

Influence of Paleoenvironmental Factors on Preservation of Organic Matter in Middle Cretaceous Greenhorn Formation, Pueblo, Colorado¹

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ABSTRACT

Sedimentological and geochemical studies of the Upper Cretaceous Hartland Shale and overlying Bridge Creek Limestone Members of the Greenhorn Formation reveal close associations between abundance of current-induced sedimentary structures, extent of bioturbation, and type of preserved organic matter. Abundant hydrogen-rich organic matter (4-5 wt. %) and low sulfur to organic carbon ratios are characteristic of the laminated facies, which lack current-induced sedimentary structures. Sparse hydrogen-poor organic matter (0.1-0.5 wt. %) and relatively high sulfur to organic carbon ratios are characteristic of the bioturbated facies, which contain numerous sedimentary structures indicative of currents. The concentration of oxygen in the benthic environment and the degree of bioturbation of the sediment apparently were determined principally by the rate that oxygen was supplied advectively (by currents) rather than by the rate of oxygen consumption (by decomposition). Thus, paleoclimatic and paleo-oceanographic factors that influenced mixing and current strength in the water column profoundly affected the amount and type of organic matter preserved in these units. It is proposed that episodes of high river discharge lead to density stratification of the water column and in turn to quiescent oxygen-depleted bottom water and high preservation of organic matter, thus accounting for the intermittent widespread deposition of organic-rich strata during maximum transgression and depth of the Greenhorn sea. The lateral association of voluminous deltaic deposits with deep-water black shales in other elongate or restricted marine basins may have causes similar to those envisioned for the Hartland Shale and Bridge Creek Limestone Members.

INTRODUCTION

Organic geochemical data are widely used to characterize crude oils and evaluate potential source rocks of petro-

leum. With appropriate sampling, the amount and composition of organic matter preserved in sedimentary rocks have been shown to be useful indicators of environment of deposition, paleoclimate, and paleo-oceanographic conditions (e.g., Didyk et al, 1978; Arthur and Natland, 1979; Demaison and Moore, 1980; Tissot et al, 1980). The use of organic geochemical data for interpreting paleoenvironmental conditions in epicontinental seas is impaired, however, by a lack of comparative studies in which both detailed sedimentological and organic geochemical data are presented. This study was undertaken with the objective of integrating a wide range of sedimentological data with organic geochemical data to gain new insights into the chemical and physical factors that influenced widespread deposition of organic-rich strata during the middle Cretaceous (Cenomanian and Turonian) in the central Western Interior basin of North America.

The Bridge Creek Limestone Member and the underlying Hartland Shale Member of the Greenhorn Formation (Figure 1) were chosen as the focus of this study because of their potential as petroleum source rocks (Clayton and Swetland, 1980; Merewether and Claypool, 1980), the lateral continuity of individual beds (Hattin, 1971, 1975), their well-established biostratigraphic indices (Kauffman, 1969, 1977; Eicher and Worstell, 1970; Cobban and Scott, 1972), and the availability of radiometric age dates on major bentonites (Obradovich and Cobban, 1975). Fresh samples of the Bridge Creek and Hartland were obtained from a 295-ft (90-m) core (PU-79-Pueblo) drilled in 1979 near Pueblo, Colorado (Figure 2) by Princeton University, the U.S. National Museum, and the U.S. Geological Survey. The PU-79-Pueblo core starts in the upper Bridge Creek and is continuous down to the top of the Dakota Sandstone. The upper part of the core (Figure 1) includes the rhythmically interbedded limestone and marlstone or calcareous shale in the lowest 39 ft (12 m) of the Bridge Creek and 54 ft (16.5 m) of the underlying calcareous and marly shale in the Hartland. This upper part of the PU-79-Pueblo core was sawed lengthwise, and one half of it was impregnated with epoxy resin and replicated by means of continuous acetate peels (Figure 3). The other half was subsampled for sedimentologic and organic geochemical analyses.

Studies of the PU-79-Pueblo core reported here and in Pratt (1981) document the variation in small-scale sedimentary structures, body and trace fossils, and clay mineral content associated with differences in the amount and composition of organic matter preserved in the various lithofacies of the Hartland and Bridge Creek. From these

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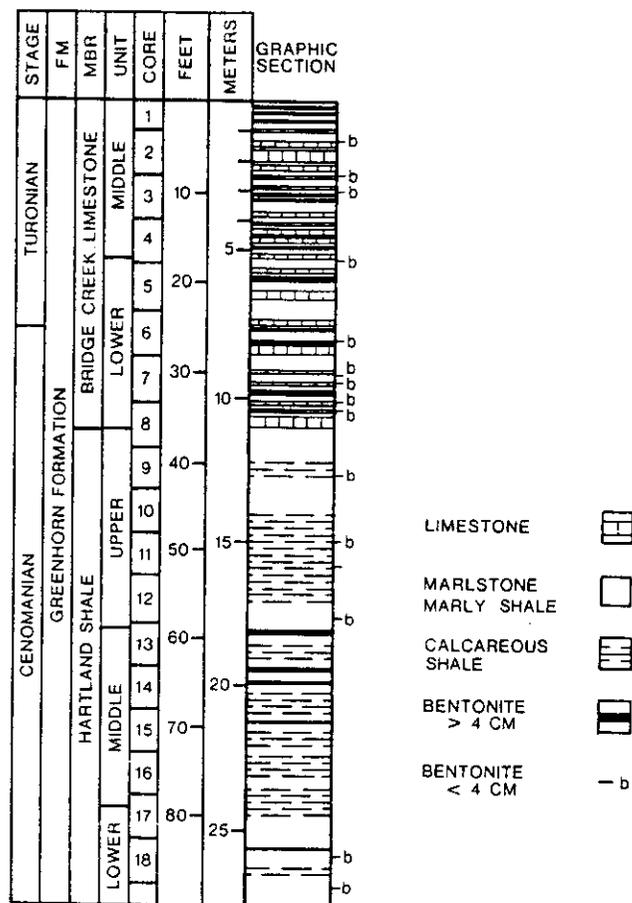


Figure 1—Stratigraphic units and rock types of Upper Cretaceous Greenhorn Formation in PU-79-Pueblo core (Princeton University, PU-79-Pueblo; NW¹/₄, NW¹/₄, NE¹/₄, Sec. 31, T20S, R65W.

data, it is inferred that the amount and composition of organic matter preserved in the sediment was determined largely by the concentration of oxygen in the bottom water and the extent to which the sediment was disrupted by burrowing organisms. Further, the close association between abundance of current-induced sedimentary structures, extent of bioturbation, and amount of organic matter suggests that the strength and frequency of benthic currents determined the rate at which oxygen was supplied to the bottom water and largely controlled the concentration of oxygen in the benthic environment.

GEOLOGIC SETTING

During the Late Cretaceous, the Western Interior seaway extended southward from the Arctic Ocean and northward from the Gulf of Mexico (Figure 2). At times of maximum transgression, such as the early Turonian, the seaway linked the Atlantic-Tethyan region with the Arctic (Jeletzky, 1971; Williams and Stelck, 1975). The position of the western shoreline in the early Turonian can be reconstructed from facies changes where marine shales grade into littoral and alluvial sandstones. The position of the eastern shoreline in the early Turonian is unknown, but

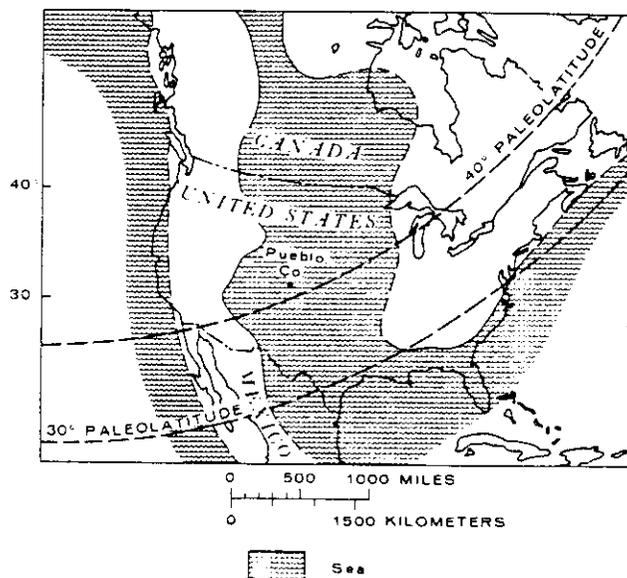


Figure 2—Early Turonian paleogeography and paleolatitude of North America. Map shows inferred maximum extent of Western Interior seaway during deposition of Greenhorn cyclothem (shoreline dashed where shallow water deposits are not preserved). Paleogeographic reconstruction of seaway is based on Jeletzky (1971) for Canada part and on Williams and Stelck (1975) and Reeside (1957) for U.S. and Mexico part. Cretaceous paleolatitude is based on Couillard and Irving (1975).

certainly it was east of a belt of fossiliferous marine beds that outcrop in northern and western Minnesota (Bergquist, 1944; Shurr, 1980) and in parts of Iowa and Kansas, making the width of the seaway at least 550 mi (900 km).

Along the Arkansas River and its tributaries immediately west of Pueblo, Colorado, all of the units in the Greenhorn cyclothem are well exposed. Cobban and Scott (1972) studied the ammonite faunas, Kauffman (1973, 1977) studied the bivalve assemblages, and Eicher and Worstell (1970) described the vertical distribution of planktonic and benthic foraminifera from these outcrops. Potassium-argon age determinations on major bentonite beds provide a chronostratigraphic framework for studying the Pueblo section (Obradovich and Cobban, 1975; Kauffman, 1977). Correlation of strata in the Pueblo core with nearby outcrops and with outcrops in Kansas is possible because of the regional continuity and parallel bedding of bentonites and limestones in the central basin area (Hattin, 1971, 1975).

The Hartland Shale Member and the overlying Bridge Creek Limestone Member of the Greenhorn Formation were deposited during maximum transgression of the Greenhorn sea. The Hartland is late Cenomanian in age, and the Bridge Creek is latest Cenomanian and earliest Turonian in age (Cobban and Scott, 1972; Kauffman, 1977). The base of the Turonian in the Western Interior generally is placed at the first bed above strata containing the diverse *Sciponoceras gracile* fauna. No conspicuous change in lithofacies is associated with the Cenomanian-Turonian boundary at Pueblo.

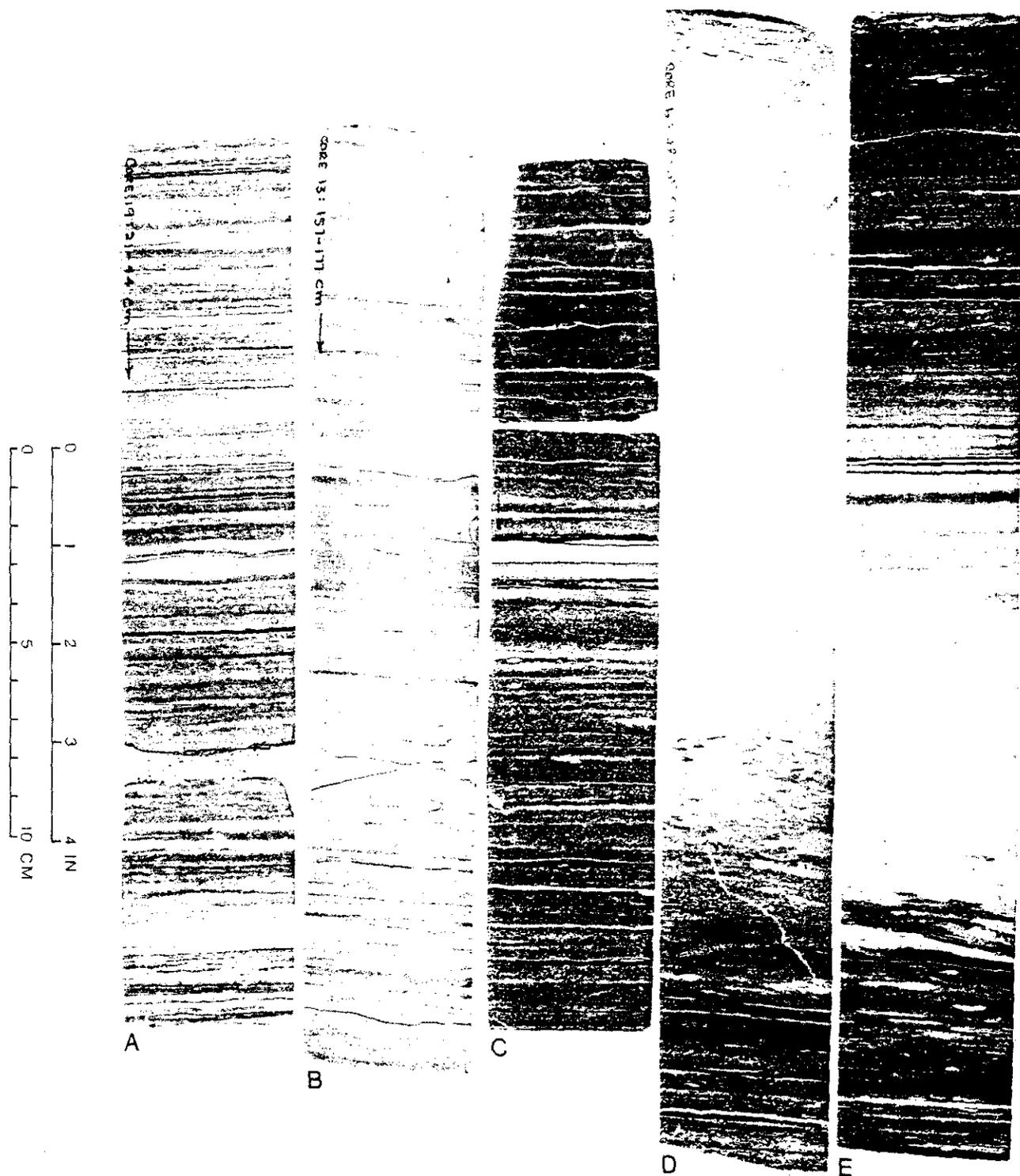


Figure 3—Acetate-peel replicas of representative sections from PU-79-Pueblo core. (A) Core 19: 44-21 cm. Well-sorted foraminiferal calcarenite/calcsiltite. Peel is interrupted by a 1-cm thick bentonite in lower half of section. (B) Core 13: 153-177 cm. Finely laminated calcareous shale containing a few thin intervals of microburrowed marly shale. Extremely fine, submillimeter laminations are preserved in lower half of section. Peel is interrupted by two cracks in lower half of this core section. Mottled light color of peel is due to relatively low carbonate content in this core section and to difficulty in obtaining a uniform acetate peel. Actual color of rock is dark gray to grayish black. (C) Core 9: 133-110 cm. Microburrowed marly shale containing a few lenses and laminae of foraminiferal calcarenite/calcsiltite and rare inoceramid fragments. Peel is interrupted by several partings and thin cracks within dark layers. (D) Core 6: 58-28 cm. Marly shale grading upward through marlstone into macroburrowed limestone. Note calcite-filled fracture that diagonally cuts across transitional marlstone. Peel is interrupted by a single thin crack near the bottom of the section. (E) Core 4: 29-0 cm. Thin macroburrowed limestone between two microburrowed marly shales. Peel is interrupted by several thin cracks in section.

LITHOFACIES AND SEDIMENTARY STRUCTURES

The polished core and acetate peels (Figure 3) of the PU-79-Pueblo core provide an unusually complete and detailed record of epicontinental pelagic sedimentation that was punctuated by ash-fall, current, and biogenic events. During deposition of the Hartland Shale Member, the benthic environment was relatively stable and changes in the composition of sediment occurred gradually. In contrast, the rhythmically interbedded limestones and marlstone or calcareous shale of the Bridge Creek Limestone Member reflect deposition in two alternating and distinct benthic environments.

Based on the distribution of major lithofacies (Table 1)

Table 1. Classification of Fine-Grained Calcareous Rocks

Percent Mud	Percent Carbonate	Predominantly Nonlaminated Rocks	Predominantly Laminated Rocks
0-25	75-100	Limestone	Laminated limestone*
25-50	50-75	Marlstone	Marly shale
50-90	10-50	Calcareous mudstone	Calcareous shale
90-100	0-10	Mudstone*	Mudshale*

*Not observed in the PU-79-Pueblo Core.

and sedimentary structures, five units are recognized in the PU-79-Pueblo core (Table 2). These units are named, in ascending order, the lower, middle, and upper units of the Hartland, and the lower and middle units of the Bridge Creek. The lower Hartland unit consists of marly shale interlayered with numerous laminae of foraminiferal calcarenite/calcsiltite and a few thin intervals of finely laminated calcareous shale (Figure 3A). The middle Hartland consists of nearly uninterrupted, finely layered calcareous shale composed of pelletal and silty laminae (Figure 3B). The upper Hartland consists of a basal marlstone overlain by marly shale containing many inoceramid fragments and laminae of foraminiferal calcarenite/calcsiltite (Figure 3C). The lower Bridge Creek unit consists of highly bioturbated limestone rhythmically interbedded with marlstone and calcareous mudstone (Figure 3D). The middle Bridge Creek is the uppermost unit recovered in the Pueblo core and consists of burrow-mottled limestone rhythmically interbedded with marly shale and marlstone (Figure 3D). The sedimentary structures and an interpretation of the environment of deposition for each unit are summarized in Table 2.

ANALYTICAL RESULTS

Substantial differences are evident in the amount and type of organic matter between the predominantly laminated lithofacies (marly and calcareous shales) and the predominantly nonlaminated lithofacies (limestones, marlstones, and calcareous mudstones) in the PU-79-Pueblo core. Thirty-eight samples of this core, encom-

passing all major lithofacies, were selected for organic geochemical and mineralogic study. Initial characterization of samples included determination of organic carbon (C_{org}), total sulfur (TS), carbonate carbon (C_{carb}), mineral composition, and pyrolysis assay of the organic matter. The results of these analyses are given in Table 3, and the analytical techniques are described in the Appendix. Based on the results of these initial analyses, 26 samples were chosen for analysis of extractable organic matter (Table 4). The extraction and chromatography techniques are given in the Appendix.

Optical examination of organic matter in kerogen separates and decalcified thin sections revealed that structured fragments (woody or cuticular particles) compose 10-15% of the total organic matter in the lower and middle Hartland. Structured fragments decrease in abundance upward through the upper Hartland unit and make up less than 10% of the total organic matter in the overlying lower and middle Bridge Creek units. Thus, recognizable terrestrial plant debris appears to have been a small component of the organic matter deposited within the Hartland and Bridge Creek Members. Organic matter in the predominantly laminated rocks is mostly pelletized or clumped amorphous material. In contrast, organic matter in the predominantly nonlaminated rocks is mostly finely disseminated amorphous material.

Organic-carbon contents of the PU-79-Pueblo core samples range from 0.1 to 5.1% (Table 3) and are linearly proportional to TS contents (Figure 4) except where pyrite nodules or pyritized burrows are present. However, the TS to C_{org} relationship for shale has a markedly different slope than that for limestone, marlstone, and mudstone. The ratio of TS to C_{org} has a mean value of 0.73-0.82 for the limestone, marlstones, and mudstone samples, and a mean value of 0.27-0.30 for the calcareous and marly shale samples (Table 5).

Pyrolysis data (Table 3) reveal substantial differences in the composition of organic matter preserved in the various rock types of the PU-79 Pueblo core. On a plot of hydrogen indices versus oxygen indices (Figure 5), three groups of samples can be distinguished. The limestone samples have low hydrogen indices and variable oxygen indices, and they plot in the general region of type III kerogen described by Espitalié et al (1977) and residual carbon described by Tissot et al (1980). The marlstone and calcareous mudstone samples plot along a vertical trend and have intermediate hydrogen indices. The marly and calcareous shale samples have high hydrogen indices and plot along a vertical trend. This shale trend follows the vertical portion of the maturation pathways for kerogen types I and II described by Espitalié et al (1977). The same three groups of samples can be distinguished using the ratio of pyrolytic hydrocarbon yield, ($S_1 + S_2$) to C_{org} , which is given in Table 5, converted to a percentage. The ratio of volatile hydrocarbon yield, (S_1) to C_{org} , is not useful for separating the types of organic matter because there is considerable overlap in the range of values for the various rock types.

Saturated hydrocarbons (C_{15+}) extracted from common rock types in the PU-79-Pueblo core and analyzed by capillary gas chromatography have similar distributions of n -

Table 2. Summary of Stratigraphy and Sedimentology for PU-79-Pueblo Core

Stratigraphic Unit	Lithofacies and Sedimentary Structures	Depositional Environment
Middle unit, Bridge Creek Limestone	Partially macroburrowed limestone rhythmically interbedded with marly shale. Limestone beds are less bioturbated and in sharper contact with adjacent marly beds than in the lower Bridge Creek unit. Marly shale contains roughly equal amounts of laminated strata and microburrowed strata. Lenticular foraminiferal calcarenite/calcsiltite is common in the microburrowed strata. Quartz silt (apparently wind blown) is abundant in some limestone beds.	Bottom water alternating between being moderately oxygenated (limestone) and poorly oxygenated to anoxic (marly shale). Benthic currents consistently present during deposition of limestone, intermittently present during deposition of microburrowed strata, and rare during deposition of laminated strata.
Lower unit, Bridge Creek Limestone	Highly macroburrowed limestone rhythmically interbedded with microburrowed marlstone and calcareous mudstone. Limestone beds are nearly homogeneous as a result of multiple phases of bioturbation. Contacts between limestone beds and marly or muddy beds are disrupted by bioturbation. Marly and muddy beds contain mostly microburrowed strata. Lenticular to wavy foraminiferal calcarenite/calcsiltite is common in the microburrowed strata. Quartz silt (apparently wind blown) is abundant in some of the limestone beds.	Bottom water alternating between being well oxygenated (limestone) and poorly oxygenated (marly and muddy beds), anoxic conditions rare. Benthic currents consistently present during deposition of limestone and intermittently present during deposition of marly and muddy strata.
Upper unit, Hartland Shale Member	Basal macroburrowed marlstone overlain by microburrowed marly shale containing a few thin intervals of laminated calcareous shale. Inoceramid fragments and foraminiferal calcarenite/calcsiltite are abundant in the basal marlstone, common in the marly shale, and rare in the calcareous shale. Scoured surfaces are common in the basal marlstone but rare in the overlying shale. A thin wavy-bedded layer (0.5 cm thick) composed of bone fragments, phosphatic pebbles, and quartz sand is scoured into the uppermost marly shale.	Bottom water moderately oxygenated. Erosive currents common during deposition of basal marlstone. Current strength and concentration of oxygen rapidly diminishing following deposition of basal marlstone. Intermittent gentle currents and poorly oxygenated bottom water present during deposition of microburrowed marly shale; quiescent and anoxic conditions present during deposition of the laminated calcareous shale. Current strength and oxygenation of bottom water increasing during deposition of uppermost marly shale.
Middle unit, Hartland Shale Member	Finely laminated calcareous shale interlayered with thin intervals of microburrowed marly shale. Inoceramid fragments and foraminiferal calcarenite/calcsiltite are rare. Several intervals contain sub-millimeter laminae composed of alternating pelletal and silty sediment.	Anoxic and quiescent bottom water present during deposition of laminated shale; poorly oxygenated bottom water and intermittent gentle currents present during deposition of thin intervals of microburrowed shale. Seasonal or longer cycles in surface-water conditions are recorded by alternating laminae of pelletal and silty sediment.
Lower unit, Hartland Shale Member	Microburrowed marly shale interlayered with thin intervals of laminated calcareous shale. Lenses, wavy laminae, and cross-laminated foraminiferal calcarenite/calcsiltite are abundant in the lower marly shale but decrease in abundance upward and are rare near the top of the unit.	Poorly oxygenated bottom water intermittently mixed by gentle to erosive currents during deposition of lower marly shale. Current strength and frequency decreasing through time. Erosive currents not present during deposition of upper marly shale. Anoxic and quiescent bottom water present during deposition of laminated calcareous shale.

alkanes (Figure 6). In extracts of shale and marlstone, pristane is the most abundant compound in the saturated fraction; n -C₁₅, n -C₁₇, and in some cases n -C₂₂ are the next most abundant constituents. In extracts of limestone, n -C₁₉ is the most abundant saturated hydrocarbon. Pristane/phytane ratios are between 1.1 and 3.8 in all samples of the core (Table 4) and are generally lower in the nonlaminated rock types than in the laminated ones. Relative to n -C₁₇ and n -C₁₈, pristane and phytane are less abundant in the nonlaminated rock types than in the laminated

ones. Alkane chains longer than n -C₂₈ are minor constituents of the saturates from all rock types. Unresolved branched paraffins and cycloalkanes form a noticeable hump (with a maximum at about n -C₂₂) on the chromatograms for the limestone and marlstone samples but not on chromatograms for the shale samples. Sterane and terpane biomarkers in the range of n -C₂₇ to n -C₃₂ are more abundant and diverse in extracts from the shale samples than in extracts from the limestone, marlstone, and mudstone samples.

Table 3. Whole Compositions and Pyrolysis Data for PU-79-Pueblo Core¹

Sample No.	Organic Carbon (C _{org})	Total Sulfur	CaCO ₃	Quartz	Discrete Illite	Illite/Smectite	Kaolinite	Chlorite	Production Index [S ₁ /(S ₁ +S ₂)]	H ₂ Index (S ₂ /C _{org})	O ₂ Index (S ₃ /C _{org})	T _{max} (°C)
Calcareous Shale												
9-75	3.3	0.94	46.0	21	8	15	2	1	.05	333	18	433
12-73	3.1	0.84	37.1	21	6	27	3	Tr ²	.03	357	17	441
13-73	3.1	0.75	34.4	26	14	16	2	1	.05	416	24	440
14-73	4.1	1.44	20.9	33	10	27	1	1	.04	383	27	432
15-72	2.9	1.07	38.9	20	14	20	3	1	.04	403	31	434
16-72	4.5	1.50	24.9	24	18	19	3	1	.04	380	11	439
18-73	4.4	1.23	40.6	24	3	20	3	Tr	.05	470	39	431
Marly Shale												
3-20	4.2	1.09	53.3	14	6	13	3	1	.04	590	25	434
3-55	2.6	0.77	67.9	12	3	9	3	Tr	.05	362	17	439
3-120	4.4	0.81	70.3	12	2	4	2	Tr	.05	537	38	434
4-108	5.1	0.93	54.4	13	3	18	2	Tr	.05	476	22	436
4-150	4.1	0.86	62.6	11	1	17	2	0	.04	503	35	435
6-20	4.2	1.04	68.1	11	1	10	2	Tr	.04	477	19	437
6-73	4.3	0.89	68.2	9	2	12	2	Tr	.05	404	42	431
10-73	2.3	0.93	59.9	16	6	11	2	Tr	.04	451	26	440
11-79	2.5	0.99	58.6	18	5	12	2	1	.06	447	19	434
17-73	3.3	1.01	50.2	18	7	15	5	Tr	.05	460	46	432
19-73	4.5	1.10	59.1	14	2	8	8	Tr	.05	445	34	437
Marlstone and Calcareous Mudstone												
5-72	0.9	0.90	72.1	13	1	11	Tr	Tr	.07	203	47	440
5-137	0.6	0.58	67.4	7	2	18	4	0	.07	193	25	442
7-6	1.6	1.15	45.0	19	Tr	31	Tr	Tr	.10	71	13	435
7-75	1.8	1.34	39.2	19	Tr	8	Tr	Tr	.03	114	17	442
8-5	0.1	0.91	67.7	7	2	21	1	Tr	UD ³	UD	UD	UD
8-30	0.5	0.72	66.7	6	2	20	1	1	.06	138	32	441
8-119	1.2	0.75	56.2	12	3	23	3	Tr	.04	324	35	441
13-20	1.4	0.39	70.6	12	2	12	Tr	Tr	.06	382	41	438
Limestone and Quartzose Limestone												
2-73	0.6	0.42	82.1	5	1	9	1	Tr	.05	122	20	436
2-119	0.3	0.18	85.7	8	Tr	3	Tr	Tr	.17	136	93	438
4-19	0.3	0.22	79.8	5	2	8	1	1	.14	158	103	439
4-72	0.4	0.15	86.6	6	UD	UD	UD	UD	.09	265	60	440
4-120	0.2	0.15	92.3	3	0	4	0	0	.35	68	31	425
5-20	0.2	5.66	77.6	5	0	7	Tr	Tr	.07	65	55	475
5-108	0.1	0.17	84.7	10	0	5	Tr	Tr	UD	UD	UD	UD
6-38	0.2	0.12	73.5	17	1	8	Tr	Tr	.07	130	70	433
6-124	0.3	0.13	64.7	22	1	11	Tr	Tr	.07	132	70	433
7-52	0.2	0.27	89.0	1	0	9	Tr	Tr	.00	9	38	442
7-91	0.2	0.11	82.7	12	0	5	Tr	Tr	.04	30	105	430
8-73	0.4	0.13	88.3	5	1	4	Tr	Tr	.51	10	69	439

¹Values are in weight percent except for ratios and T_{max}. See appendix for description of analytical methods and definitions of S₁, S₂, and S₃.
²Tr = trace.
³UD = unable to determine.

Consistent differences exist in the ratio of extractable organic matter (EOM) to organic carbon from the various rock types (Table 5). The nonlaminated rock types (limestone, marlstone, and calcareous mudstone) yield a mean 4.5 wt. % of the organic carbon as EOM compared to a mean yield of 7.5 wt. % for marly shale and 6.6 wt. % for calcareous shale. Thus, organic matter preserved in the nonlaminated types of rock is depleted in chloroform-extractable compounds (both hydrocarbons and nonhy-

drocarbons) compared to organic matter in the predominantly laminated types of rocks.

DEPOSITIONAL AND EARLY DIAGENETIC CONDITIONS

Sedimentological and geochemical data from the PU-79-Pueblo core indicate that the amount and type of organic matter in the various lithofacies correlate strongly with the extent to which the sediment was bioturbated. The rela-

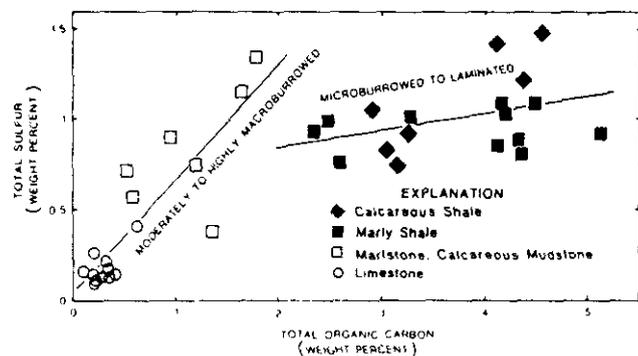


Figure 4—Plot of total sulfur vs. total organic carbon for samples of Greenhorn Formation from PU-79-Pueblo core. The two labeled lines are linear least-squares fits of the data from the macroburrowed samples and the microburrowed to laminated samples.

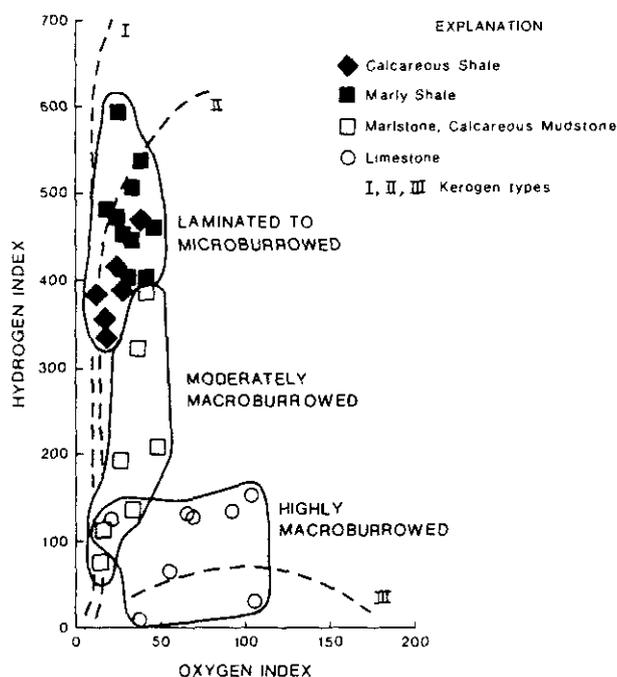


Figure 5—Plot of hydrogen indices vs. oxygen indices for organic matter in Greenhorn Formation from PU-79-Pueblo core. Kerogen types I, II, and III are from Espitalié et al (1977).

relationship between bioturbation and composition of organic matter in the PU-79-Pueblo core is shown clearly on a plot of hydrogen indices vs. oxygen indices (Figure 5). Samples that are predominantly laminated (shale) have substantially higher hydrogen indices than the predominantly nonlaminated samples, which are either moderately bioturbated (marlstone, mudstone) or highly bioturbated (limestone). Several lines of evidence indicate that this trend is not related to changes in the proportion of terrestrial organic matter deposited in the sediment or to differences in thermal maturity. All of the core samples are at the same level of thermal maturity, just prior to or at the onset of oil generation (early catagenic stage). Woody and cuticular particles make up less than 15% of the total

Table 4. Chloroform Extraction Data from PU-79-Pueblo Core¹

Sample No.	Organic Carbon (wt. %)	Extractable Organics/Organic Carbon (%)	Saturated Hydrocarbons (ppm)	Aromatic Hydrocarbons (ppm)	Nonhydrocarbons (ppm)	Pristane/Phytane (Pr/Ph)
Calcareous Shale						
9-73	3.3	5.9	577	456	981	2.4
13-73	3.1	5.4	462	553	990	2.5
15-72	2.9	7.4	660	627	950	2.1
Marly Shale						
3-20	4.2	7.2	798	835	1385	2.9
3-55	2.6	5.8	430	475	835	3.0
3-120	4.4	8.9	998	906	1942	2.8
4-108	5.1	7.3	948	971	1951	3.2
4-150	4.1	7.7	912	975	1412	3.2
6-73	4.3	6.2	676	864	1130	3.8
11-79	2.5	7.1	532	526	596	2.4
17-75	3.3	8.3	795	962	1070	2.1
19-75	4.5	7.4	997	1053	1270	2.8
Marlstone and Calcareous Mudstone						
5-72	0.9	4.6	118	120	200	2.9
5-137	0.6	5.4	75	91	143	3.2
7-6	1.6	3.2	126	143	252	3.7
7-75	1.8	3.3	137	94	193	3.4
8-30	0.5	3.7	46	45	99	2.3
8-119	1.2	5.1	140	159	311	2.7
13-20	1.4	7.1	236	236	496	2.6
Limestone and Quartzose Limestone						
4-72	0.4	4.5	35	38	108	UD ²
4-120	0.2	2.0	2	8	29	1.1
5-24	0.2	3.2	12	10	29	UD
6-38	0.2	5.6	28	26	62	UD
6-124	0.3	4.2	23	25	64	1.5
7-52	0.2	2.9	22	7	29	2.3
7-95	0.2	1.2	8	1	17	UD

¹See appendix for description of methods and definition of terms.
²UD = unable to determine owing to low concentration.

organic matter in the lower and middle Hartland units and less than 10% of the total organic matter in the remainder of the core. The *n*-alkanes extracted from the core have essentially smooth distributions without significant odd-carbon predominance and have only small amounts of the long-chain paraffinic compounds that are typical of the homologs from terrestrial plant debris (Bray and Evans, 1961; Clark and Blumer, 1967; Palacas et al, 1972). Thus, terrestrial organic matter appears to have been a relatively small percentage of the original organic matter and too small a contribution to account for the differences in composition of organic matter observed between the various facies of the PU-79-Pueblo core. The most obvious difference between the lithofacies in this core is the extent to which the sediment was bioturbated.

Studies of modern depositional environments have shown that the burrowing and scavenging activities of benthic organisms are controlled largely by the concentration of oxygen in the bottom water (Theede et al, 1969; and extensive references to earlier literature therein; Rhoads and Morse, 1971; Rosenberg, 1977). Based on these studies of modern marine environments, the density and size of burrows in the PU-79-Pueblo core are interpreted in terms of inferred oxygen concentrations in the bottom water at the time of deposition. This approach leads to an improved understanding of the paleo-

Table 5. Summary of Organic Geochemical Properties for PU-79-Pueblo Core¹

Lithofacies	Organic Carbon (C _{org} wt. %)			Ratio Total Sulfur (TS) to C _{org} (TS/C _{org})			Pyrolytic Hydrocarbon (PHC) to C _{org} [(S ₁ + S ₂)/C _{org} × 100]			Extractable Organic Matter (EOM) to C _{org} (EOM/C _{org} × 100)		
	n	w	\bar{x}	n	w	\bar{x}	n	w	\bar{x}	n	w	\bar{x}
Predominantly laminated												
Marly shale	11	2.5-5.1	3.8	11	.18-.40	.27	11	37.9-61.5	49.1	9	7.1-8.9	7.4
Calcareous shale	7	2.9-4.5	3.6	7	.24-.37	.30	7	35.2-49.8	41.0	3	5.4-7.4	6.6
Predominantly nonlaminated												
Limestone and quartzose limestone	12	.1-0.6	0.3	11	.37-1.70	.73	10	0.9-18.4	10.3	7	1.2-5.6	3.4
Marlstone and calcareous mudstone	8	.2-1.8	1.0	7	.29-1.38	.82	8	5.3-40.6	19.6	7	2.3-7.1	4.5

¹n = number of samples analyzed; w = range of values; \bar{x} = arithmetic means of values.

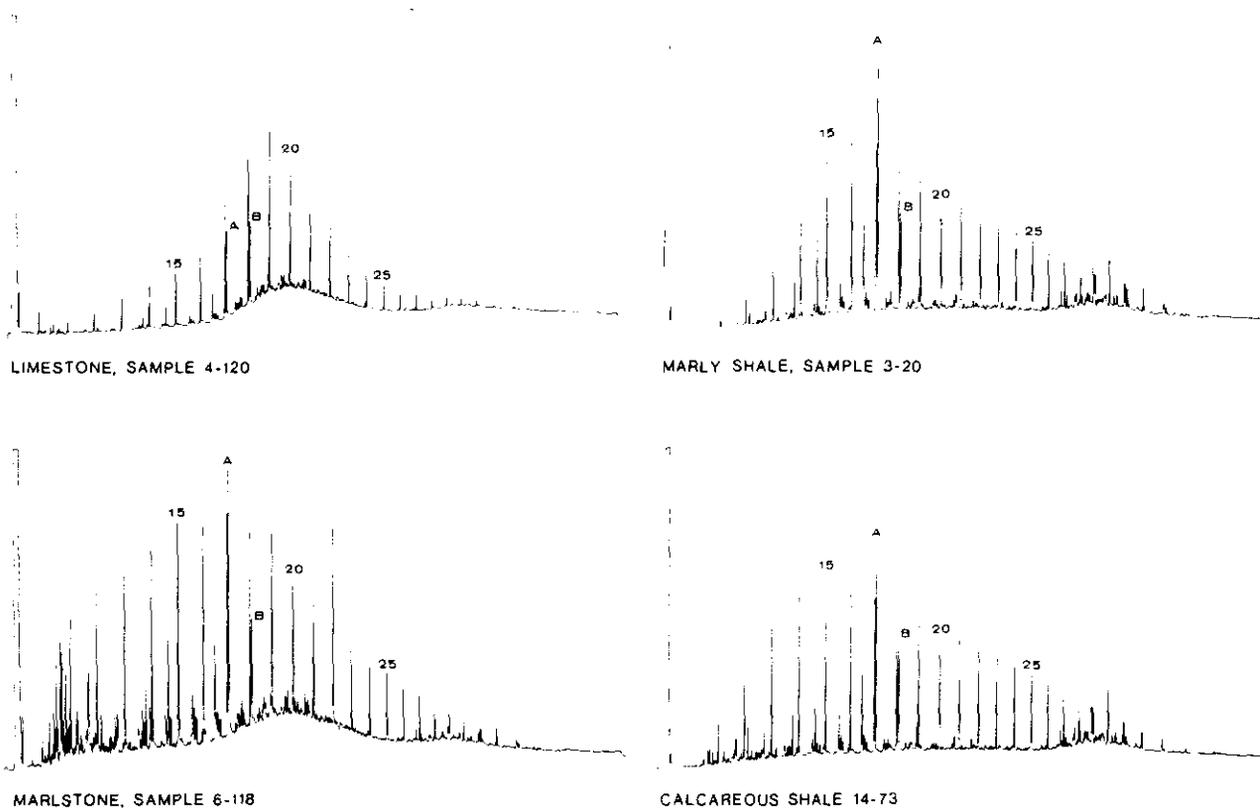


Figure 6—Representative gas chromatograms of saturated hydrocarbons (heptane eluates) extracted from limestone, marlstone, and shale in Greenhorn Formation from PU-79-Pueblo core. (A = pristane; B = phytane.)

oceanographic and paleoclimatic conditions present during the middle Cretaceous in the Western Interior region.

Effects of Bioturbation

Four degrees of bioturbation are distinguished in the PU-79-Pueblo core. Each degree is inferred to reflect the oxygen concentration in the bottom water during and shortly after deposition. "Highly macroburrowed strata" are extensively disrupted by vertical and horizontal burrows greater than 1 mm in diameter and are considered

indicative of well-oxygenated bottom water (e.g., limestone shown in Figures 3D, E). "Moderately macroburrowed strata" are partially disrupted by short vertical and extensive horizontal burrows greater than 1 mm in diameter and are considered indicative of moderately oxygenated bottom water (e.g., marlstone shown in Figure 3D). "Microburrowed strata" are slightly disrupted by horizontal burrows less than 1 mm in diameter and are considered indicative of poorly oxygenated (dysaerobic) bottom water (e.g., marly shale shown in Figure 3C). "Laminated strata" are finely layered and not disrupted by burrows

and are considered indicative of anoxic bottom water (e.g., calcareous shale shown in Figure 3B). The highly and moderately macroburrowed strata compose the predominantly nonlaminated lithofacies referred to earlier; the microburrowed and laminated strata are the predominantly laminated lithofacies.

As can be seen in peels of the Pueblo core (Figure 3), with decreasing bioturbation there is a decrease in the abundance of current-induced sedimentary features such as lenses and laminae of well-sorted foraminiferal calcarenite/calcsiltite and scour-and-fill features. The lack of current-induced structures indicates little mixing of the bottom water and slow advection of oxygen during times when microburrowed and laminated sediments rich in organic matter were deposited. The close association between current-induced sedimentary features, degree of bioturbation, and C_{org} suggests that a major control on the amount of organic matter preserved in the sediment was the rate at which oxygen was supplied to the bottom water by currents.

With increasing bioturbation there is a marked decrease in the hydrogen richness of organic matter remaining in the sediment (Figure 5). Compositional changes in the sedimented organic matter caused by bioturbation are indicated also by lower EOM/ C_{org} ratios (Tables 4, 5) and higher proportions of intermediate-molecular-weight branched alkanes and cycloalkanes relative to *n*-alkanes (Figure 6) in the macroburrowed samples (limestone and marlstone) compared to the microburrowed and laminated samples (shale). Regardless of the degree of bioturbation, however, the ratio of saturated to aromatic hydrocarbons is close to 1, and the ratio of pristane to phytane (Pr/Ph) is between 1 and 4 in the PU-79-Pueblo core samples (Table 4). The use of low Pr/Ph ratios as an indicator of anoxic paleoenvironments (Powell and McKirdy, 1973; Didyk et al, 1978) is not supported by data from the PU-79-Pueblo core. In particular, Pr/Ph ratios are much greater than 1 in the laminated facies, which clearly were deposited under anoxic conditions. The greater thermal maturity of the Pueblo section may explain why its Pr/Ph ratios are somewhat higher than the immature sediments described by Didyk et al (1978). However, relatively high Pr/Ph ratios (generally > 2) seem to be a primary genetic characteristic of extractable organic matter in Upper Cretaceous marine rocks of the Western Interior regardless of lithofacies (limestone vs. shale) or depositional environment (oxygenated vs. anoxic). Thermally immature, organic-rich chalks from the Upper Cretaceous Niobrara Formation in the eastern Denver basin, analyzed by Rice (1984), have Pr/Ph ratios greater than 2, which supports an interpretation of a primary origin for Pr/Ph ratios from the PU-79-Pueblo core. Thus, other organic geochemical properties must be sought as indicators of oxygenated vs. anoxic depositional conditions for the Bridge Creek and Hartland.

Bioturbation is an important influence on the composition of the pore water and solid constituents in the anoxic zone of sediments deposited under an oxygenated water column (e.g., Rhoads, 1974; Aller, 1978). Experimental studies by Aller (1978) have shown that burrowing and burrow irrigation (for respiration and feeding) increase the exchange of pore water with overlying water and,

thereby, enhance the diffusion of solutes into the sediment beneath the reworked zone. The relatively high ratios of total sulfur to organic carbon in the macroburrowed lithofacies of the Pueblo core (Figure 4) may reflect, in part, the biogenically enhanced diffusion of sulfate ions into the anoxic zone.

Anoxic Diagenesis of Organic Matter

In sediments deposited under anoxic water or below the zone of bioturbation and oxygenated pore water, sulfate reduction and methane generation are important processes in early diagenesis (Claypool and Kaplan, 1974; Goldhaber and Kaplan, 1974; Berner, 1981). The ubiquity of framboidal and euhedral pyrite in the PU-79-Pueblo core attests to the activity of sulfate-reducing bacteria during early diagenesis of these sediment (Kaplan et al, 1963; Berner, 1964; Goldhaber and Kaplan, 1975). Metabolic activities of anoxic bacteria in zones below those of sulfate reduction are more difficult to document in ancient sediments. Isotopically heavy authigenic carbonates sometimes form as a consequence of the removal of ^{12}C -enriched CO_2 during methane generation by anoxic bacteria (Irwin et al, 1977; Pisciotto and Mahoney, 1981). In addition, polar lipids that are attributable to archaeobacteria, particularly methanogens, have been identified in organic-rich rocks and petroleum by Chappe et al (1982). These "molecular fossils" provide evidence that reworking of sedimented organic matter by certain anaerobic bacteria is significant in the development of some source rocks containing extremely hydrogen-rich types of organic matter. Polar lipids were not analyzed in this study, but the presence of highly hydrogen-rich organic matter in the laminated lithofacies in the PU-79-Pueblo core may reflect metabolic activities of microbes living below the zone of sulfate reduction.

In the moderately and highly macroburrowed lithofacies, scavenging by burrowing organisms and associated oxidative processes appear to have removed nearly all of the organic matter from the sediment as it passed through the bioturbated zone. In the underlying anoxic zone, the residual organic matter was further decomposed by a microbial assemblage that included sulfate-reducing bacteria. High rates of sulfate-ion diffusion into those sediments that were highly irrigated by burrows are reflected in high TS/ C_{org} ratios for the predominantly nonlaminated lithofacies. The fate of organic matter in the microburrowed and laminated lithofacies was quite different than in the macroburrowed lithofacies. Scavenging of sedimented organic matter by benthic organisms in the microburrowed sediment was inefficient and limited to the uppermost few millimeters; there is no evidence of scavenging activities in the laminated sediments. The ratios of TS/ C_{org} are lower and organic carbon contents are higher in the microburrowed and laminated lithofacies than in the macroburrowed lithofacies (Figure 4). Because there was abundant organic matter in the microburrowed and laminated sediments, it is possible that low rates of sulfate diffusion limited the metabolism of sulfate-reducing and associated bacteria. Other groups of anaerobic bacteria,

however, probably were active in these organic-rich sediments. The relatively hydrogen-rich type of organic matter and high content of extractable organic compounds in the marly and calcareous shale are probably a result of relatively unoxidized organic matter reaching the sediment (rapidly transported through the water column in pellets) and conversion of some amount of this sedimented organic matter into anaerobic-bacterial biomass.

PALEO-OCEANOGRAPHIC AND PALEOCLIMATIC CONDITIONS

The shape of the Western Interior seaway (Figure 2) suggests that its connections with the Atlantic-Tethyan and circumpolar oceans were restricted during all but the most transgressive phases of its history. Voluminous deltaic and nonmarine sediments preserved along the western margin of the basin (Weimer, 1960) were deposited by numerous large rivers raining into the seaway from the Sevier highlands. In addition, the absence of many normal marine organisms from the faunas in the Western Interior basin suggests that salinity of the seaway was usually less than normal marine salinity (Reeside, 1957; Kauffman, 1969, 1977).

The distribution of clay minerals in the PU-79-Pueblo core (Figure 7) indicates substantial variations in the

amount of discrete illite entering the basin during deposition of the Hartland Shale and Bridge Creek Limestone Members. Discrete illite, clay-size quartz, and woody or cuticular organic particles are considered indicators of river-borne detritus that settled out of the water column over the central basin area (Pratt, 1981). The amount of discrete illite can be quantified and, therefore, is used to evaluate the riverine input to the seaway. From the data in Table 3, it is evident that the weight percent of discrete illite is highest in the marly and calcareous shale (average 6.6 wt. %), intermediate in the marlstone and calcareous mudstone (average 1.5 wt. %), and lowest in the limestone (average 0.5 wt. %). A relationship between abundance of discrete illite and rock type is also shown in Figure 7. In comparison, mixed-layer illite/smectite dominates the clay mineral fraction of all rock types in the core (Figure 7), and the weight percentage of illite/smectite (Table 3) does not vary systematically with rock type. The volume of river discharge into the seaway apparently controlled the abundance of discrete illite, and a combination of river discharge and wind dispersal of volcanic ash controlled the abundance of illite/smectite in the Hartland and Bridge Creek. River discharge was highest during deposition of calcareous shale in the Hartland (highest weight percent discrete illite) and lowest during deposition of limestone beds in the Bridge Creek (lowest weight percent discrete illite). In terms of climate, limestone beds reflect dry periods, whereas calcareous shale reflects wet periods. Intermediate climatic conditions are inferred for the marly shale and mudstone beds. Thus, climatic cycles of dry phases alternating with wetter conditions apparently existed during deposition of the rhythmically bedded lower and middle Bridge Creek.

Based on evidence of large fluctuations in runoff entering the seaway, many rivers draining into the seaway from the western highlands, a subtropical to warm-temperate climate (Kauffman, 1973), and relatively deep water, it is proposed that buoyant plumes of brackish water and suspended mud intermittently extended from the western shoreline nearly across the seaway. Seasonal and longer term fluctuations in rainfall, river discharge, wind strength, and sea surface area controlled the areal extent and thickness of this brackish-water layer. During maximum transgression of the Greenhorn sea, strong salinity stratification of the water column would have developed during wet periods, which were characterized by seasonally high rainfall and river discharge. Strong stratification decreased the effects of wind-driven currents and turbulent mixing in the water column, thereby leading to weak circulation or stagnation of the bottom water. A thoroughly mixed water column would have existed during dry periods, which were characterized by low annual rainfall and river discharge. During deposition of all the Hartland, except the uppermost few feet, the central seaway appears to have been moderately to strongly salinity stratified with little or no oxygen in the bottom water. Weakly stratified conditions alternated with thoroughly mixed conditions during deposition of the uppermost Hartland and the rhythmically bedded lower Bridge Creek. Moderately to strongly stratified conditions alternated with thoroughly mixed conditions during deposition of the rhythmically bedded middle unit of the Bridge Creek.

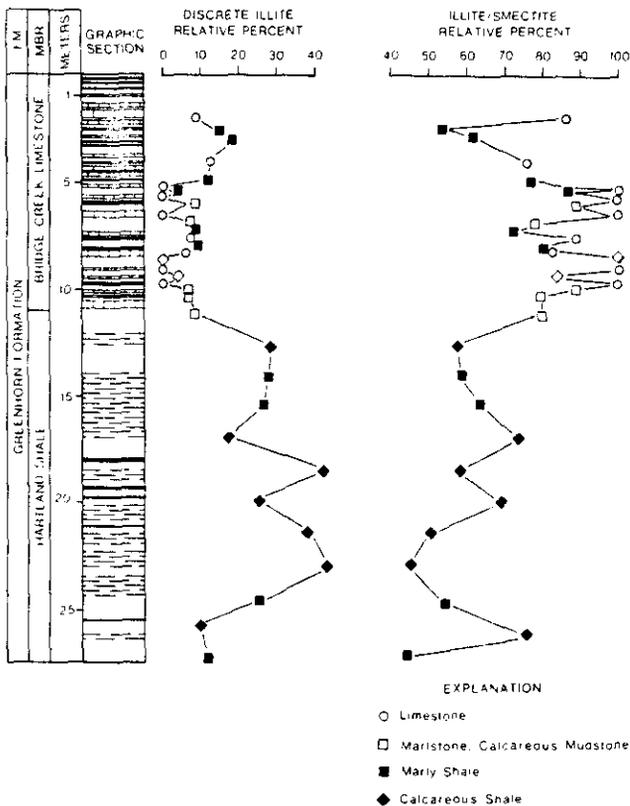


Figure 7—Relative percentages of discrete illite and mixed-layer illite/smectite clay for Greenhorn Formation from PU-79-Pueblo core.

A similar cause-and-effect chain from heavy rainfall, to a stratified water column, to stagnant bottom waters and organic-rich sediments is widely invoked to explain the formation of sapropels in the Mediterranean during the late glacial and early Holocene (e.g., Luz, 1979; Adamson et al, 1980; Rossignol-Strick et al, 1982). The deposition of organic-rich strata in restricted basins during other short geologic intervals may be related, in some cases, to climatic factors similar to those envisioned for the middle Cretaceous Greenhorn Formation and recent sapropels of the Mediterranean. It is important to note that the proposed relationship between climate and organic richness of the sediment requires a sufficiently deep water column for the establishment of stable salinity stratification. Recognizing the possibility of association between voluminous deltaic deposits and deeper water black shales is useful in predicting the distribution of potential petroleum source rocks in elongate or otherwise restricted marine basins that received high river input.

CONCLUSIONS

Study of the amount and composition of organic matter and sedimentary structures in the Greenhorn Formation from the PU-79-Pueblo core has resulted in a better understanding of the factors that influenced widespread deposition of strata rich in organic matter during the middle Cretaceous in the Western Interior basin. Sedimentological and organic geochemical data indicate a close association between paleoclimate, salinity of the surface-water layer, strength of currents in the bottom water, and the amount and composition of organic matter preserved in the sediment. Paleoclimatic and paleo-oceanographic conditions in the Western Interior ranged from dry periods characterized by a well-mixed water column, highly macroburrowed sediments (now limestone), and low preservation of organic matter, to wet periods characterized by salinity stratification of the water column, finely laminated sediments (now calcareous shale), and high preservation of organic matter.

Based on the lateral association of relatively deep-water black shales with extensive fluviodeltaic deposits in the Cretaceous Western Interior, it is proposed that in tropical to temperate climatic regimes, heavy rainfall channeled by large rivers into long linear or otherwise restricted marine basins can induce development of a brackish-water surface layer. If the sea is sufficiently deep, salinity and density contrasts between this surface layer and the underlying water layer can lead to stable stratification of the water column and sluggish circulation or stagnation of the bottom water. Reduced currents and reduced advection of oxygen to the benthic environment limit reworking of the sediment by burrowing organisms and the associated deep diffusion of oxidants, thereby enhancing preservation of organic matter.

The close association between current-induced sedimentary structures, extent of bioturbation, and the amount and hydrogen richness of organic matter in the PU-79-

Pueblo core suggests that the concentration of oxygen in the bottom water was primarily controlled by the strength and frequency of benthic currents rather than by the rate of oxygen consumption in the benthic environment. In the Western Interior basin and other restricted marine basins, paleoclimatic and paleogeographic factors that affect vertical mixing and benthic currents can influence profoundly the amount and composition of organic matter preserved in the sediment.

APPENDIX

METHODS OF GEOCHEMICAL ANALYSES

Carbon and Sulfur Content

Total carbon and organic content were measured using a LECO³ induction furnace and a volumetric CO₂ analyzer. Prior to combustion of the organic carbon samples, 250 mg of powdered rock were treated with 0.5 N HCl for 24 hr, followed by 1 N HCl for 15 min to remove mineral carbon. The insoluble residues were concentrated on a glass filter, using rinses of distilled water and then dried in a 60°C (140°F) oven. Carbonate carbon content was calculated as the difference between total carbon and organic (acid-insoluble) carbon. Total sulfur content was measured using a LECO induction furnace and sulfur analyzer. Duplicate measurements of total carbon, organic carbon, and total sulfur were made on each sample. The reported values are the averages of these two measurements.

Pyrolysis of Organic Matter

Thermal evolution (pyrolysis) was done using a Rock-Eval instrument that was calibrated by analysis of a synthetic standard (*n*-C₂₀H₄₂) and solid CO₂. S₁ is the integral of the first hydrocarbon peak detected after heating the powdered sample in flowing helium at 250°C (482°F) for 5 min. This peak represents the free or adsorbed hydrocarbons in the rock and is roughly proportional to the content of organic matter that can be extracted from the rock with organic solvents. S₂ is the integral of the second hydrocarbon peak, produced mainly by cracking of solid organic matter when the rock is heated from 250° to 550°C (482° to 1022°F) at a rate of 25°C (45°F) per min. These hydrocarbons are probably produced by thermal cracking of the kerogen and to a small degree by the cracking of resins and asphaltenes (Espitalié et al, 1977). S₃ is the integral of the carbon dioxide peak measured on a split of the gas trapped during the heating interval from 250° to 390°C (482° to 734°F). This temperature range is lower than the temperature of thermal dissociation for carbonate minerals under most circumstances. Therefore, S₃ is considered to be a measure of the CO₂ produced by pyrolysis of the organic matter in the rock. S₁, S₂, and S₃ are reported in milligrams of hydrocarbon or CO₂ per gram of dry rock.

The hydrogen index is defined as S₂ divided by the organic carbon content of the rock (S₂/C_{org}) and is reported in milligrams of hydrocarbon per gram of organic carbon. The oxygen index is defined as S₃ divided by the organic carbon of the rock (S₃/C_{org}) and is reported in milligrams of CO₂ per gram of organic carbon.

Thermal maturity is interpreted from the temperature of maximum yield of pyrolytic hydrocarbons [T_{max}(S₂)] and the transformation ratio or production index [S₁/(S₁ + S₂)]. In general, the transition from immature to mature petroleum source rocks is indicated by T_{max}(S₂) values of about 435°C (815°F) and production indices of about 0.1 (Tissot and Welte, 1978).

To minimize the effects of complicating factors on whole-rock pyrolysis (Katz, 1981; Orr, 1983), the amount of whole-rock powder that was pyrolyzed was varied such that each sample contained close to 0.5 mg of organic carbon. In addition, pyrolysis was done on 15 representative pairs of whole-rock and decalcified (acid-leached) samples. The data from these two sets of sam-

³Use of brand or trade names in this report is for descriptive purposes only and does not imply endorsement by the U. S. Geological Survey.

ples were used to evaluate the influence of the carbonate matrix and varying concentrations of organic carbon on pyrolytic results (Table 6). The organic carbon contents and clay mineral compositions of the decalcified limestone and marlstone samples are comparable to the compositions of the whole-rock shale samples. The data in Table 6 show that the hydrogen indices of the decalcified samples are consistently higher than the whole-rock samples, but the trend of sharply decreasing hydrogen indices, from shale to marlstone to limestone, is the same for both sets of samples. The oxygen indices are somewhat lower for the decalcified samples than the whole-rock samples and do not appear to vary systematically with rock type.

Chloroform Extraction and Elution Chromatography

Chloroform extraction was done for 24 hr in a Soxhlet apparatus, using 25 to 40 g of powdered rock. Bitumen concentration was determined by weight from an aliquot of extract concentrated by evaporation at room temperature under flowing nitrogen. The bitumen was treated with *n*-heptane and filtered to separate the asphaltene fraction. The deasphalted extracts were fractionated by column chromatography, eluting successively with heptane, benzene, and 1:1 benzene-methanol. The

asphaltene precipitates and each of the three eluates were dried under flowing nitrogen and weighed to determine concentrations.

Saturated hydrocarbons (heptane eluate) were analyzed on a Hewlett Packard 5880A series gas chromatograph, using a 60 m by 0.315 mm capillary column coated with J and W Scientific DB5. The programmed conditions were from 80°C to 400°C (176° to 752°F) at 4°C (7.2°F) per min.

Clay Mineral Content

Clay mineral groups were identified from x-ray diffraction spectra generally following the techniques described by Schultz (1964, 1978). Approximately 10 g of powdered rock was treated with 3% acetic acid buffered with sodium acetate to remove the carbonate fraction. Hydrogen peroxide (30%) was added in small amounts when necessary to disaggregate samples rich in organic matter. The insoluble residue was neutralized with distilled water and dispersed with an ultrasonic probe. The fraction less than 2 μm in size (clay size) was separated by settling. The clay-size fraction was vacuum-mounted onto porous ceramic tiles or smear-mounted onto glass slides. X-ray diffractograms were taken successively of the sample when air-dried, saturated with ethylene glycol vapors, and heated to 300°C (572°F). Per-

Table 6. Pyrolysis Data for Whole-Rock and Decalcified Pairs of Samples from PU-79-Pueblo Core

Sample No.	Type of Sample	Organic Carbon (wt. %)	Production Index $[S_1/(S_1 + S_2)]$	H ₂ Index (S_2/C_{org})	O ₂ Index (S_3/C_{org})	T _{max} (°C)
3-20	Whole rock	4.2	.04	590	25	434
3-20	Decalcified	8.9	.05	656	22	434
3-120	Whole rock	4.4	.05	537	38	434
3-120	Decalcified	4.7	.05	610	24	432
4-72	Whole rock	0.4	.09	265	60	440
4-72	Decalcified	2.5	.05	336	12	440
4-150	Whole rock	4.1	.04	503	33	435
4-150	Decalcified	10.8	.04	664	21	433
5-19	Whole rock	0.2	.01	65	55	475
5-19	Decalcified	0.9	.03	98	23	481
5-72	Whole rock	0.9	.07	203	47	440
5-72	Decalcified	3.4	.08	214	11	432
6-38	Whole rock	0.2	.07	130	70	433
6-38	Decalcified	0.8	.06	240	23	429
6-124	Whole rock	0.3	.07	130	70	433
6-124	Decalcified	0.8	.09	280	16	429
6-73	Whole rock	4.3	.05	404	42	431
6-73	Decalcified	13.4	.05	580	33	430
7-6	Whole rock	1.6	.10	71	13	435
7-6	Decalcified	2.9	.14	98	15	432
9-70	Whole rock	3.3	.05	333	18	433
9-70	Decalcified	6.7	.07	432	27	432
14-73	Whole rock	4.1	.04	383	27	432
14-73	Decalcified	5.2	.06	415	20	433
15-71	Whole rock	2.9	.04	403	31	431
15-71	Decalcified	4.7	.06	478	20	434
17-69	Whole rock	3.3	.05	460	46	432
17-69	Decalcified	6.6	.06	515	29	431
18-73	Whole rock	4.4	.05	470	39	431
18-73	Decalcified	7.5	.06	506	28	430

centages of discrete illite and mixed-layer illite/smectite clay were determined as described by Schultz (1978). The percentage of clay in the rock was calculated by assuming that calcite + quartz + pyrite + organic matter + clay = total rock. Organic matter was estimated as $1.5 \times C_{org}$. Pyrite was estimated as $1.87 \times$ total sulfur.

Quartz Content

Quartz content was determined by quantitative x-ray diffractometry of whole-rock powders, following a method described by Cubitt (1975). Splits of each sample were spiked with 0.005 g and 0.01 g quartz powder. The weight percent quartz was calculated by the difference in area of the 26.6° reflection between the whole rock, the 0.005-g spike, and the 0.01-g spike. Reproducibility of results was good, and the calculated weight percent quartz increased linearly with the integrated peak area above about 8 wt. % quartz.

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