. 56 W., Sioux County, Nebraska																
81	2,360	21.5	25,300	–	–	–	–	981	32,648	0.97	3.9	5.5	5.0	106.9	496	428
14. GAO Hawk Fee 1–35, sec. 35, T. 21 N., R. 62 W., Goshen County, Wyoming																
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
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																
15. Sun M. Segelke 1, sec. 26, T. 11 N., R. 53 W., Logan County, Colorado																
89	2,304.5	3.3	–	–	–	–	–	–	–	–	0.3	11.0	1.5	8.9	274	443
90	2,304.8	10.1	–	–	–	–	–	–	–	–	–	–	3.2	38.2	378	440
91	2,306	8.3	–	–	–	–	–	–	–	–	2.2	3.8	2.0	31.5	381	443
16. Sun Roelle 1, sec. 24, T. 12 N., R. 53 W., Logan County, Colorado																
92	2,272	5.8		–	–	–	–	–	–	–	0.7	8.3	1.9	22.4	382	439
17. Hunt 1–33 Brunkhardt, sec. 33, T. 5 N., R. 54 W., Washington County, Colorado																
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	474	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

Table 2. Organic geochemical data for rocks, northern Denver Basin and southeastern Powder River Basin—Continued

Sample number	Sample depth	C_{org}[1]	EOM[2]	SAT. HC[3]	S/A[4]	Pr/Ph[5]	Pr/nC_{17}	NiP[6]	VOP[7]	V/V+Ni[8]	S_T[9]	C_{org}/S_T	S_1[10]	S_2[11]	HI[12]	T_{max}
MISCELLANEOUS CORES AND OUTCROPS FROM KANSAS, MISSOURI, AND OKLAHOMA																
100[13]	637	21.6	6,300	–	–	–	1.7	202	436	0.68	–	–	–	64	280	440
101[13]	678	14.9	3,800	–	–	–	1.9	18	448	0.96	–	–	–	41	260	449
102[13]	964	8.2	3,850	–	–	–	–	959	4,774	0.83	1.0	8.2	–	–	–	330
103[13]	889	12.8	7,720	–	–	–	–	381	4,141	0.92	2.2	5.8	–	–	–	340
104[13]	1,382	11.1	6,120	–	–	–	–	–	776	–	2.2	5.0	–	–	–	360
105[13]	1,004	10.0	8,190	–	–	–	–	1,215	2,790	0.70	1.8	5.6	–	–	–	–
106[13]	1,130	6.9	3,640	–	–	–	–	2,209	584	0.21	–	–	–	–	–	270
107[13]	Outcrop	15.4	6,250	–	–	–	–	328	1,314	0.80	–	–	–	–	–	438
108[13]	Outcrop	13.2	5,700	–	–	–	–	781	2,374	0.75	–	–	–	–	–	360
109[14]	Not known	16.9	–	–	–	–	–	–	181	–	3.7	4.6	–	–	–	–
110[14]	Not known	9.95	–	–	–	–	–	–	339	–	1.5	6.6	–	–	–	–
111[14]	Not known	18.3	–	–	–	–	–	–	609	–	2.6	7.0	–	–	–	–
112[14]	Not known	13.1	–	–	–	–	–	–	580	–	1.8	7.3	–	–	–	–
113[14]	Not known	16.6	–	–	–	–	–	–	1,232	–	1.2	13.8	–	–	–	–
114[14]	Not known	20.1	–	–	–	–	–	–	1,141	–	–	–	–	–	–	–
115[14]	Not known	15.7	–	–	–	–	–	–	993	–	2.6	6.0	–	–	–	–
116[14]	Not known	9.15	–	–	–	–	–	–	815	–	–	–	–	–	–	–

[1] Weight percent organic carbon.

[2] Chloroform-extractable organic matter (parts per million relative to dry rock weight).

[3] C_{15}+ saturated hydrocarbons (parts per million relative to dry rock weight).

[4] Saturated to aromatic hydrocarbon ratio.

[5] Pristane to phytane ratio.

[6] Nickel porphyrins (parts per million relative to extractable organic matter).

[7] Vanadium porphyrins (parts per million relative to extractable organic matter).

[8] Ratio of VOP/NiP+VOP.

[9] Total sulfur from Leco combustion.

[10] S_1 from Rock-Eval pyrolysis (mg/g rock).

[11] S_2 from Rock-Eval pyrolysis (mg/g rock).

[12] Temperature of maximum pyrolysis yield (°C).

[13] Data from Hatch and others (1989) and G.A. Desborough, J.R. Hatch, and J.S. Leventhal (U.S. Geological Survey, unpub. data, 1991); S_1+S_2 yields are combined.

[14] Data from Wenger and Baker (1986).

eluting approximately 20 mL of toluene using an alumina column. The residual oil containing porphyrins and other nonhydrocarbons was analyzed using the diode array detector above. 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 N_2 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 HP5880A gas chromatograph equipped with a 50 m by 0.32 mm SE54 fused silica capillary column. The gas chromatograph was programmed from 50°C to 320°C at 4°C per minute using hydrogen as the carrier gas. The detector output was digitized and stored on computer disk using the Nelson chromatography software.

Gas chromatography–mass spectrometry (GC–MS) analysis was performed using the gas chromatograph described above coupled to a Kratos MS30 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.

Stable 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 hr. The CO_2 formed was collected and purified using a cryogenic vacuum line. Carbonate carbon was collected as CO_2 by digestion of the samples in 100 percent anhydrous phosphoric acid at 25°C. The CO_2 generated by acid digestion was collected according to the procedure described above.

Carbon isotope ratios of the CO_2 collected above were measured using a Finnigan MAT251, 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),

$$\delta^{13}C(‰)=[(R_{sample}/PDB)-1]\times10^3,$$
$$R={}^{13}C/{}^{12}C.$$

Isotope ratios are reproducible within 0.5‰. Duplicates of several samples were analyzed (including duplicate CO_2 preparation) to monitor reproducibility. $\delta^{13}C$ values of kerogen and carbonate carbon are reproducible within 0.13‰ and 0.85‰, respectively.

Total sulfur was separated into various forms (pyrite, anhydrite, acid-volatile, organic) using the method of Tuttle and others (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 multiacid digestion (with HCl, HF, $HClO_3$, and HNO_3, successively). The solution was dried and redissolved in 1.0 mL aqua regia and diluted to 10.0 g with 1.0 percent HNO_3. 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. SiO_2 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 settings 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} contents are all less than about 2.0 weight percent (Clayton and Ryder, 1984). Between individual black shale units at any given location, the C_{org} content varies somewhat, 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 environments, 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 shales is 0.3–5.0 weight percent; most values are between 2 and 4.5 percent (table 2). C/S ratios (C_{org}/S_T) of restricted-basin samples (average 3.7) are generally lower than those of open-marine samples (average 6.5) (fig. 3). 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~3) (Berner, 1970; Sweeney, 1972; Goldhaber and Kaplan, 1974; Leventhal, 1983), whereas the open-marine samples generally have higher ratios.

Total sulfur content of the oils is about 0.5–4.11 weight percent, in the same range as Paleozoic oils from the Big Horn Basin (Orr, 1974). In general, increasing sulfur content correlates inversely with API gravity (R^2=0.74) (table 3).

Whole-rock iron content correlates weakly with total sulfur content (fig. 4). 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 we did not determine the degree of pyritization (DOP), 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 samples from 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. 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 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 (fig. 5) (Tissot and others, 1974; Espitalié and others, 1977). Rocks from the margins of the seaway and the sill 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, unpub. data) and predominantly type III organic matter.

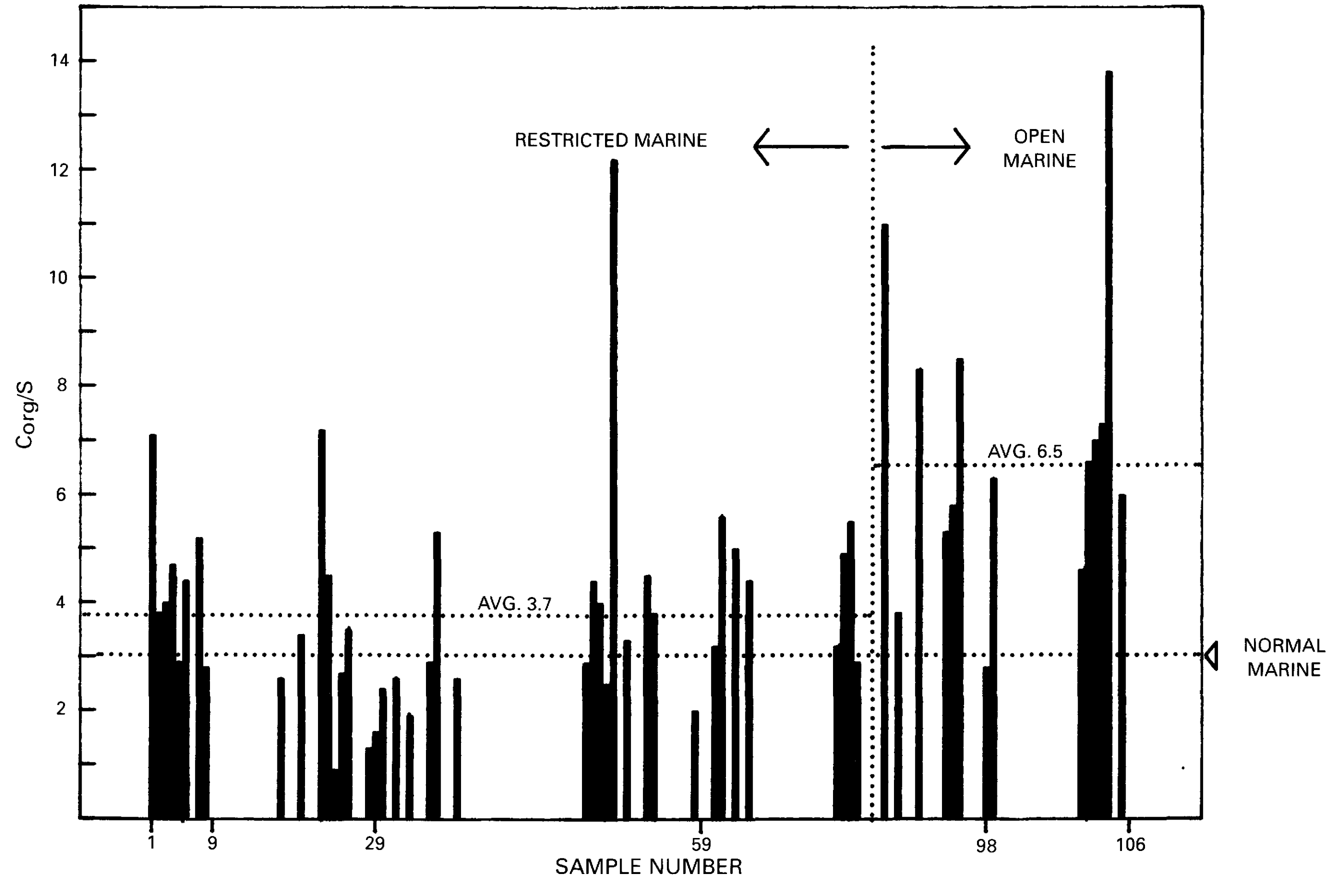


Figure 3. C_{org} to sulfur ratios for rock samples in study. C_{org} to sulfur ratio for normal marine sediments is about 3 (Berner, 1970; Sweeney, 1972; Goldhaber and Kaplan, 1974, Leventhal, 1983). See table 2 and figure 1 for sample locations.

Table 3. API gravity and sulfur and porphyrin content of oils produced from the Minnelusa Formation and equivalent-age rocks, northern Denver Basin and southeastern Powder River Basin

[Depth of producing interval given in meters in parentheses. VOP, vanadyl porphyrin, in parts per millions; NiP, nickel porphyrins, in parts per million; T, trace amount; leader (–), not determined. Unless otherwise noted all oils produced from Minnelusa Formation. Duplicate values for samples 1, 2, and 3 are replicate determinations including sample preparation]

Sample number and well name	Location (county, state)	Field name	Producing interval	API gravity	Sulfur (percent)	VOP	NiP	VOP/ (VOP+NiP)
1. Government Meng 1	Sec. 25, T. 38 N., R. 62 W. (Niobrara, Wyoming)	Red Bird	Ming sandstone, middle member (945)	32	1.74	349 338	34 35	0.91 0.91
2. Pfister Fee	Sec. 25, T. 38 N., R. 62 W. (Niobrara, Wyoming)	Red Bird	1st Leo sandstone, middle member (1,006)	29	2.01 2.06	451	38	0.92
3. 3–16 State	Sec. 16, T. 12 S., R. 1 E. (Fall River, South Dakota)	Indian Creek	2nd Leo sandstone, middle member (1,115–1,117)	38	1.17	217 228	17 7	0.93 0.97
4. 33–5	Sec. 5, T.36N., R. 63 W. (Niobrara, Wyoming)	Leimser	2nd Leo sandstone, middle member (1,993–2,000)	36	0.52	15	2	0.91
5. 42–18 Federal A	Sec. 18, T. 36 N., R. 63 W. (Niobrara, Wyoming)	Buck Creek	1st Leo sandstone, middle member (1,876–1,884)	38	0.79	14	2	0.87
6. Federal 1	Sec. 15, T. 35 N., R. 63 W. (Niobrara, Wyoming)	Pine Lodge	1st Leo sandstone, middle member (809-810)	22	1.28	–	–	–
7. 12–19 Pfister	Sec. 19, T. 38 N., R. 61 W. (Niobrara, Wyoming)	Red Bird	3rd Leo sandstone, middle member (1,041)	30	–	353	19	0.95
8. Raven Creek Unit 12–11	Sec. 11, T. 48 N., R. 69 W. (Campbell, Wyoming	Raven Creek	A sandstone, upper member (2,546–2,553)	34	1.04	21	7	0.76
9. Bishop 1–8	Sec. 8, T. 47 N., R. 69 W. (Campbell, Wyoming)	Dillinger	A sandstone, upper member (2,767–2,778)	37	0.85	3	1	–
10. A. Breen 14–12A	Sec. 12, T. 47 N., R. 72 W. (Campbell, Wyoming)	Breen	Upper member (3,269–3,275)	30	–	21	3	0.88
11. Rule Federal 41–17	Sec. 17, T. 52 N., R. 68 W. (Crook, Wyoming)	Semlek	B sandstone, upper member (2,180)	35	–	104	2	0.98
12. Not available	T. 54 N., R. 71 W. (Campbell, Wyoming)	Camp Creek	Camp Creek sandstone, upper member (~2,256)	23	2.73	97	18	0.85
13. Dunlap 2–6	Sec. 6, T. 47 N., R. 71 W. (Campbell, Wyoming)	Breen	Upper member (~3,165)	37	–	8	2	0.78
14. LeSeur 1	Sec. 17, T. 49 N., R. 70 W. (Campbell, Wyoming)	Timber Creek	Upper member (~2,857)	32	1.29	8	3	0.82
15. (W4–60)	Sec. 17, T. 49 N., R. 70 W. (Campbell, Wyoming)	Timber Creek	A dolomite, upper member (2,854)	25	1.29	12	2	0.86

Table 3. API gravity and sulfur and porphyrin content of oils produced from the Minnelusa Formation and equivalent-age rocks, northern Denver Basin and southeastern Powder River Basin—Continued

Sample number and well name	Location (county, state)	Field name	Producing interval	API gravity	Sulfur (percent)	VOP	NiP	VOP/ (VOP+NiP)
16. 1 Pownall Ranch	Sec. 7, T. 53 N., R. 70 W. (Campbell, Wyoming)	Pownall Ranch	B sandstone, upper member (2,225–2,227; 2,218–2,222)	25	–	32	4	0.89
17. Simpson 24–12	Sec. 12, T. 51 N., R. 69 W. (Campbell, Wyoming)	Simpson	B sandstone, upper member (~2,317)	20	3.4	158	14	0.92
18. Wolff Federal 31–28	Sec. 28, T. 49 N., R. 71 W. (Campbell, Wyoming)	T.A. Buttes	A sandstone, upper member (~3,085)	21	–	57	14	0.80
19. Hayden 5–28	Sec. 28, T. 47 N., R. 71 W. (Campbell, Wyoming)	Maysdorf South	A sandstone, upper member (~3,232)	37	–	45	7	0.86
20. Fowler 3–5	Sec. 5, T. 54 N., R. 67 W. (Crook, Wyoming)	Fowler	Upper member (1,703–1,709)	20	–	206	9	0.96
21. Burrows B–16	Sec. 8, T. 49 N., R. 68 W. (Crook, Wyoming)	Donkey Creek	Upper member (~3,049)	34	–	24	T	–
22. Not available	T. 51 N., R. 70 W. (Campbell, Wyoming)	Keuhne Ranch	Upper member (~2,430)	26	2.14	63	5	0.93
23. Not available	T. 45 N., R. 80 W. (Campbell, Wyoming)	Pheasant	C sand and D dolomite, upper member (~ 4,580)	35	0.94	T	T	–
24. Not available	T. 51 N., R. 71 W. (Campbell, Wyoming)	Springer Ranch	Upper member (~2,284)	32	1.33	53	5	0.91
25. 21–1	Sec. 21, T. 45 N., R. 79 W. (Johnson, Wyoming)	Reno East	D dolomite, upper member (4,573)	36	0.84	T	T	–
26. Not available	Sec. 19, T. 50 N., R. 69 W. (Campbell, Wyoming)	East Rozet	Upper member (~2,114)	21	3.07	89	9	0.91
27. 11–162X Corman	Sec. 11, T. 25 N., R. 56 W. (Sioux, Nebraska)	Spotted Tail	Late Pennsylvanian (Missourian-Virgilian) (equiv. to upper member) (2,317–2,330)	33	~0.5	45	5	0.90
28. Morel 1–17	Sec. 17, T. 53 N., R. 68 W. (Crook, Wyoming)	Morel	Upper member (2,112–2,117)	25	–	102	11	0.91
29. 12X–19A	Sec. 19, T. 45 N., R. 79 W. (Johnson, Wyoming)	Reno	C sandstone, upper member (4,630–4,639)	38	0.82	19	T	–
30. Not available	T. 25 N., R. 56 W. (Crook, Wyoming)	Mellot Ranch	A and B sandstone, upper member (~2,070)	21	3.64	179	18	0.91

Table 3. API gravity and sulfur and porphyrin content of oils produced from the Minnelusa Formation and equivalent-age rocks, northern Denver Basin and southeastern Powder River Basin—Continued

Sample number and well name	Location (county, state)	Field name	Producing interval	API gravity	Sulfur (percent)	VOP	NiP	VOP/ (VOP+NiP)
31. Not available	T. 48 N., R. 71 W. (Campbell, Wyoming)	Rainbow Ranch	Upper member (~3,050)	25	1.67	20	T	–
32. Not available	T. 51 N., R. 68 W. (Crook, Wyoming)	Prong Creek	Upper member (~1,950)	19	4.11	222	16	0.93
33. Not available	Sec. 6, T. 49 N., R. 69 W. (Campbell, Wyoming)	Halverson Ranch	Upper member (~2,600)	21	2.63	73	9	0.89
34. Not available	Sec. 14, T. 2 N., R. 69 W. (Campbell, Wyoming)	Little Mitchell Creek	Upper member (~2,330)	24	2.27	67	T	–
35. Not available	Sec. 30, T. 56 N., R. 68 W. (Crook, Wyoming)	Driscoll Creek	B sandstone, upper member (1,616)	22	3.16	155	7	0.96

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) (fig. 6), although on an absolute basis bitumen contents are as high as about 25,000 ppm (relative to rock weight) (fig. 7) 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 samples of organic-rich black shale contain predominantly low-molecular- weight compounds ($<C_{20}$), and isoprenoids are present in high amounts relative to *n*-alkanes in most samples (fig. 8). 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 (fig. 8). Rocks containing low amounts of organic matter ($C_{org}<1.0$ percent) are interbedded with the black shales. The organic-lean rocks (not shown in fig. 8) typically contain relatively greater amounts of higher molecular-weight *n*-alkanes (C_{25+}), are depleted in isoprenoids relative to *n*-alkanes, and, in some cases, exhibit an odd-carbon preference (C_{25}–C_{31}).

Figures 9 and 10 show GC–MS results for aromatic hydrocarbons extracted from samples of black shale of the restricted-basin and open-marine settings. Peak identifications 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

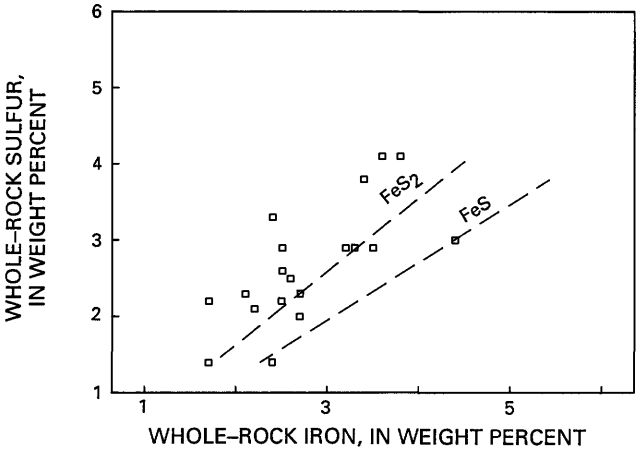


Figure 4. Iron versus total sulfur for some rock samples in the study. Dashed lines indicate stoichiometric amounts of iron and sulfur in FeS_2 and FeS.

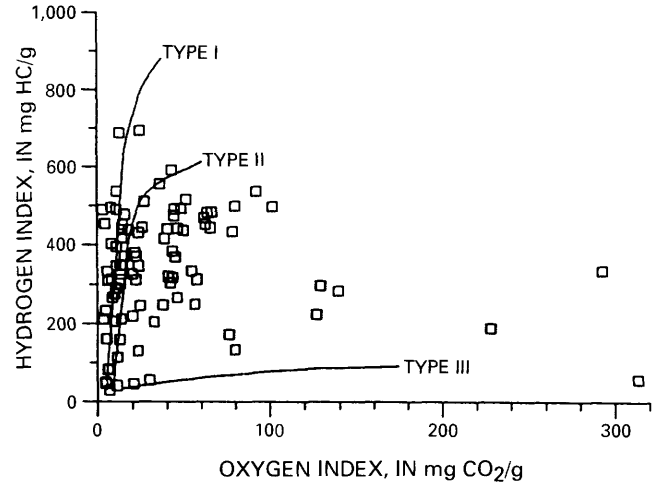


Figure 5. Hydrogen index versus oxygen index for rock samples in the study.

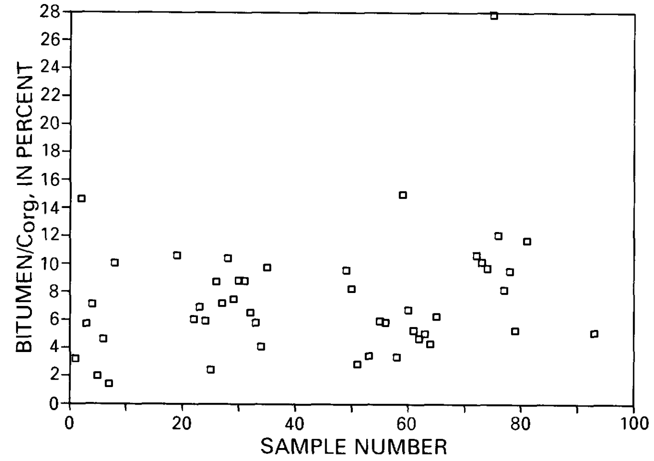


Figure 6. Extractable organic matter (bitumen) normalized to C_{org} for some rock samples in study. See table 2 and figure 1 for sample locations.

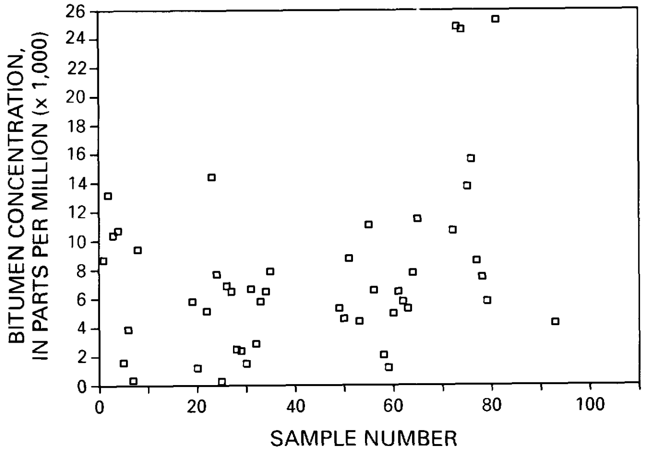


Figure 7. Extractable organic matter (bitumen) relative to dry rock weight. See table 2 and figure 1 for sample locations.

rocks (fig. 10). Comparison of mass spectra of these compounds (fig. 9) 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; however, all of the samples in the present study are predominated by homologues of lower carbon number (fig. 9) than samples studied by Summons and Powell (1986).

Results of GC–MS analysis of steranes (m/z 217) and terpanes (m/z 191) extracted from samples of organic-rich black shale of the restricted-basin and northernmost open-marine setting in Colorado are compared in figure 11. 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 only from northern Colorado. Diasteranes are present in secondary amounts relative to regular steranes, and C_{27} compounds are the most abundant regular steranes present in the C_{27}–C_{29} fraction. C_{30} steranes were not analyzed in the present study.

The terpane distributions are quite variable with respect to relative amounts of tricyclic and pentacyclic compounds (fig. 11) (see also Clayton and Ryder, 1984), although in most samples the pentacyclic compounds are more abundant than the tricyclic compounds. The hopanoids are predominantly of 17α, 21β stereochemistry, although small amounts of 17β, 21α compounds (moretanes) are present in some samples (fig. 11, top).

Porphyrins

Total porphyrin contents (relative to bitumen) of restricted-basin samples are as high as about 40,000 ppm and in most samples are higher than 10,000 ppm (table 1). Similarly high porphyrin contents have been reported in the Cretaceous La Luna Formation of Venezuela (Didyk and others, 1975), the Cretaceous Toolebuc Formation of Australia (Boreham and Powell, 1987), and the Permian Kupferschiefer Formation of Germany (Eckardt and others, 1989). A porphyrin content 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 and others, 1989). With the exception of one sample (number 94) from northeastern Colorado, the total porphyrin content in samples of black shale from the open-marine setting is less than about 5,000 ppm.

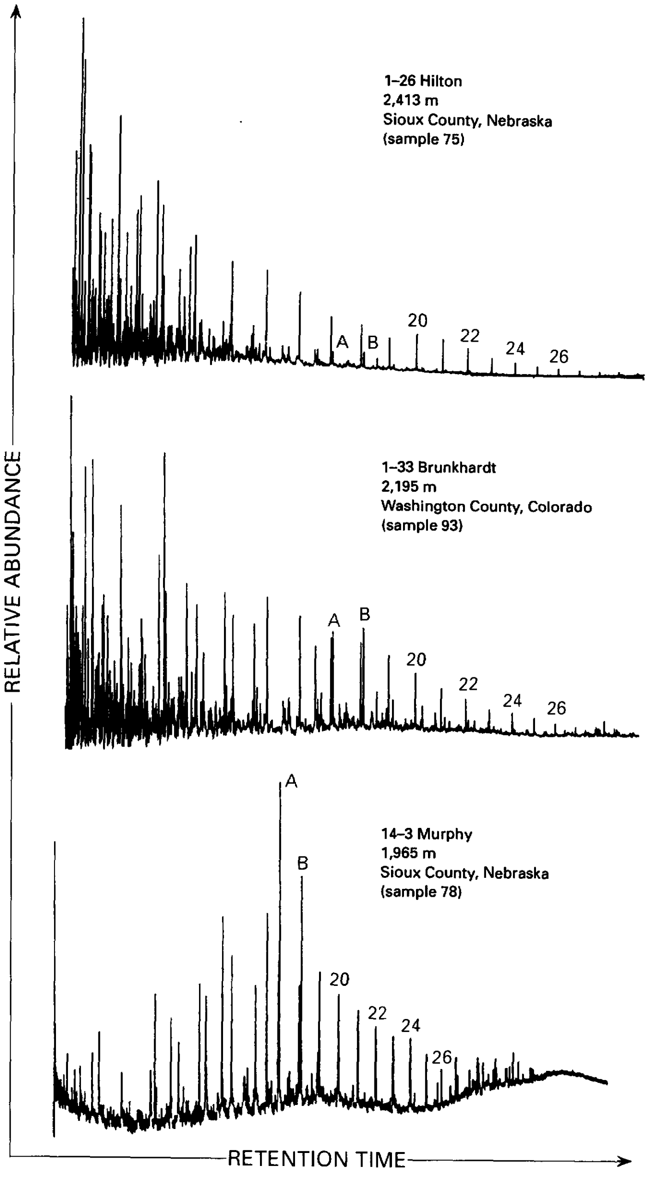


Figure 8. Typical gas chromatograms of saturated hydrocarbons from rock extracts. See table 2 and figure 1 for sample locations. Relative amounts of isoprenoids vary markedly between samples of similar thermal maturity as indicated by samples from the Hrubetz 1-26 Hilton and True 14-3 Murphy wells. In most samples, isoprenoids are abundant (see table 2). The sample from the Hunt 1-33 Brunkhardt well was run under slightly different conditions than other samples, and some evaporative loss of light hydrocarbons occurred during sample preparation.

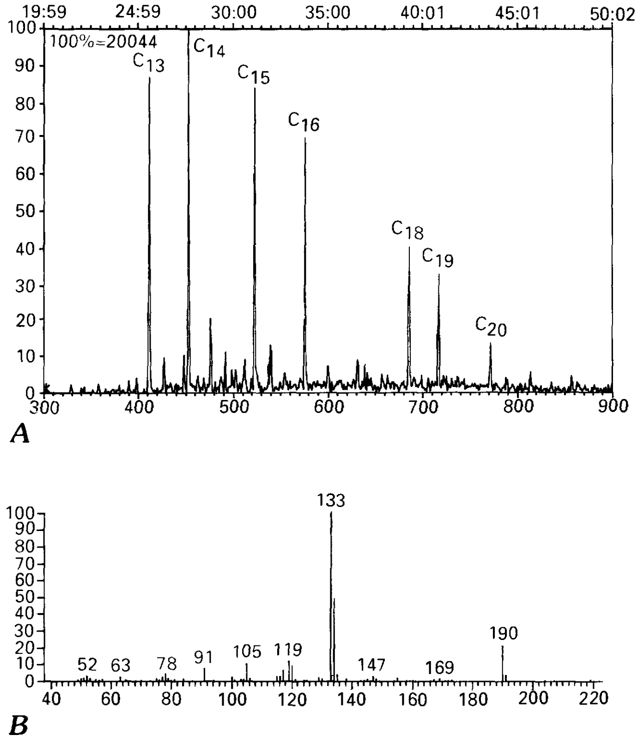


Figure 9. Mass chromatograms of m/z 133 showing (*A*) typical molecular distribution for aryl isoprenoids in a restricted-basin sample and (*B*) example mass spectrum of the C_{13} compound obtained from scanning a whole aromatic fraction of that sample (mass resolution of 3,000 at 5 percent valley, background subtracted). The low intensity of the m/z 134 fragment suggests a methyl substitution similar to that suggested by Summons and Powell (1987) (that is, methyls at both *ortho* positions). Bird 11-16 Corman well, 2,386 m; see table 2 and figure 1 for well location.

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).

The total porphyrin content (VOP+NiP) of oils produced from the Minnelusa Formation ranges from trace amounts (below detection limits) in deeply buried reservoirs of the upper member (such as the Pheasant Field) to 489 ppm in oil of the middle member (Red Bird Field) (table 3). Like the restricted-basin rock extracts, vanadyl porphyrins are predominant over nickel porphyrins. Such high porphyrin contents in oils having API gravity values of about 30 or greater are very unusual. For example, oils produced from Paleozoic reservoirs in the Big Horn Basin having API gravity values of less than about 23 have porphyrin contents of approximately 200 ppm, but those having API gravity values of 30 or greater have porphyrin contents between 0 and 50 ppm (Baker and Louda, 1986; Baker and others, 1987). A compilation of porphyrin data for oils worldwide (Filby and Van Berkel, 1987) shows that porphyrin contents greater than about 500 ppm have been reported for only biodegraded oils (such as Boscan crude, Venezuela; Athabasca oil sand, Canada).

Interestingly, the porphyrin content of oils from the Minnelusa Formation correlates with sulfur content, a correlation also observed for other oils in a number of other studies (Baker and Louda, 1986), but is largely independent of API gravity, especially in oils of the middle member (fig. 12).

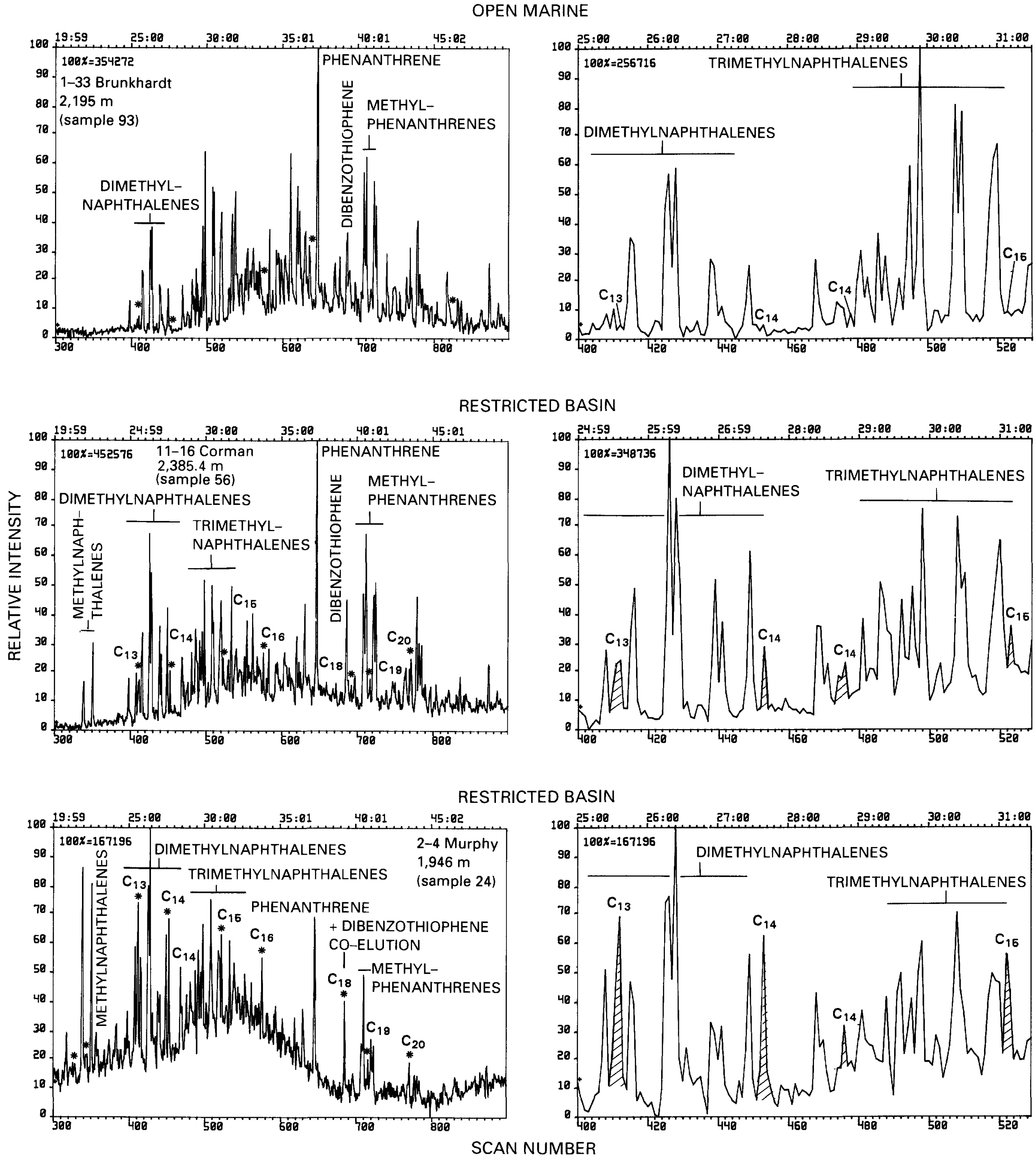


Figure 10. Gas chromatography–mass spectrometry (total ion current) of representative aromatic hydrocarbon fractions from open-marine and restricted-basin shales from northeastern Colorado and western Nebraska, respectively. Chromatograms on right show enlargement of scans 499–530. Aryl isoprenoid compounds, indicated by asterisks and crosshatches, are major peaks in restricted-basin samples but are present in trace amounts in open-marine samples and are commonly not detectable. See table 2 and figure 1 for well locations.

Stable Carbon Isotopes

Stable carbon isotope ratios were determined for kerogen, saturated and aromatic hydrocarbons (C_{15+}), and carbonate carbon for selected samples (table 4). $\delta^{13}C$ values for kerogens are from −23.70‰ to −28.97‰. $\delta^{13}C$ values for saturated and aromatic hydrocarbons are from −25.76‰ to −29.55‰ and from −26.41‰ to −29.68‰, respectively. These values are similar to those reported by Wenger and Baker (1986) and Wenger and others (1988) for black shales of Pennsylvanian age in Oklahoma. Values for 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

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

The molecular distribution of saturated hydrocarbons extracted from samples of black shale both from the restricted basin and from northeastern Colorado is dominated by low-molecular-weight components and acyclic isoprenoids (fig. 8). 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 C_{27} 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 the nonreactive organic matter that might have been 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 coal deposits or transport from adjacent land masses (by water and possibly air) during transgression of the sea when the black shales were deposited. This second explanation was discussed by Wenger and Baker (1986) to explain the presence of various higher-plant-derived organic constituents in Desmoinesian shales of Oklahoma. The same or similar process probably occurred during deposition of the Desmoinesian and Missourian black shales in the northern part of the epicontinental sea in Colorado and the restricted-basin in western Nebraska and eastern Wyoming. Erosion of the coaly organic matter 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 and others, 1984; Wenger and Baker, 1986). One problem with the interpretation of erosion of coal is that coal occurrence within the Desmoinesian sequence in northeastern Colorado or Nebraska is poorly documented. Although we did find one coal of Desmoinesian age in the Sun Fay 1 State well (sec. 36, T. 1 S., R. 46 W., Yuma County, Colorado) (64 percent C_{org}), 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 Desmoinesian-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.

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 multiparameter 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 consists 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 high relative amounts of aryl isoprenoids in the restricted-basin shales suggest 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

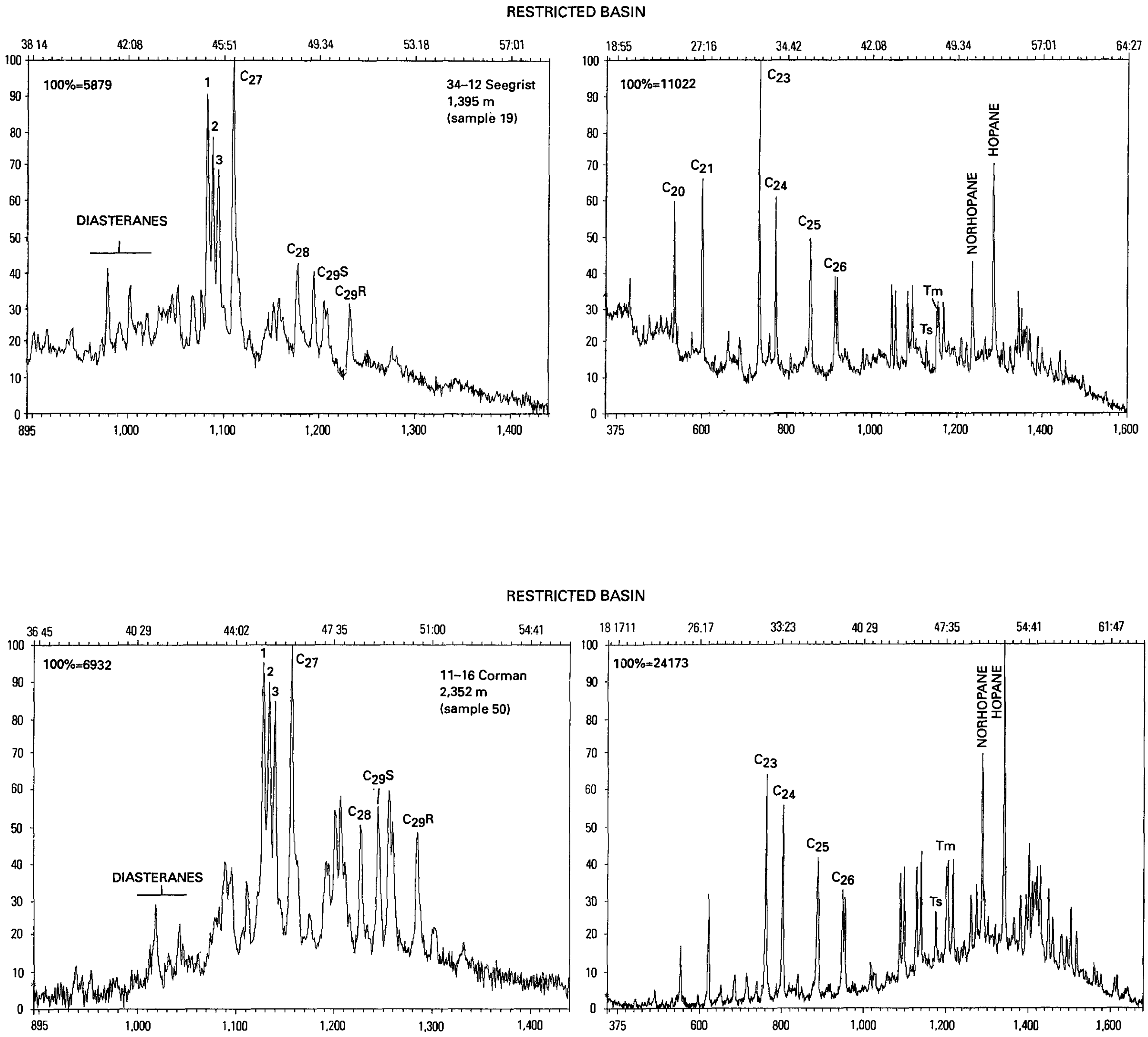
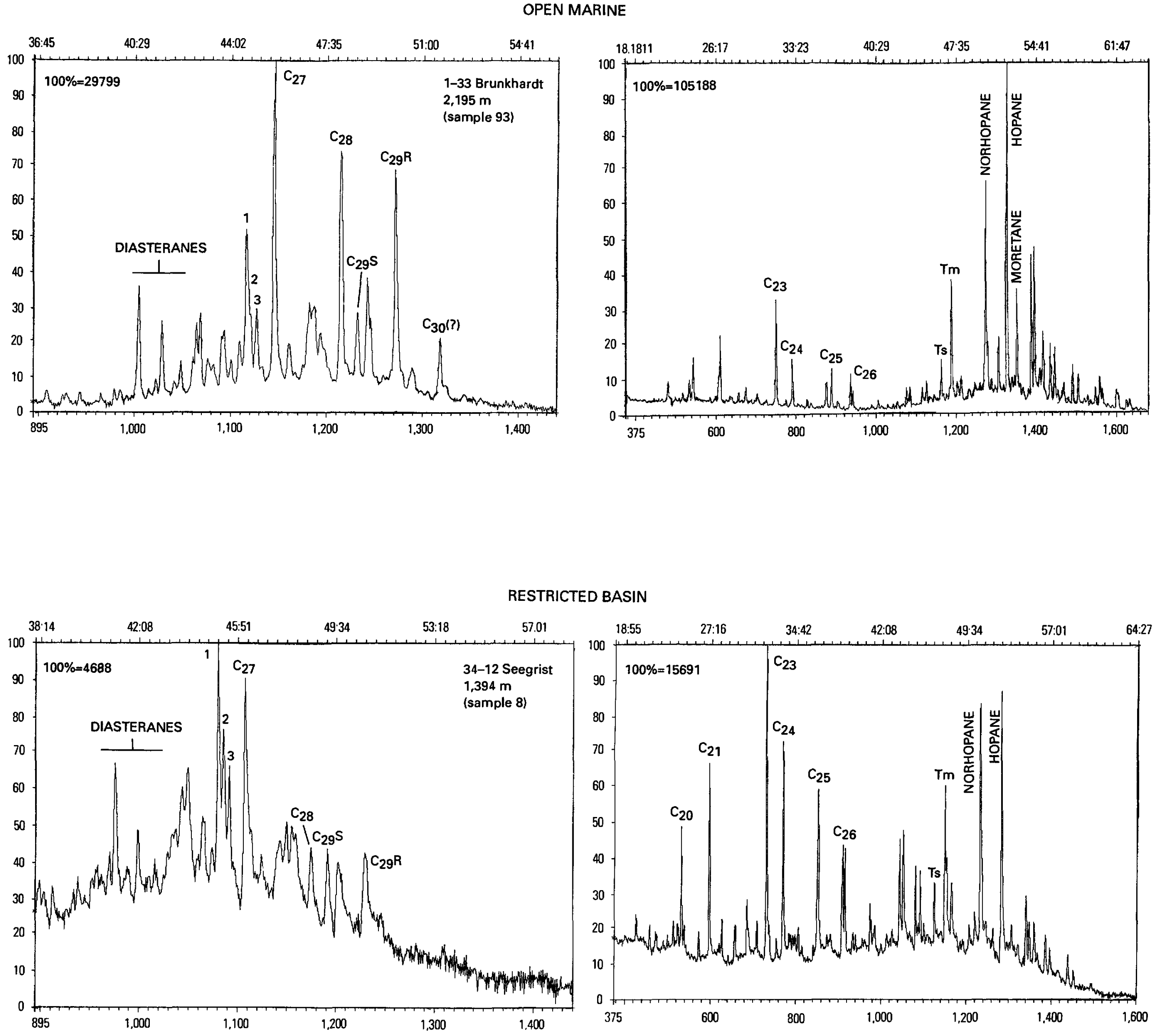


Figure 11 (above and facing page). Gas chromatography-mass spectrometry of steranes (m/z 217, left) and terpanes (m/z 191, right) in whole bitumens from rock extractions. Carbon numbers of steranes refer to compounds having ααα configuration. Sterane peaks labeled 1, 2, and 3 are ααα 20S C_{27}, αββ 20R C_{27}+minor C_{29} diasterane, and αββ 20S C_{27}, respectively. Tm is 17α(H)-trisnorhopane. Ts is 18α(H)-trisnorneohopane. See table 2 and figure 1 for well locations.

reduced sulfur species as the reducing agent to incorporate CO_2 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 CO_2 through oxidation of sulfide is energetically more favorable (more negative ΔG) than is photosynthesis in which H_2O 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 13 compares relative abundances of farnesane and pristane in restricted-basin and



open-marine samples; the open-marine samples include several from wells in Kansas (fig. 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 9–25 percent of the total annual organic matter produced in some Japanese lakes containing sulfidic waters. Likewise, Kepkay and others (1979) reported that chemoautotrophic fixation of CO_2 by sulfur bacteria constituted an appreciable proportion of the organic carbon in sulfidic marine waters of Nova Scotia. Guerrero and others (1985) found that 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 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 that they attributed to photosynthetic sulfur

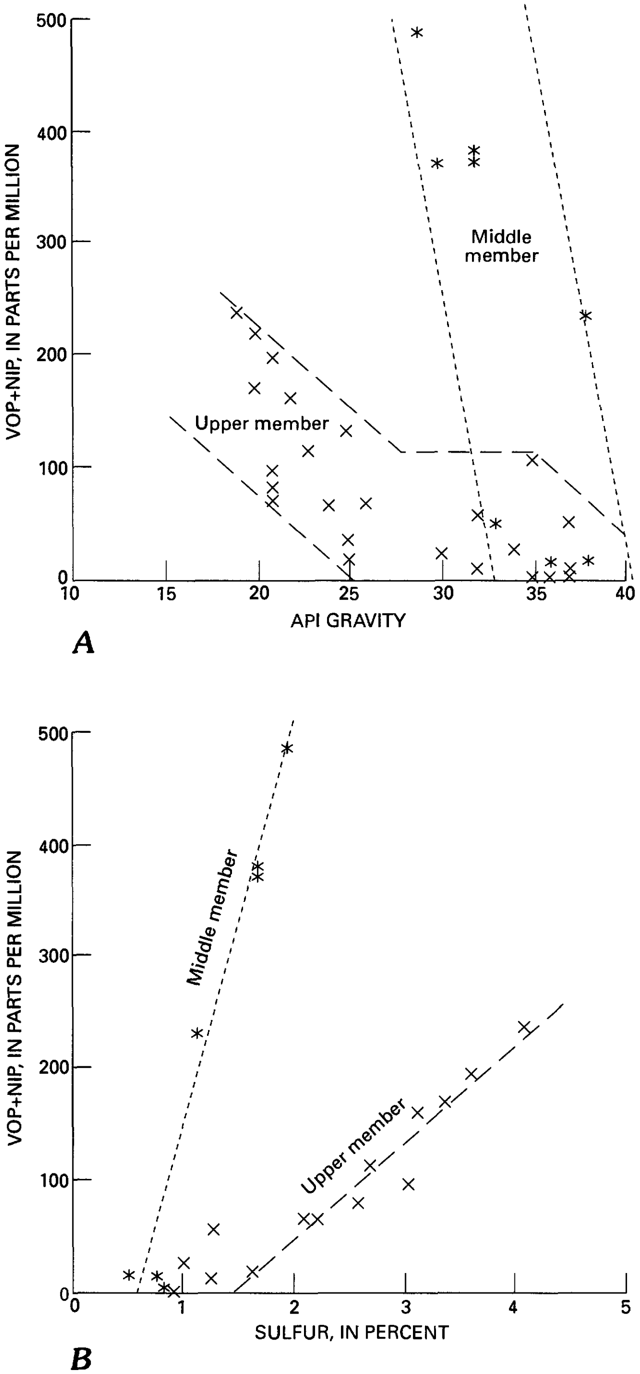


Figure 12. Porphyrin (VOP+NiP) content versus weight percent sulfur and API gravity for oils produced from the middle (*) and upper (x) members of the Minnelusa Formation, northern Denver Basin and southeastern Powder River Basin.

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 sulfate-reducing bacteria were present (table 5). $\delta^{34}S$ values of anhydrite are similar to that reported by Claypool and others (1980) for 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 sulfate-reducing bacteria, 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, support the notion of significant input of bacterial organic matter, including archaebacteria (Michaelis and Albrecht, 1979).

Biomarker compounds indicative of methanogens such as diphytanyl (Tornabene, Wolfe, and and others, 1978; Holzer and others, 1979; Tornabene, Langworthy, and others, 1979; Tornabene, Lloyd, and others, 1980) are not present in significant 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 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 4). Further, petroleum exploration drilling in black shales in both the restricted-basin and open-marine settings has not revealed significant quantities of methane-rich gas. It should be emphasized, however, that although some microbial gas has been reported in Pennsylvanian strata (Jenden and others, 1988), preservation of gas formed during early diagenesis is unlikely in such old rocks.

The relatively high sulfur contents and generally low carbon to sulfur ratios of the restricted-basin samples (fig. 3) are consistent with the interpretation of euxinic water conditions (Leventhal, 1983). In contrast, the higher carbon to sulfur ratios in the open-marine samples (fig. 3, table 1), along with the low aryl isoprenoid and farnesane contents, suggest that the water column in the open-marine environment may not have contained significant quantities of sulfide. It should be noted, however, that the fairly low iron contents of the restricted-basin samples may have been a limiting factor for sulfur incorporation in the sediments. The same is likely true for the open-marine sediments. Iron contents are less than 3.0 weight percent in open-marine shales of northeastern Colorado, although only two samples were analyzed.

Table 4. Stable carbon isotopic ratios ($\delta^{13}C$ in per mil versus PDB) for kerogen, saturated and aromatic hydrocarbons, and carbonate carbon in rock samples, northern Denver Basin and southeastern Powder River Basin

[Locations of wells shown by numbers in figure 1. Sample depth in meters. Leader (–), not determined; slash (/), duplicate analysis]

Sample number	Sample depth	Kerogen	Saturated hydrocarbon	Aromatic hydrocarbon	Carbonate carbon
1. Shell 31–16, sec. 16, T. 42 N., R. 62 W., Westin County, Wyoming					
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	–	-28.84	+0.13
4	1,860	-28.89	-29.42	-29.68	-2.46
5	1,879	-24.98	–	–	+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., Dawes County, Nebraska					
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	–	–	+1.51
10	1,394.57	-28.90	–	–	-1.59
11	1,394.60	-28.97	–	–	-1.68
12	1,394.63	-28.62	–	–	-1.94
13	1,394.66	-28.74	–	–	-1.97
14	1,394.69	-28.84	–	–	-1.58
15	1,394.72	-28.97	–	–	-1.47
16	1,394.75	-28.72	–	–	-1.52
17	1,394.78	-28.94	–	–	-1.50
18	1,394.81	-28.53	–	–	-1.49
19	1,395	-28.92	-29.55	-29.60	-1.98
20	1,395.4	–	-29.50	-29.32	–
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., Sioux County, Nebraska					
24	1,946	–26.28	–	–	+1.46
25	1,948	–25.47	–	–	–0.16
26	1,955.4	–27.88	–	–	+0.95
27	1,955.7	–27.54	–	–	+0.39
4. Bird 18–8 Downer, sec. 18, T. 24 N., R. 56 W., Sioux County, Nebraska					
28	2,363.7	–26.22	–28.59	–28.86	–0.60
29	2,364	–	–28.77	–28.45	–
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	–	–27.95	–	–
32	2,393	–26.58	–27.18	–26.89	+0.03
5. Bird 2–3 Laucomer, sec. 5, T. 24 N., R. 55 W., Sioux County, Nebraska					
33	2,256	–26.29	–	–	+1.55/+1.54
34	2,260	–26.23	–	–	+1.38/+1.42
34a	2,263	–25.12	–	–	+0.80
34b	2,267	–26.28	–	–	+1.91/+1.90
35	2,271	–27.82	–	–	+0.27/+0.31
35a	2,292	–24.11/–24.06	–	–	–1.29
35b	2,293	–23.82/–23.70	–	–	–1.00/–1.06
36	2,303	–28.83	–	–	–0.21
37a	2,303.4	–28.72	–	–	–0.20

Table 4. Stable carbon isotopic ratios ($\delta^{13}C$ in per mil versus PDB) for kerogen, saturated and aromatic hydrocarbons, and carbonate carbon in rock samples, northern Denver basin and southeastern Powder River Basin—Continued

[Locations of wells shown by numbers in figure 1. Sample depth in meters. Leader (–), not determined; slash (/), duplicate analysis]

Sample number	Sample depth	Kerogen	Saturated hydrocarbon	Aromatic hydrocarbon	Carbonate carbon
6. True 13–18 Laucomer, sec. 8, T. 25 N., R. 55 W., Sioux County, Nebraska					
37	2,267	–26.28	–	–	+1.91
44	2,303	–28.83	–	–	–0.07
45	2,303.4	–28.72	–	–	–0.07
7. Bird 11–16 Corman, sec. 11, T. 25 N., R. 56 W., Sioux County, Nebraska					
47	2,350.9	–28.76	–	–	–0.64/–0.29
48	2,351.2	–28.80	–	–	–0.58/–1.29
49	2,351.5	–28.51	–	–	–0.47
50	2,351.8	–28.16	–	–	–0.26/–0.27
51	2,364.0	–27.95	–	–	–0.22
52	2,364.3	–26.73/–26.65	–	–	+1.39/+1.19
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	–	–	+0.54/+0.11
56	2,385.4	–27.89	–	–	+0.65
57	2,385.6	–27.46	–	–	+0.91
57a	2,386	–27.02	–	–	+0.76/+0.75
57b	2,395	–25.58	–	–	+1.09/+0.24
8. Conoco 23–1 Perkins, sec. 23, T. 25 N., R. 57 W., Sioux County, Nebraska					
58	2,461	–26.05	–	–	+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 W., Sioux County, Nebraska					
60	2,416	–28.83/–28.84	–	–	+1.15
61	2,417	–28.66	–29.36	–29.35	–1.30
62	2,418	–28.80	–	–	–1.14/–1.12
63	2,428	–24.74	–	–	+1.56
63a	2,428.4	–23.92	–27.11	–27.40	+1.62
64	2,431	–25.88	–	–	+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., Logan County, Colorado					
89	2,304.5	–26.37	–	–	–0.73
90	2,304.8	–26.51	–	–	–0.49
91	2,306	–	–27.47	–27.15	–
16. Sun Roelle 1, sec. 24, T. 12 N., R. 53 W., Logan County, Colorado					
92	2,272	–26.31	–27.21	–27.24	–0.97
92a	2,271	–	–28.61	–27.27	–
17. Hunt 1–33 Brunkhardt, sec. 33, T. 5 N., R. 54 W., Washington County, Colorado					
93	2,195	–28.21	–	–	–3.48
95	2,256	–26.94	–	–	–2.70
96	2,268	–26.72	–	–	–0.84
97	2,277	–26.61	–	–	–1.56
98	2,284	–26.46	–	–	–1.29
99a	2,381	–24.85	–28.85	–28.78	–2.82

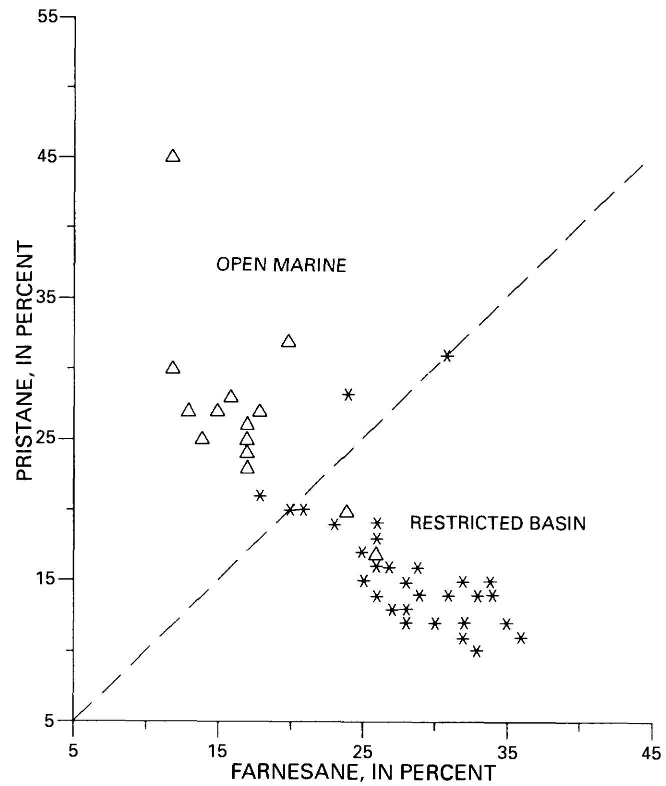


Figure 13. Relative abundance of pristane (C_{19}) versus farnesane (C_{15}) determined from gas chromatography of saturated hydrocarbon fractions of samples from the open-marine (triangles) and restricted-basin (asterisks) settings. Amounts shown are normalized percentages of the C_{15}–C_{20} isoprenoid fraction.

Table 5. Sulfur isotope ratios of Desmoinesian black shale samples from the western Nebraska Panhandle (Sioux County))

Sample description	$\delta^{34}S$ (‰ 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

Evidence from Stable Carbon Isotopes

A major objective of carbon isotope studies in organic geochemistry is to interpret the biological source(s) of sedimentary organic matter (kerogen). Although the $\delta^{13}C$ values for various living organisms are well known (Galimov, 1974, 1980; Fuex, 1977), isotope fractionation may occur during deposition of sedimentary organic matter and during the formation of kerogen (Fuex, 1977; Dean and others, 1986; Hayes and others, 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 generally still evident. For example, most modern terrestrial plants are depleted in ^{13}C ($\delta^{13}C$ about −25‰ to −30‰) relative to marine plants ($\delta^{13}C$ 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 materials 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; Sackett and others, 1965; Deuser and others, 1968; 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 $^{12}C/^{13}C$ ratio of CO_2 fixed during photosynthesis can vary (McKenzie, 1982; Schoell, 1984; Lewan, 1986).

Dean and others (1986) and Dean and Anders (1991) proposed that comparison of $\delta^{13}C$ of kerogen and hydrogen index allows separation of the effects of parent organic-matter source and environment—that is, alteration of $^{13}C/^{12}C$ 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 and others, 1984). Underlying assumptions in this approach are that (1) hydrogen index reflects the source of organic matter and (2) bacterial organic matter is not an important contributor to sedimentary organic matter. Dean and others (1986) argued that a correlation should exist between $\delta^{13}C$ values and the hydrogen index of kerogen because higher hydrogen indices correlate with greater proportional input of algal organic matter and attendant shift in $\delta^{13}C$ values.

In their study of Cretaceous rocks, Dean and others (1986) hypothesized that a positive correlation should exist between these parameters; that is, $\delta^{13}C$ 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 $\delta^{13}C$ values were about −27‰. Similarly, data on amorphous ("algal") kerogens of Phanerozoic age show uniformly light values (Lewan, 1986). A compilation of isotope data for kerogens of various origins (Schoell, 1984) shows values of about −26‰ for type III kerogen and about −28‰ for type II kerogen; the widest range of values was for type I kerogen (−23‰ to −33‰).

Kerogen isotopic composition does not show any correlation with either hydrogen index or C_{org} content in the

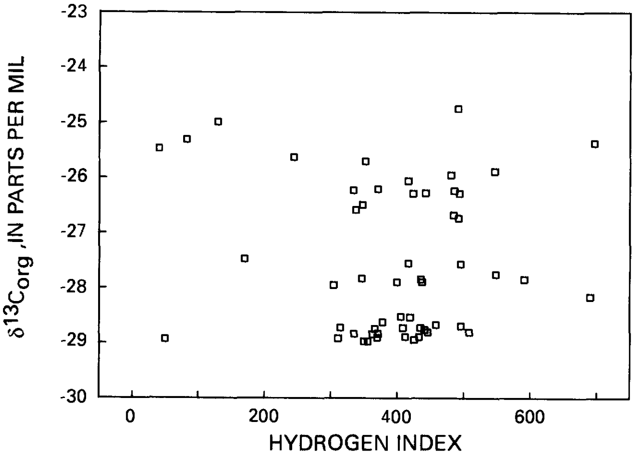


Figure 14. Hydrogen index versus $\delta^{13}C$ of total organic carbon (kerogen).

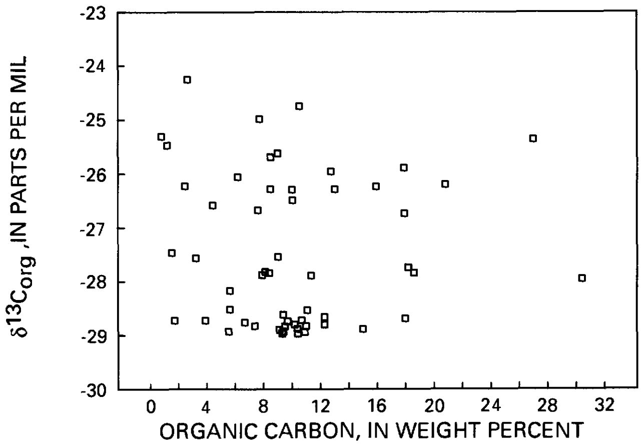


Figure 15. C_{org} versus $\delta^{13}C$ of total organic carbon (kerogen).

samples of Desmoinesian shale of the present study (figs. 14, 15). It might be expected that lower C_{org} contents 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 do 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, which are discussed in the following 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 phototropic 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 and others, 1990; Hayes and others, 1990). Coffin and others (1989) reported a wide range of $\delta^{13}C$ values in bioassays of bacteria harvested from a marine estuary (−11.5‰ to −27.4‰), but experimental data showed that bacteria had $\delta^{13}C$ values within 2‰ of their growth substrates. Therefore, Coffin and others (1989) suggested that $\delta^{13}C$ values of bacteria could be used as tracers for assessing growth substrates.

Second, as noted previously, the organic matter in these Desmoinesian and Missourian shales was 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 lowering 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 $\delta^{13}C$ values of about −28‰ to −30‰ for samples of Pennsylvanian rocks 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 was not in equilibrium with oceanic bicarbonate ($\delta^{13}C$ about 0‰) was the predominant source of CO_2. Wenger and others (1988) reported $\delta^{13}C$ values of about −27‰ for kerogen in Pennsylvanian black shales from Kansas and Oklahoma. Approximately half of the samples analyzed in the present study have $\delta^{13}C$ values between −28‰ and −30‰.

The importance of source of CO_2 is that a large $\delta^{13}C$ 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) (fig. 14). Wenger and others (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 organic matter occurred because pure undegraded algal organic matter has much higher hydrogen indices (about 800–900 mg/g). Therefore, the $\delta^{13}C$–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 commun., 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 figs. 14, 15) 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, both of 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, data are insufficient to adequately evaluate this hypothesis.

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

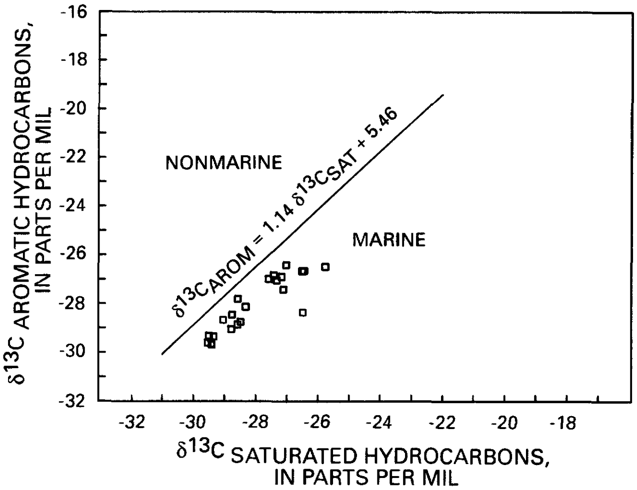


Figure 16. Carbon isotopic composition of saturated versus aromatic hydrocarbons. Line separates marine from nonmarine sources (Sofer, 1984).

Figure 16 shows a comparison of $\delta^{13}C$ 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 ("nonmigrated oil") as well as for oils in reservoirs, then hydrocarbons plotted in figure 15 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‰ (fig. 17). 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 about 15‰ as compared to carbohydrates, lignin, and proteins (Degens and others, 1968). Humin is generally regarded an important precursor to kerogen (Tissot and Welte, 1984), and humin 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 $\delta^{13}C$ 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

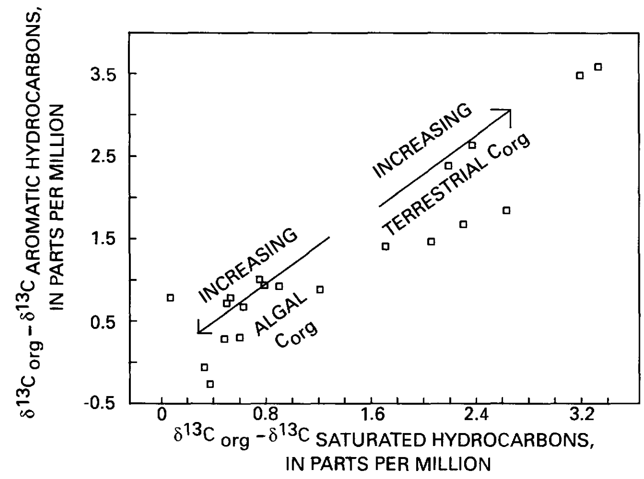


Figure 17. $\delta^{13}C$ (kerogen) $-\delta^{13}C$ (saturated hydrocarbons) versus $\delta^{13}C$ (kerogen)$-\delta^{13}C$ (aromatic hydrocarbons).

isotopically lightest of the lipid fraction. This expectation is supported by isotopic studies of various compound classes contained within the lipid fraction (saturates, aromatics, resins, asphaltenes) (Stahl, 1977) and the data of the present study in which the saturated hydrocarbons are consistently lighter than the aromatic hydrocarbons (fig. 16).

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, likely 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 $\delta^{13}C$ 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 [$\delta^{13}C(C_{org}) - \delta^{13}C$(saturated or aromatic hydrocarbons)] have a large range (fig. 17) despite the 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 $\Delta\delta^{13}C$ 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 18 shows a positive correlation between $\delta^{13}C$ values of kerogen and Δ values. These data are consistent with the interpretations that most of the soluble organic matter was derived from the water column and that 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, lower $\delta^{13}C_{org}$ values are accompanied by lower Δ values because more algal 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 including organic productivity, sedimentation rate, thermal maturity, and redox conditions of the sedimentary environment (Orr and others, 1958; Lewan and Maynard, 1982; Baker and Louda, 1986; Baker and others, 1987). Long residence time in oxygenated water, either because of slow settling velocity or a long water column (Lewan and Maynard, 1982) (fig. 19), 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 and others (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 1 percent of the total pigment flux from the overlying water column was preserved in oxygenated marine sediments from Dabob Bay, Washington, and that in marine waters pheopigment decomposed 5–20 times faster than 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

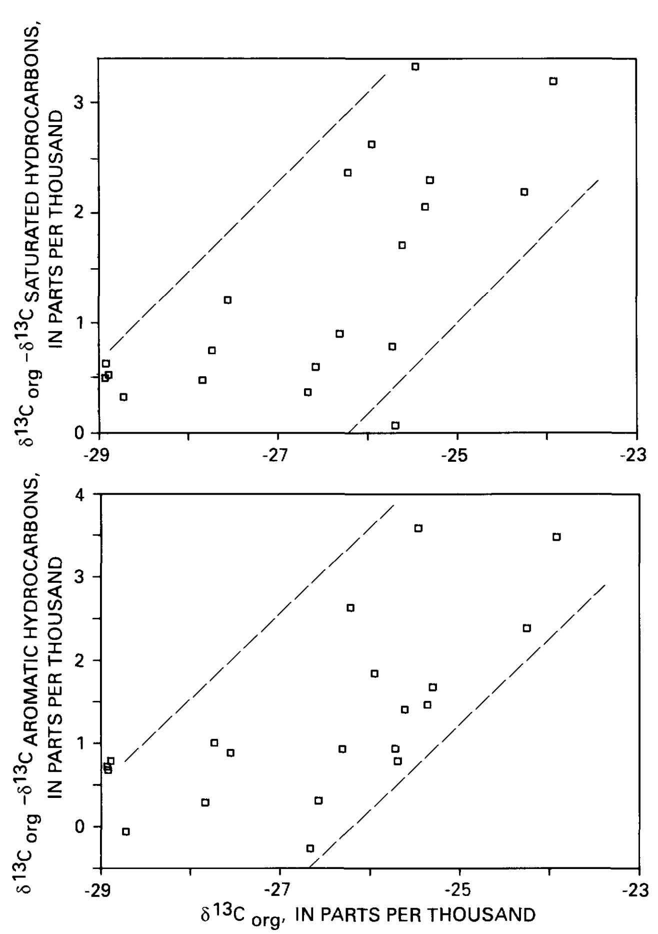


Figure 18. Comparison of kerogen (C_{org}) $\delta^{13}C$ values and Δ values (difference in $\delta^{13}C$ values between C_{org} and hydrocarbon fractions).

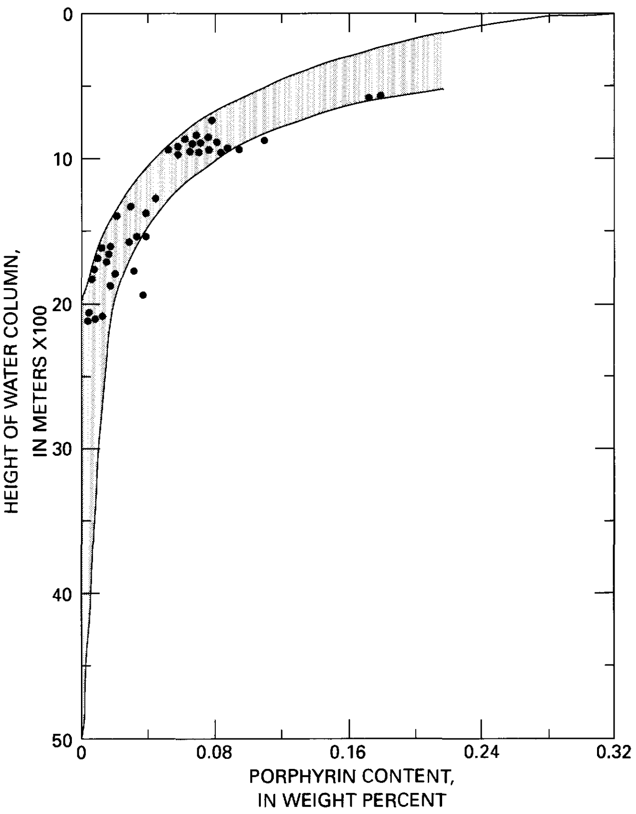


Figure 19. Concentration of tetrapyrroles (pheophytins) in organic matter from surface sediments in offshore basins of California versus height of water column. Median grain diameter of sediments ≤10 µm. Modified from Lewan and Maynard (1982) and Orr and others (1958).

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 contents 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 and others, 1986; Hurley and Armstrong, 1990); however, several studies show that planktonic grazing by zooplankton can enhance preservation of pheopigments through rapid settling of fecal particles (Downs and Lorenzen, 1985; Carpenter and others, 1986; Hurley and Armstrong, 1990). Carpenter and others (1986) observed a relationship between body mass of zooplanktonic herbivores and pigment flux that suggests large zooplankters provide 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 g m^{-2} yr^{-1}).

Samples of Desmoinesian and Missourian black shales from the restricted basin that have hydrogen indices as low as about 300 mg HC/g C_{org} have porphyrin contents 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 and type III or even as type III organic matter (Espitalié and others, 1977; Tissot and Welte, 1984). This paradox between bulk organic-matter type and high porphyrin content 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 content (VOP+NiP) in figure 20. Samples having hydrogen indices greater than 300 mg HC/g C_{org} have variable porphyrin contents, but samples having lower hydrogen indices (190–300 mg HC/g C_{org}) all have porphyrin contents less than 5,000 ppm. Only a few samples having the lower hydrogen indices were

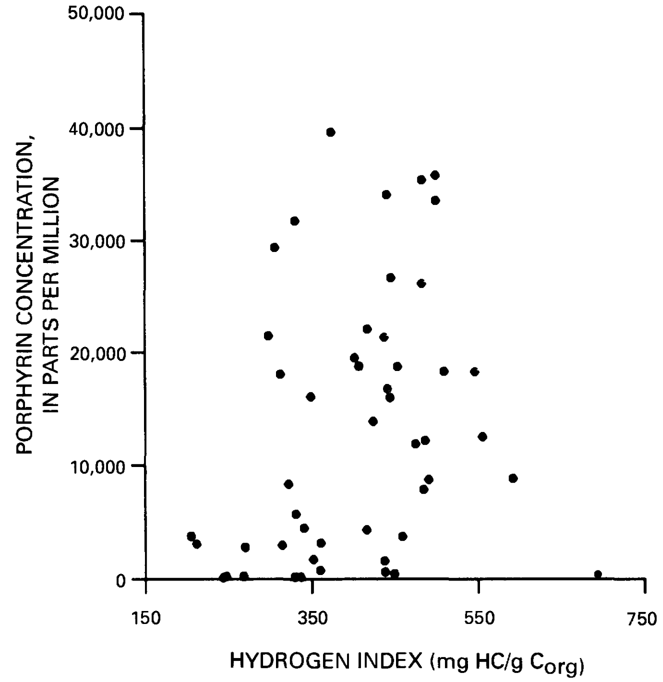


Figure 20. Hydrogen index versus total porphyrin content (VOP+NiP) relative to bitumen.

analyzed for porphyrins because these samples have light-colored extracts that obviously have low porphyrin contents. These low porphyrin contents are interpreted to indicate that low hydrogen indices are caused by poor preservation of primary organic matter combined with abundant allochthonous organic matter that results in high C_{org} contents. This situation would result in low porphyrin contents. Samples having higher hydrogen indices (300–600 mg HC/g C_{org}) have variable porphyrin contents 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 content for hydrogen indices above some minimum value associated with a threshold level of organic productivity and preservation. Because porphyrins are more rapidly degraded than 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 oxygen levels.

No systematic relationship exists between C_{org} content and porphyrin content (fig. 21). The C_{org} content of some open-marine samples is as high as about 24 weight percent and the porphyrin content 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 contents (restricted-basin samples). High C_{org} contents combined with low porphyrin contents 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.

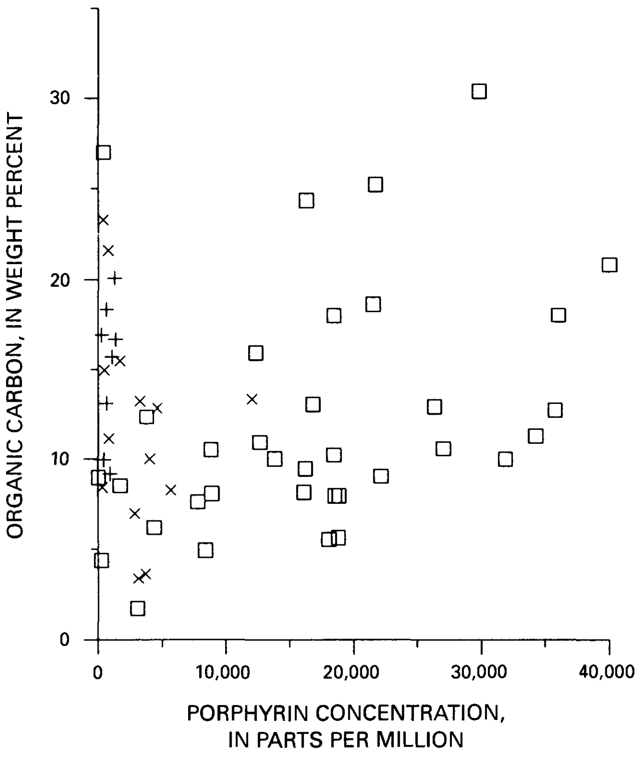


Figure 21. C_{org} versus total porphyrin content (VOP+NiP) relative to bitumen. Squares indicate restricted basin-shales; +'s indicate open-marine shales from northeastern Colorado near the restricted basin; x's indicate open-marine samples from Kansas and Oklahoma.

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} contents. 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.

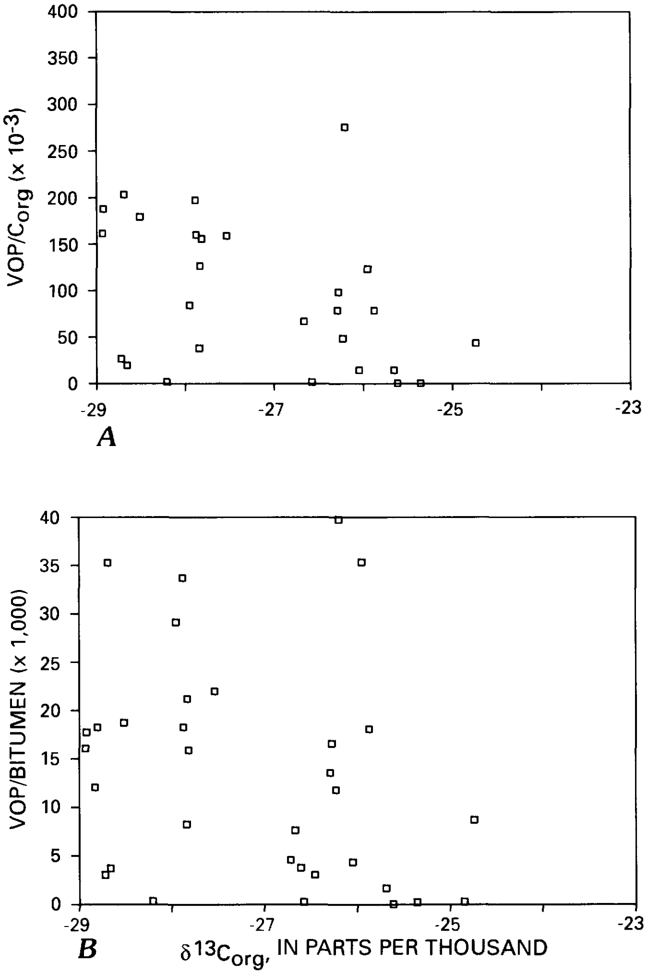


Figure 22. Comparison of $\delta^{13}C_{org}$ and porphyrin contents (VOP) normalized to (*A*) C_{org} and (*B*) bitumen.

Alternatively, the porphyrin data could be normalized to C_{org} if an independent method were available to assess the proportions of algal (autochthonous) and terrestrial (allochthonous) organic input to the kerogen. As noted previously, comparison of the carbon isotopic compositions of kerogen and extractable hydrocarbons (fig. 18) can provide a qualitative assessment of allochthonous organic-matter input. The isotopically light C_{org} samples (about –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 content normalized to C_{org} and bitumen in figure 22. 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 content would depend mostly on degree of mixing of organic matter from two sources. It is evident from figure 22 that the normalized porphyrin content is highly variable for a given organic matter source as indicated by isotopic composition. Therefore, we propose that the porphyrin content (normalized to bitumen) reflects mainly preservation rather than mixing of organic matter.

Figure 23 shows geochemical data for 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). The essentially constant $\delta^{13}C$ values of the kerogen (–28.53‰ to –28.97‰) indicate that organic-matter type is uniform throughout the entire interval. The hydrogen index also varies little (table 2), although C_{org} contents decrease from bottom to top through most of the interval. The average bitumen content is 8,575 ppm, and bitumen contents of all but one sample (no. 15, table 2) are within ±10 percent of this value.

The purpose of analyzing this downhole set of samples was to test the applicability of porphyrin content 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 almost constant. 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 content relative to bitumen is interpreted to indicate relative preservation differences rather than variable degree of dilution by allocthonous organic matter.

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) varies widely over the same interval. This variation is interpreted to reflect differing amounts of preservation, and no systematic relationship exists between productivity and preservation. Even though productivity decreases from bottom to top of the core according to the C_{org} data, the relative preservation does not show any systematic change. Interestingly, VOP/C_{org} ratios of figure 23 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 fig. 23).

All but one sample from the open-marine setting have relatively low porphyrin contents even though most C_{org}

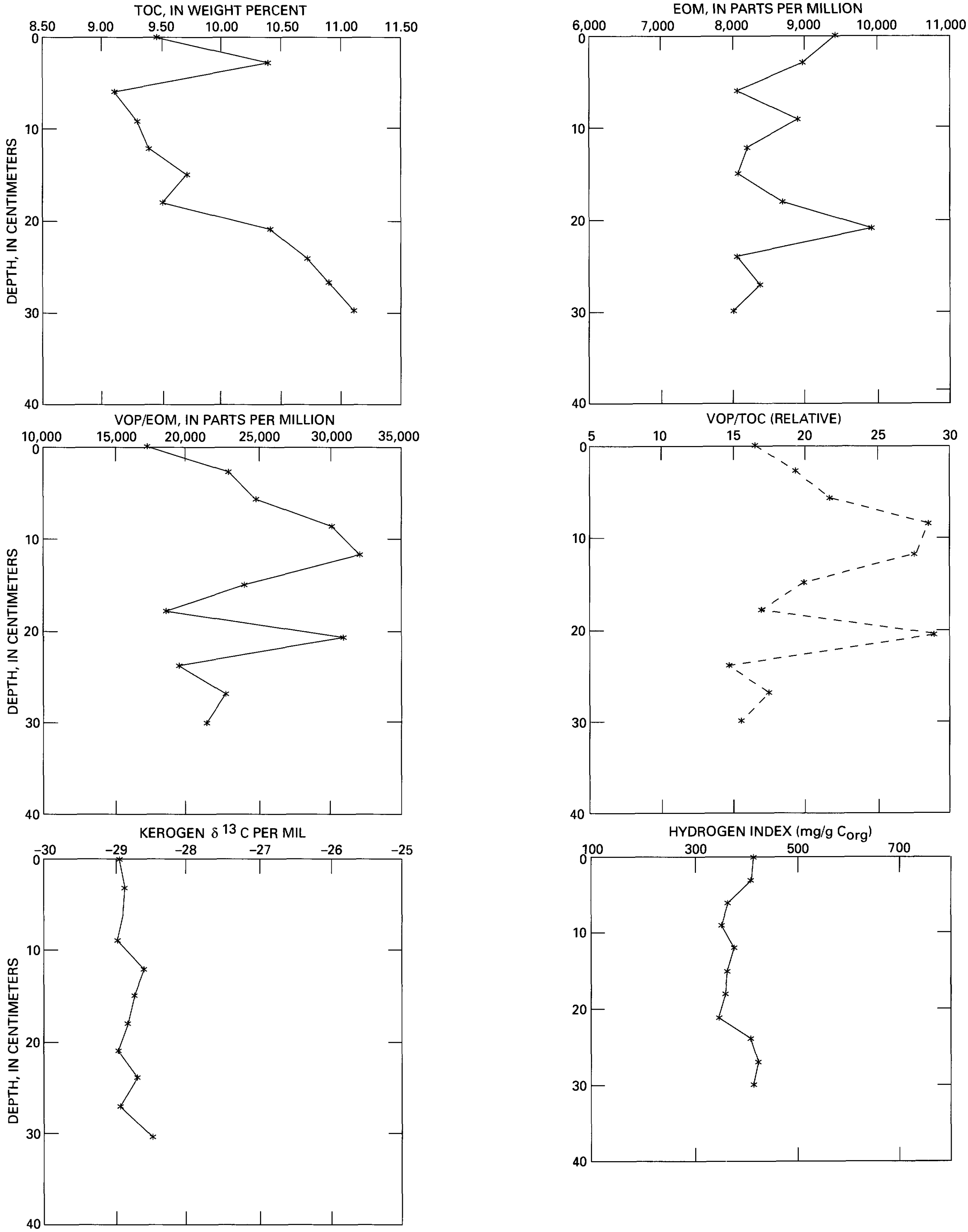

TOC, IN WEIGHT PERCENT
8.50
9.00
9.50
10.00
10.50
11.00
11.50
EOM, IN PARTS PER MILLION
6,000
7,000
8,000
9,000
10,000
11,000
VOP/EOM, IN PARTS PER MILLION
10,000
15,000
20,000
25,000
30,000
35,000
VOP/TOC (RELATIVE)
5
10
15
20
25
30
KEROGEN δ 13 C PER MIL
-30
-29
-28
-27
-26
-25
HYDROGEN INDEX (mg/g Corg)
100
300
500
700
DEPTH, IN CENTIMETERS
0
10
20
30
40

Figure 23 (facing page). Geochemical parameters of core samples collected at 1-cm intervals through a single black shale bed in the Mitchell 34–12 Seegrist well (samples 9–18, table 1). Parameter abbreviations and units of measurement are described in table 2.

contents are quite high (table 2). Considering the water depths of 50–100 m postulated for the epicontinental sea (Heckel 1977, 1980, 1984), higher porphyrin contents 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 the high amounts of organic-matter accumulation were the result primarily of high productivity combined with recycling of preexisting organic matter. This model explains not only the combination of high C_{org} contents and low porphyrin contents but also the relatively low sulfur contents (high C/S ratios) and the absence of biomarkers indicative of photosynthetic sulfur bacteria (aryl isoprenoids) in extracts from the open-marine environment. Relatively high *absolute* sulfur contents in the open-marine rocks suggest that anoxic conditions may have existed in the sediments or in a narrow water layer immediately overlying the sediments.

RECOGNITION OF HYPERSALINITY

An important research objective in molecular organic geochemistry is determining diagnostic criteria for recognizing specific depositional environments of both dispersed sedimentary organic matter and oils. Criteria have been established for distinguishing general depositional environment, such as marine or continental. 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, de Leeuw, and Schenck, 1985, 1986; Sinnighe Damsté and de Leeuw, 1986; Brassell, Eglinton, and Howell, 1987; Brassell, Sheng Guoying, and others, 1988; ten Haven, de Leeuw, and others, 1988; Jiang, 1988; Mello and others, 1988; Volkman, 1988). Although several of the earlier studies focus on geochemical criteria for recognition of "hypersaline" environments (ten Haven, de Leeuw, and Schenck, 1985; ten Haven, de Leeuw, and others, 1988; Schwark and Püttman, 1990), the term "hypersaline" is somewhat ambiguous (Hite and Anders, 1991). According to Hite and Anders, the term "hypersaline" indicates all environments in which the salinity is greater than normal seawater (greater than 35 parts per thousand), 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 are classified as hypersaline but may represent a fairly broad range of salinity. For example, ten Haven, de Leeuw, and Schenck (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 predominate at salinities below 140‰–150‰, whereas salinities of about 150‰ or more may be required for gypsum precipitation. Mello and others (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 the individual rock types contained within the sequence in order to avoid ambiguities in the application of geochemistry to paleoenvironmental assessment. Hite and Anders (1991) pointed out that organic productivity in the water column is commonly extremely high during highly saline conditions (100‰–150‰), but preservation in the underlying sediments is generally quite low. In contrast, although water-column productivity may be lower, preservation of organic matter commonly is 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 (~150‰) deposits such as anhydrite (gypsum) is very low. Only a few samples were analyzed, and these are not included in table 2 because C_{org} contents 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 above normal marine salinity. 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 environment characterized by normal or slightly elevated salinity, a density-stratified water column, and euxinic conditions in the lower water layer.

As noted by Hite and Anders (1991), when water salinity increases the diversity of living organisms decreases, although the total biomass may be quite high. Research

Table 6. Geochemical characteristics of rocks and oils in hypersaline sequences

[Leader (–) indicates not available. 4-Me is 4-methy steranes. Sulfur and diasterane values in percent]

Reference	Pr/Ph	CPI	GI	S	R_{22} index	Diasteranes	C_{35} hopane	C_{25} isoprenoid	4-Me
1	<1.0	<1.0	–	–	–	–	–	–	–
2	<1.0	–	–	–	–	–	–	Abundant	–
3	0.3–1.2[a]	<1.0	–	–	>1.0	–	–	–	–
4	–	–	–	–	–	–	$>C_{34}$	–	–
5,6[b]	0.3	<1.0	11	3.6	–	–	–	–	Abundant
7	0.3–0.9	<1.0	–	–	>1.0	Low[c]	$>C_{34}$	Absent	Abundant
8	<<1.0	<1.0	~40	–	>1.0	Low	$>C_{34}$	Abundant[d]	Abundant
9	–	–	–	–	>1.0	–	–	–	Abundant
10	0.5–1.0	≥1.0	76–132	–	>1.0	9–27[e]	$>C_{34}$	–	–
11	<<1.0	<1.0	~100	–	>1.0	Low	$>C_{34}$	Abundant	Abundant
12	0.1–0.5	≤1.0	35–216	High	–	–	$>C_{34}$	–	Abundant
13	<1.0	≤1.0	70–120	0.3–2.5	~1.0	Low	$>C_{34}$	Abundant	Abundant
14	0.3	<1.0	~100	–	>1.0	–	–	–	–
This study	0.7–1.4	≤1.0	<10–113[f]	0.5–5.0	≥1.0	Low	$<C_{34}$	Rare	–

[a] 0.3 for anhydrite-rich sample; 1.2 for dolomite-rich sample.

[b] Both studies include same sample from evaporite sequence.

[c] Except one nodular anhydrite sample had high diasteranes.

[d] Only in marl sample, absent in gypsum.

[e] Relative abundance in whole sterane fraction.

[f] All samples except one have values less than about 40.

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

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 result when a decrease of overall diversity of organisms is 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 for a slight even carbon predominance among n-alkanes in the C_{25} region (fig. 8), low diasterane content (fig. 11), and high sulfur content (table 2). Only three samples (nos. 59–61, table 1) contain gammacerane (fig. 24) in greater abundance than C_{31} hopane (homohopane). The only sample that has an R_{22} index (ten Haven and others, 1988) greater than one is an organic-lean sample (fig. 25), and this sample has a CPI (C_{25}–C_{32}) 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 (R_{22} index) is mixed with terrestrially derived organic matter (pristane/phytane ratio >1, odd carbon preference, abundant C_{25+}). Considering the relatively low organic carbon content, it is not surprising that the terrestrial organic components are so predominant.

A possible explanation for the variability in geochemical data reported in the literature for hypersaline settings 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 and others (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 (1985) observed significant differences between the marl and gypsum samples. For example, the saturated hydrocarbons in the gypsum sample contained an even carbon preference in the C_{25}–C_{30} region, whereas the marl sample contained an odd carbon predominance in the same fraction. This finding is noteworthy because Mello and others (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 predominance is characteristic of evaporitic sequences (Welte and Waples, 1973; Dembicki and others, 1976; Spiro and Aizenshtat, 1977; Tissot and others, 1977; Guoying and others, 1980). ten Haven and others (1985) suggested that an input of "reworked" organic matter could obscure the even carbon predominance in the marl sample. Further, they found the C_{25} 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. In the present study, aryl isoprenoids in the C_{13+} range are abundant constituents of black shales and marlstones from the restricted basin but are minor components or absent entirely in 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. In the present study, 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 that 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 salinity may be nonuniform through the water column. The model proposed herein for deposition of black shales includes 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, high amounts of freshwater runoff could not only preclude development of high salinity in the upper water layer but would also carry large amounts of nonindigenous organic matter to the depositional site and thus obscure the geochemical characteristics of the biological system in the water (hypersaline) and sediments.

PETROLEUM SOURCE-ROCK POTENTIAL

In this section, we discuss the petroleum source-rock potential of organic-rich Desmoinesian rocks in the northern Denver Basin and southeastern Powder River Basin. We do not consider the petroleum potential of Pennsylvanian rocks in adjacent areas outside the Denver and Powder River Basins (Kansas, Oklahoma).

The present study supports the conclusions of previous investigations that organic-rich black shales of the middle member of the Minnelusa Formation (Powder River Basin) and stratigraphically equivalent rocks of the northern Denver Basin are good to excellent petroleum source rocks (Momper and Williams, 1979; Clayton and Ryder, 1984; Clayton, 1989). Despite the relatively low thermal maturity of these rocks, large amounts of extractable hydrocarbons are present (table 2). Therefore, the total amount of hydrocarbons available in these rocks over the broad area of the northern Denver and southeastern Powder River Basins is substantial (Clayton and Ryder, 1984).

The main limitations on these rocks as effective petroleum source rocks are the low thermal maturity and possible primary migration constraints. According to Momper (1978), primary migration requires generation of sufficient quantities of hydrocarbons to overcome adsorption of free hydrocarbons by the high-molecular-weight organic matter (kerogen). Sufficient generation of hydrocarbons is required to enhance porosity by microfracturing, opening of bedding partings, and reducing kerogen volume when kerogen converts to hydrocarbons. The high S_1 and extractable hydrocarbon yields of these organic-rich rocks (table 2) indicate that sufficient hydrocarbon generation may have occurred to enhance porosity according to Momper's (1978) criteria; however, the low ratios of free hydrocarbons to C_{org} suggest that adsorption by the kerogen may be an important barrier to primary migration.

On the other hand, shales having exceptionally high organic-matter content may expel oil at fairly low maturation levels because the organic phase constitutes a high proportion of the rock volume. A continuous oil phase may be present even though much of the hydrocarbon-generation capacity of the kerogen has not been achieved. Also, thin source beds interbedded with secondary carrier beds may expel hydrocarbons more readily than homogeneous thick source-rock sequences (Brooks and others, 1987).

Previous investigators (Sheldon, 1967; Stone, 1967) concluded that oil trapped in the reservoirs in the Permian Phosphoria Formation and Pennsylvanian Tensleep Sandstone of the Big Horn and Wind River Basins and the upper (Permian) and middle (Pennsylvanian) members of the Minnelusa Formation in the Powder River Basin is all derived from source rocks in the Phosphoria Formation along the western part of the Wyoming shelf and adjacent miogeocline in Idaho. They believed that oil was expelled from the Phosphoria Formation source rocks during Late Jurassic time and migrated eastward through the Tensleep Sandstone to present-day locations of the Wind River, Big Horn, and Powder River Basins. Geologists and geochemists generally agree that oils of the Big Horn and Wind River Basins are derived from Phosphoria Formation source rocks, but the source for the oils of the Minnelusa Formation is less clear (Clayton and Ryder, 1984). Our previous oil-source correlations indicate that at least some of the oils produced from the Minnelusa Formation were derived from Desmoinesian source rocks (Clayton and Ryder, 1984).

The unusually high porphyrin content of oils of the middle member (table 3) provides additional circumstantial evidence for the hypothesis that these oils were derived from black shales and marlstones of the middle member

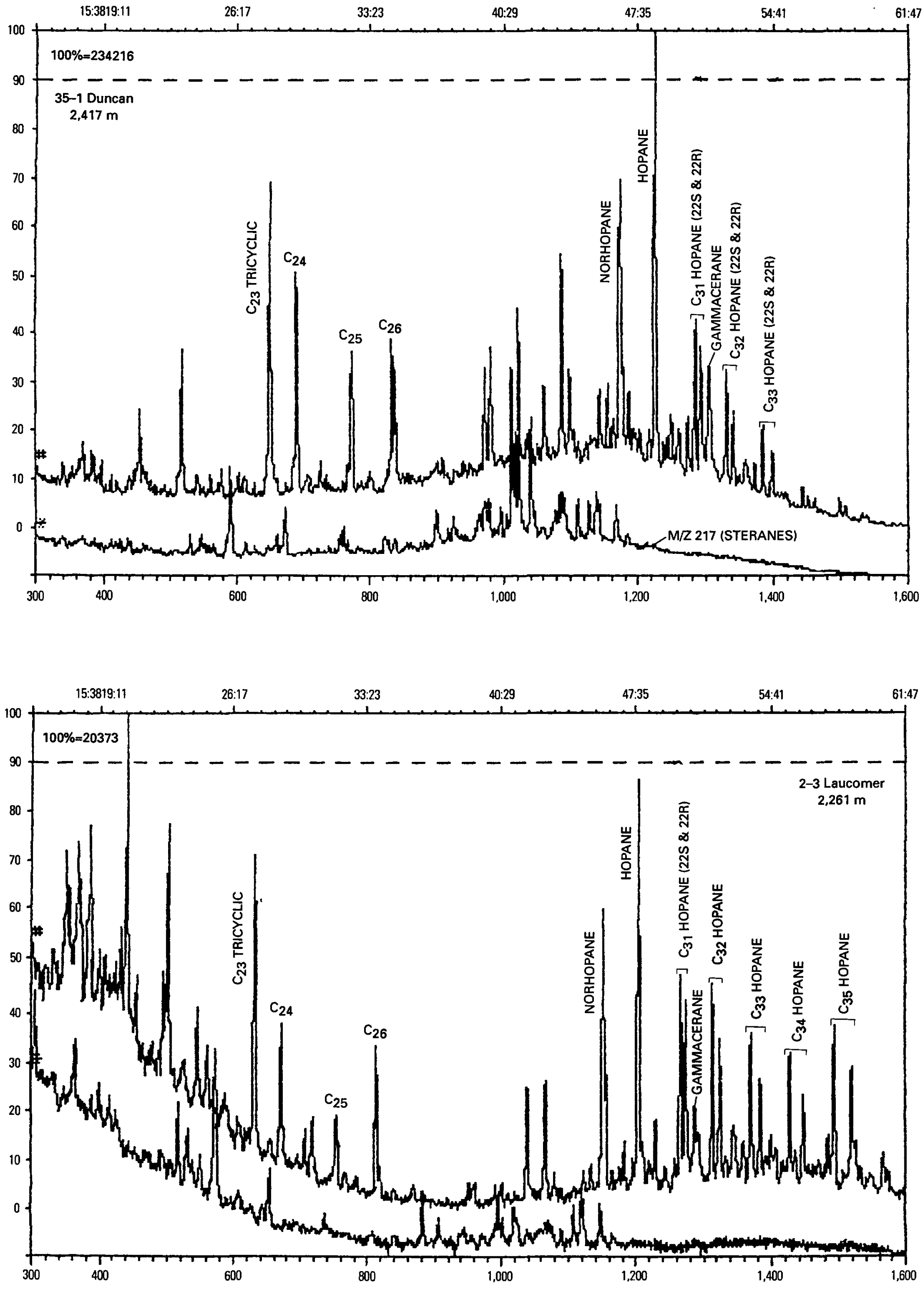
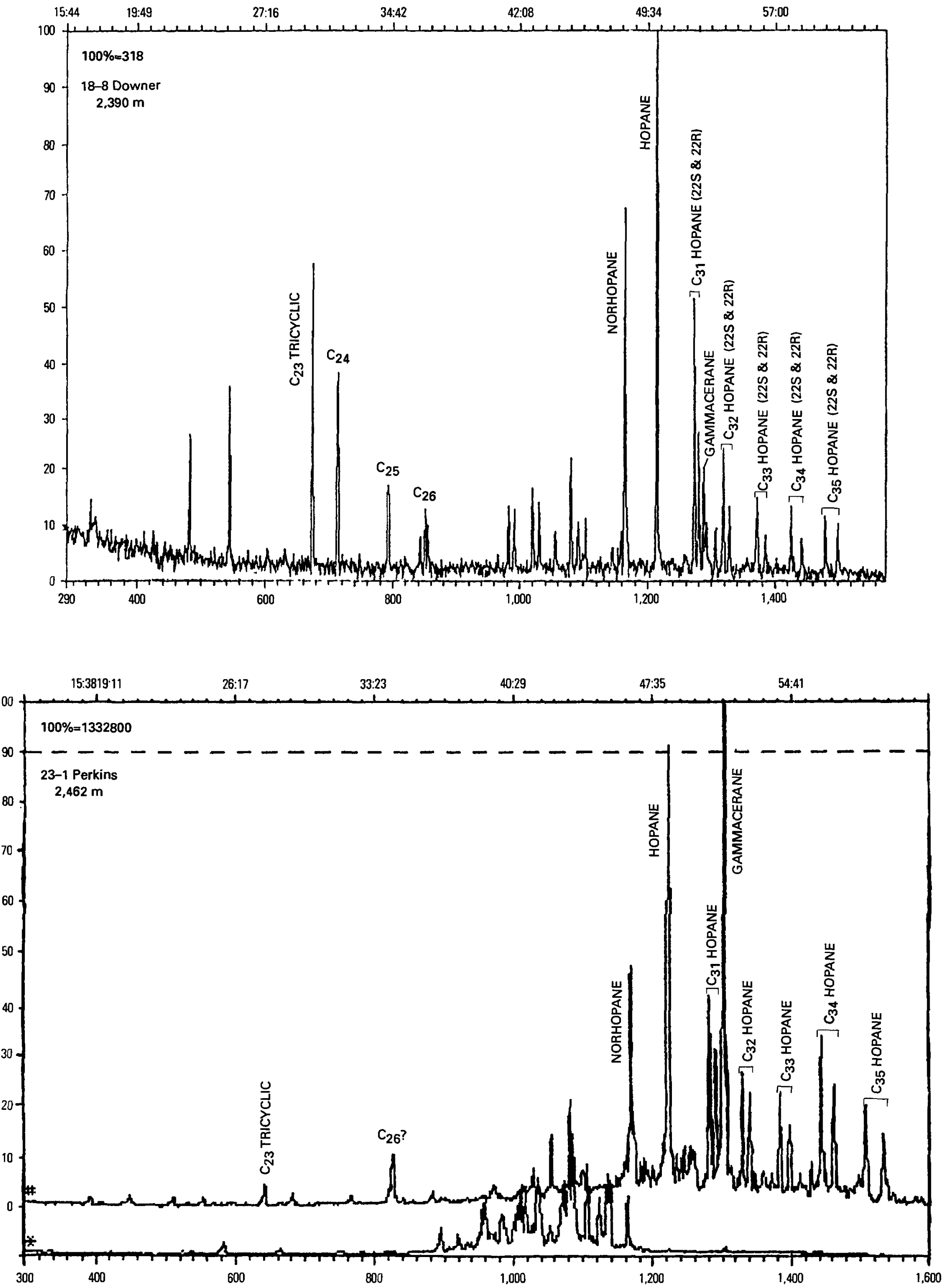


Figure 24 (above and facing page). Gas chromatography-mass spectrometry for selected samples showing some features thought to be characteristic of hypersaline environments. These are the only samples containing significant amounts of gammacerane and C_{35} hopane. See table 2 and figure 1 for well locations.



(Desmoinesian and Missourian age). It is noteworthy that porphyrin contents are high in oils of both the middle and upper member and that some of the porphyrin-rich oils have fairly high API gravity values (approximately 30 or greater) (fig. 12). In contrast, total porphyrin (VOP+NiP) contents are in the range 50 to less than 2 ppm in mature oils (API gravity about 30 or greater) produced from Paleozoic reservoirs of the Big Horn Basin (Baker and others, 1987). Although data of the present study do not fully resolve the question of the source rock for the Minnelusa Formation oil, long-distance migration might be expected to cause some loss of high-molecular-weight polar molecules such as

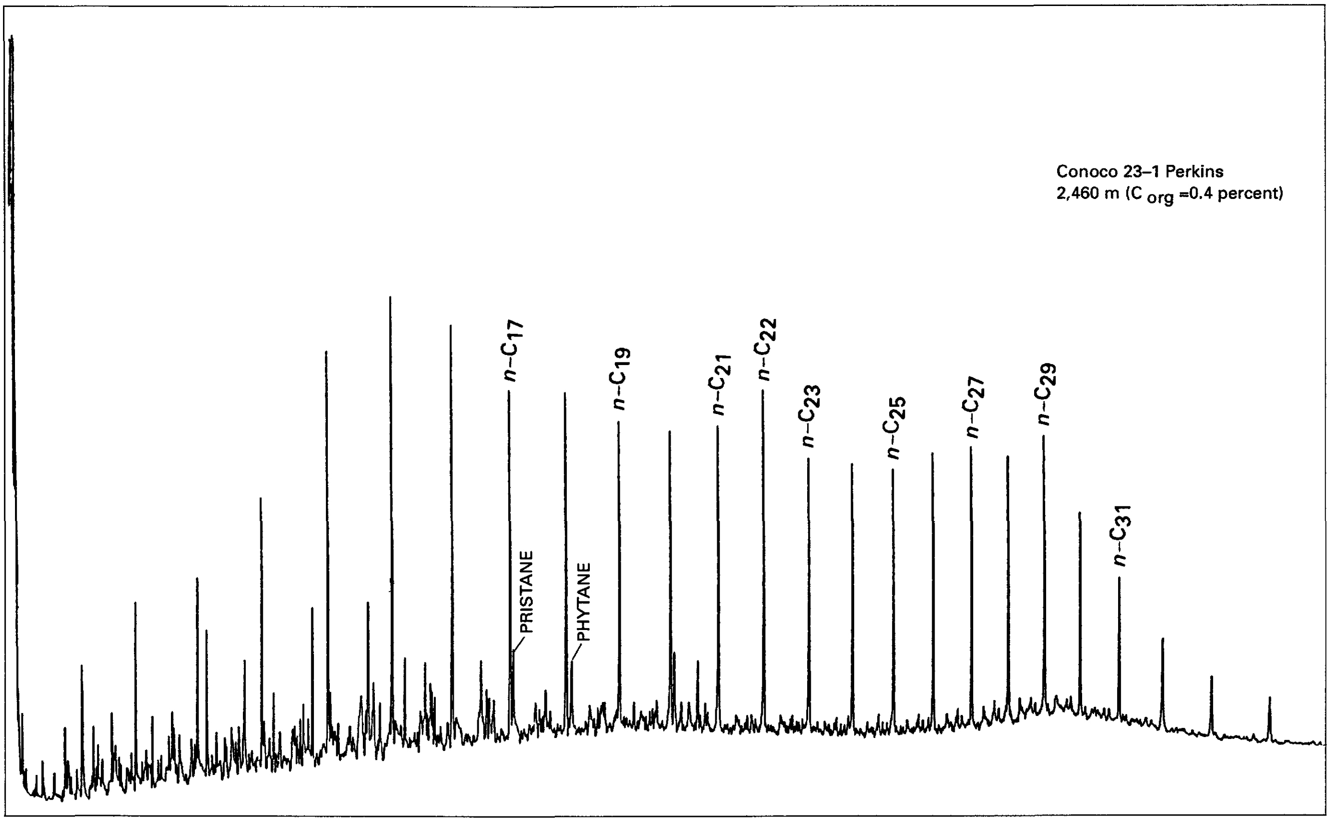


Figure 25. Gas chromatogram of rock extract containing high amounts of the proposed hypersaline indicator n-C_{22}. The odd carbon preference and high pristane/phytane ratio are interpreted to indicate input of terrestrial organic matter. See table 2 and figure 1 for well location.

porphyrins, particularly when oils thought to be of the same genetic family (oils of the Phosphoria Formation, Big Horn Basin) have generally lower porphyrin contents.

Detailed geochemical correlation of Desmoinesian or Missourian rock extracts and oils produced from the Minnelusa Formation of the Powder River Basin or equivalent rocks of the northern Denver Basin is difficult because only incipient oil generation has occurred and the expelled products (crude oils) are not compositionally identical to the residual bitumen in the source rocks. For example, the oils all have saturated to aromatic hydrocarbon ratios greater than 1.0 (Clayton and Ryder, 1984). In contrast, bitumens obtained by solvent extraction of powdered source-rock samples have low saturated to aromatic hydrocarbon ratios significantly less than 1.0 (table 1).

In order to compare the composition of oil produced from reservoirs with that of the oil phase in potential Desmoinesian source rocks, we extracted whole uncrushed core samples of source rocks. The rationale behind this experiment is that a continuous oil phase is present in the source rocks that can be extracted without extraction of bitumen still associated with the kerogen. The results are summarized in figure 26. The oil phase extracted from the potential source rocks has the same bulk composition as oils produced from reservoir rocks of Desmoinesian and Missourian age. The bitumen obtained by extracting the powdered source-rock samples contains more aromatic hydrocarbons and nonhydrocarbons (polars) than the oil phase (fig. 26). These results are consistent with the hypothesis that the oils were derived from the Desmoinesian source rocks.

Furthermore, this simple experiment demonstrates that oil-source correlations may be more strongly method dependent than previously recognized. A separate oil phase may be present in mature source rocks that represents the final step in the conversion of kerogen to oil via an intermediate bitumen phase (kerogen→bitumen→oil). Extraction of powdered rock samples yields not only the oil phase that may have begun primary migration but also extracts the bitumen that has not yet been converted to oil and does not correlate with the expelled product. We are presently conducting additional experiments to test this hypothesis. Preliminary results of these followup experiments are given in Price and Clayton (1992).

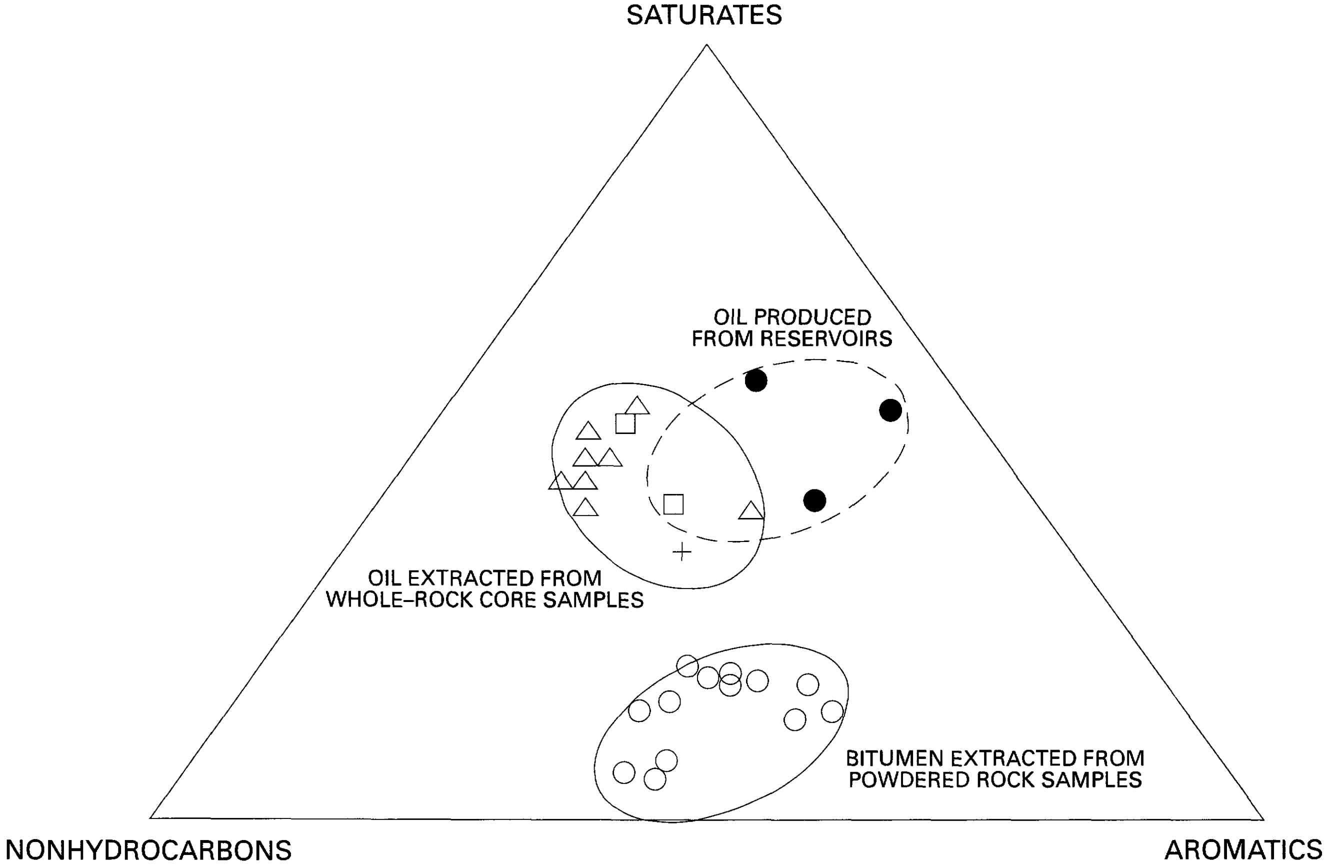


Figure 26. Ternary plot of relative abundances of saturated hydrocarbons, aromatic hydrocarbons, and nonhydrocarbons (polars) in rock extracts (both whole-core and crushed samples) and crude oils from the middle member of the Minnelusa Formation, northern Denver Basin. Open circles represent bitumen obtained from solvent extraction of powdered rock samples from the Bird 2–4 Murphy and Mitchell 34–12 Seegrist wells. Closed circles represent oil samples from producing wells. Squares (2–4 Murphy, 1,942 m), triangles (2–4 Murphy, 1,946 m), and plus (34–12 Seegrist, 1,394.5 m) represent oil obtained by extraction of whole core samples. See table 2 and figure 1 for well locations.

CONCLUSIONS

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 euxinic. High porphyrin contents resulted from a combination of high organic productivity caused by abundant nutrients in a warm shallow sea and a short oxygenated water column. It is not possible to interpret water salinity during deposition of the organic-rich rocks from either the geologic or organic geochemical data presently available, although it is likely that above-normal (>35‰) salinities prevailed at times. In the open-marine environment of eastern Colorado and adjacent areas of Kansas and Oklahoma, low porphyrin contents, high C/S ratios, and the absence of aryl isoprenoids indicate 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 contents in mixed type II–III organic matter are 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 commenced. 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.

Content 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. We suggest that preservation was enhanced by water-column stratification and euxinic conditions in the lower water layer.

High porphyrin contents in oils produced from both the middle and upper members of the Minnelusa Formation are consistent with, but do not prove, a local (middle member) source for these oils.

Extraction of organic-rich shale or marlstone using whole cores (rather than finely powdered samples) allows extraction of an *oil phase* from these oil-wet rocks that is compositionally distinct from the *bitumen* obtained from powdered samples. The oil thus obtained has a bulk composition similar to oils produced from reservoirs in the middle member of the Minnelusa Formation and from stratigraphically equivalent rocks. These rocks have apparently begun oil generation, and an oil phase separate from the bitumen formed in the rocks as primary migration commenced.

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