DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

Sulfur/carbon Ratios and Sulfur Isotope Composition of Some
Cretaceous Shales From the Western Interior of North America

by

Donald L. Gautier[1]

Open-File Report 85-514

[1]Denver

CONTENTS

Page

ILLUSTRATIONS

TABLES

SULFUR/CARBON RATIOS AND SULFUR ISOTOPE COMPOSITION OF SOME CRETACEOUS SHALES FROM THE WESTERN INTERIOR OF NORTH AMERICA

By Donald L. Gautier

ABSTRACT

Cretaceous marine sediments in the Western Interior of North America were a significant sink for organic carbon and sulfide sulfur. The Cretaceous seaway has long been suspected of having had restricted circulation, and Cretaceous shales may thus be expected to display sulfur, carbon ratios and sulfur isotopic values different from marine rocks and sediments deposited beneath fully oxygenated waters. Sulfur/carbon ratios from 129 samples analyzed for this study average 0.67, a value greater than that observed in recent marine sediments and much higher than the calculated global value for the Cretaceous. Isotopic compositions of pyrite sulfur vary systematically with the depositional environment and therefore with organic carbon abundance and organic matter type. Samples with organic carbon in excess of 4 weight percent contain disseminated pyrite which is extremely depleted in ^{34}S (mean $\delta^{34}S = -31^o/oo$); these samples are laminated clay shales that contain hydrogen-rich (Type II) organic matter. Samples containing less than 1.5 percent organic carbon display relatively "heavy" but wide ranging $\delta^{34}S$ values ($\delta^{34}S = -34.6$ to $+16.8^o/oo$; mean $\delta^{34}S = -12.4^o/oo$); these samples are highly bioturbated and contain only Type III, hydrogen-poor organic matter probably derived from terrestrial higher plants. Samples containing intermediate amounts of organic carbon contain pyrite with $\delta^{34}S$ values averaging $-25.9^o/oo$ and containing mixed Type II and Type III organic matter. The presence of higher organic carbon and the preservation of hydrogen-rich organic matter generally correlate with slow sedimentation unlike many recent marine sediments. Samples rich in organic carbon and containing isotopically "light" sulfide sulfur accumulated beneath anoxic and perhaps sulfidic bottom waters. Samples with intermediate organic matter content and intermediate sulfur isotopic compositions accumulated under mainly dysaerobic bottom waters. Samples with relatively low amounts of organic carbon and wide-ranging but less negative sulfur isotopic values were deposited beneath oxygenated bottom waters. Sulfur isotope data, then, are apparently a sensitive indicator of diagenetic or depositional facies of fine-grained Cretaceous rocks in the Western Interior.

INTRODUCTION

The Cretaceous System in the Western Interior of North America includes a thick sequence of fine-grained marine rocks that accumulated in the Western Interior seaway, a shallow epeiric sea (for review see Caldwell, 1975). Shales from the Cretaceous seaway were a significant sink for organic carbon and sulfide sulfur and have served as major source rocks for the generation of oil and gas (Rice and Gautier, 1983). The timing, rate, and intensity of aerobic oxidation and sulfate reduction during early diagenesis largely

1

determine the abundance of organic carbon and sulfide sulfur in marine sediments and, thus, greatly affect lithologic properties and petroleum source rock potential. The style of early diagenesis is generally predetermined by the depositional environment. The epeiric Western Interior seaway has long been suspected of having had restricted circulation, with periodic or episodic dysaerobic conditions or anoxia, and may thus be expected to display sulfur-carbon ratios and $\delta^{34}S$ values different from marine rocks and sediments deposited beneath fully oxygenated waters.

This paper presents the results of a study of the abundance and $\delta^{34}S$ of sulfides, and of the abundance and type of organic matter from cores of selected Cretaceous shales from the Western Interior of North America. This work is intended to (1) investigate the relative abundance of carbon and sulfur (S/C) buried in well-known marine deposits of Cretaceous age as an aid interpretating global carbon and sulfur cycles through Phanerozoic time, (2) evaluate the sulfur isotope composition of a wide variety of Cretaceous shales as an index of the depositional environment of organic carbon-rich rocks in the Western Interior and, thus, (3) provide insight into the interpretation of depositional and early diagenetic processes in ancient marine sediments.

PROCEDURE

Samples were collected from cores of fine-grained, siliciclastic marine rocks of Cretaceous age. The cores came from well locations shown on figure 1 and tabulated in table 1. Core materials were used exclusively because, in most outcrops of Cretaceous shales in the western United States, pyrite has been oxidized--at least in part (Schultz and others, 1980)-- and sulfide, organic carbon, and $\delta^{34}S$ values may be unreliable. Sample selection was limited to cores of rocks of Late Cretaceous age (Cenomanian-Campanian), thereby minimizing the effects of secular variations in the isotopic composition of marine sulfate through time (Claypool and others, 1980). Samples collected were from cores of rocks known to be thermally immature with respect to oil generation and deposited in a wide variety of settings indicated by lithologies ranging from bioturbated, gray mudrock to laminated, organic carbon-rich black shale. Cores sampled for this investigation are listed in table 1A and will be referred to as the G samples. In addition, previously unpublished carbon and sulfur data from D. L. Gautier and J. S. Leventhal, are listed in table 1B and will be referred to as the L samples.

To average the effects of minor lithologic inhomogeneities samples were collected from channels approximately 10 cm running long parallel to the long direction of the core. Because most early diagenetic pyrite occurs as finely disseminated, microscopic framboids and crystals, large crystals and (or) nodules were avoided. This was generally not difficult, as coarse crystals and pyrite nodules of pyrite are rather rare and easily identified in the fine-grained rocks in the Cretaceous of the Western Interior.

2

Table 1.—Sample localities

| Well	Location	Depth interval (feet below KB)	Number of samples	Formation(s)	Cretaceous stage
G Samples, Localities					
J. C. Paine & Assocs. Aasen 1-9	T. 129 N., R. 106 W., Bowman County, N.Dak.	1150-1300	20	Gammon Shale	Campanian
Kansas-Nebraska Natural Gas Co. 1-32 Whomble	T. 2 S., R. 43 W., Yuma County, Colo.	1466-1480	7	of Pierre Shale	Campanian
Falcon-Colorado Oil and Gas Co. 1-33 Milk River	T. 32 N., R. 33 E., Valley County, Mont.	780-900	12	Carlile Shale	Turonian
Falcon-Colorado Oil and Gas Co. 2-21 Federal	T. 33 N., R. 34 E., Phillips County, Mont.	1150-1240	12	Belle Fourche Shale/ Greenhorn Formation	Cenomanian/ Turonian
L Samples, Localities					
Coquina Oil Corp. Berthoud State #3	T. 4 N., R. 69 W., Larimer County, Colo.	2914-2918	4	Niobrara Formation	Santonian
Guy Holland No. 1 State	T. 13 S., R. 40 W., Wallace Co., Kans.	10-245	17	Sharon Springs Member of Pierre Shale/ Niobrara Formation	Santonian/ Campanian
Toltec Drilling Co. Heil No. 1	T. 3 N., R. 69 W., Boulder County, Colo.	6205-6214	4	Pierre Shale	Campanian
Turner No. 1	Hughes County, S.Dak.	78-545	25	Pierre Shale (including Sharon Springs Member)	Campanian/ Maestrichtian?
Hayes No. 2	Hughes County, S.Dak.	62-507	17	Pierre Shale	Maestrichtian?

3
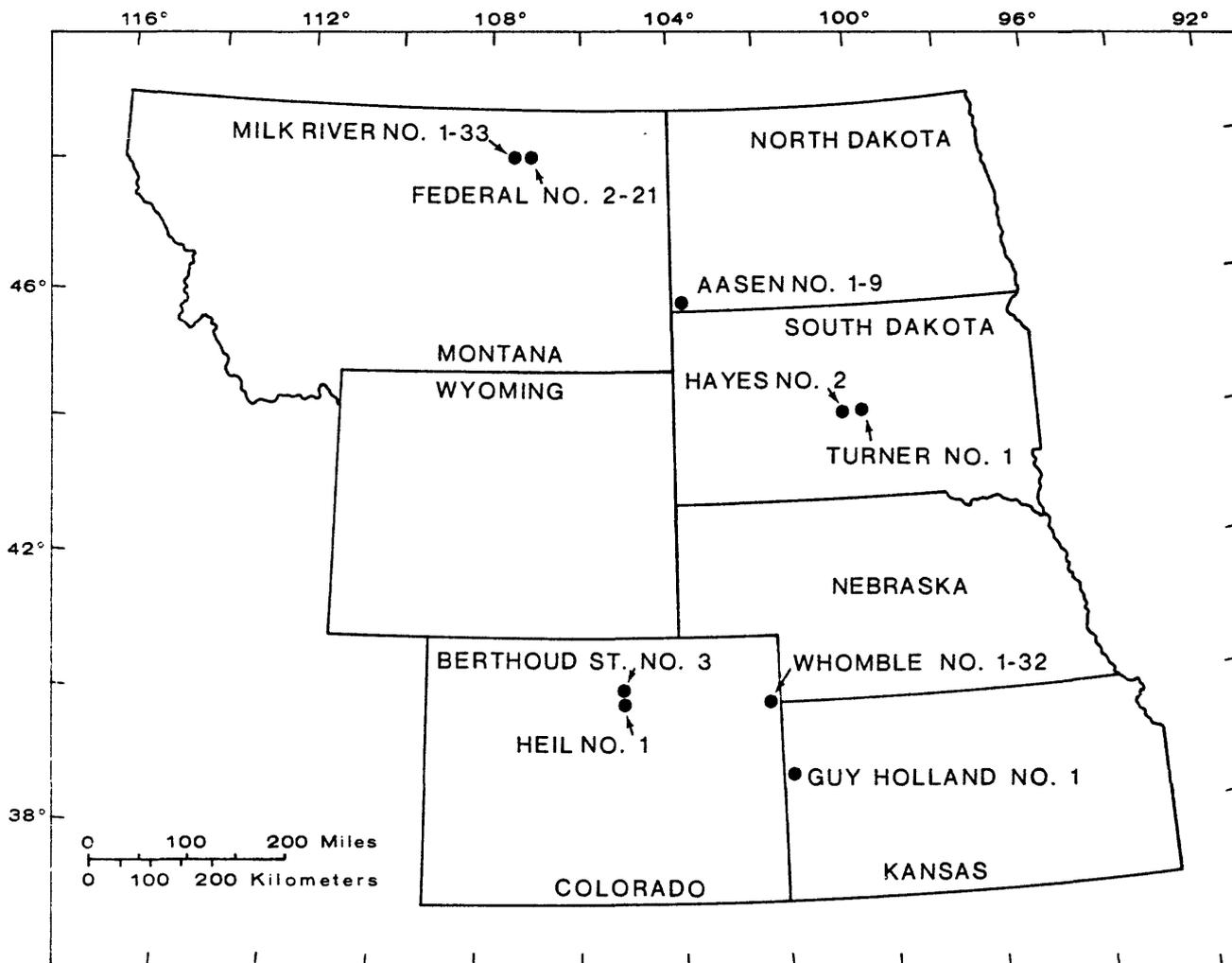
Figure 1. Locations of wells from which core samples were taken to be analyzed for this study. Well locations are listed in table 1.

The G samples were crushed, ground, and split into several portions for analysis. Weight percent organic carbon was determined by the Direct Carbon Wet-Oxidation Method (Leventhal and Shaw, 1978) at Rinehart Laboratories, Arvada, Colorado.[1] After washing with distilled water to remove any sulfates, samples were dried and weighed. Pyrite, the only metal sulfide present in the samples, was oxidized and dissolved in bromine/aqua regia. The sulfide sulfur content was then determined by weight from $BaSO_4$ precipitate. Except for selected samples used to determine precision and accuracy, isotopic analyses were conducted by Global Geochemistry Corporation of Canoga Park, California. The isotopic composition of pyrite sulfur was determined from SO_2 gas obtained from the $BaSO_4$ precipitates (Kaplan and others, 1963). The sulfur isotope data are reported in standard S-notation relative to troilite from the Canyon Diablo Meteorite (CDT). Only elemental abundance data from carbon and sulfur are available from the L samples; carbon was determined by Direct Carbon Wet oxidation as in the G samples, and sulfur was determined by means of combustion in a LECO induction furnace. Organic matter type was estimated by Rock-Eval pyrolysis (Espitalie et al., 1977) of the G samples. Data from all analyses are tabulated in table 2.

ABUNDANCE OF ORGANIC CARBON AND SULFIDE SULFUR

Samples from the G data set contain on average 2.4 percent organic carbon, and values range from as little as 0.57 percent in a silty mudstone of the Gammon Shale from southwestern North Dakota to as much as 10.66 percent in a black, laminated shale of the Sharon Springs Member of the Pierre Shale from eastern Colorado. Sulfide sulfur abundance likewise displays a considerable variation, ranging from a low of 0.05 percent in a siltstone of the Gammon Shale to as much as 7.90 percent in a black shale of the Sharon Springs Member. The average sulfide sulfur value of all samples is 1.55 percent. The L data set displays similar distributions, with an average organic carbon content of 2.9 percent, ranging from 0.25 percent for a sample of Pierre Shale from South Dakota to 10.76 percent for a duplicate of the Sharon Springs analysis in the G data set (six duplicates were run). Sulfur in the L data set averages 2.0 percent and ranges from 0.10 percent in a sample of upper part of the Pierre Shale from South Dakota to more than 7.90 percent for the Sharon Springs replicate. The grand mean for all (G and L) samples is 2.7 percent for organic carbon and 1.8 percent for sulfide sulfur, for an average S/C ratio of 0.67.

The values of carbon and sulfur abundance are highly correlated. The sulfur and carbon values from the G samples yield a correlation coefficient of 0.93. The sulfur and carbon data from the L samples have a correlation coefficient of 0.91. The correlation coefficient for the combined data set (all samples) is about 0.92 (fig. 2).

---

[1]Any use of trade names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 2.--Sample data

Well[1]	Formation	Depth	$\%C_{org}$	$\%S$	$\delta^{34}S$
	G Samples, Data				
1-33 Milk River	Carlile Shale	780	1.51	1.32	-29.49
Do................	......do.............	784	2.54	1.18	-24.40
Do................	......do.............	794	2.50	1.46	-22.82
Do................	......do.............	814	2.01	1.34	-27.25
Do................	......do.............	824	0.77	1.96	-22.19
Do................	......do.............	834	1.70	1.55	-27.11
Do................	......do.............	844	1.42	1.27	-20.49
Do................	......do.............	854	1.82	1.51	-19.35
Do................	......do.............	864	1.86	1.23	-18.81
Do................	......do.............	874	1.61	1.52	
Do................	......do.............	884	0.84	0.49	-8.08
Do................	......do.............	894	.94	.44	-23.77
2-21 Federal	Belle Fourche Shale	1240	2.41	1.92	-22.63
Do................	......do.............	1230	1.83	1.99	-25.37
Do................	......do.............	1220	2.84	1.72	-25.85
Do................	......do.............	1218	2.26	1.07	-18.53
Do................	......do.............	1210	2.49	1.15	-23.03
Do................	......do.............	1200	2.82	1.22	-27.40
Do................	......do.............	1190	2.39	1.20	-26.54
Do................	......do.............	1180	2.20	1.51	-21.51
Do................	Green Horn Formation	1170	3.10	1.27	-28.60
Do................	......do.............	1160	7.95	2.44	-28.46
Do................	......do.............	1152	3.98	0.86	-25.24
Do................	......do.............	1150	1.08	.39	-17.46
1-9 Aasen	Gammon Shale	1152	0.60	0.12	-10.60
Do................	......do.............	1153	.82	.11	-28.64
Do................	......do.............	1160	.57	.11	-14.19
Do................	......do.............	1164	.57	.16	-7.64
Do................	......do.............	1167	.62	.15	-18.24
Do................	......do.............	1173	.68	.33	16.75
Do................	......do.............	1178	.71	.18	-20.37
Do................	......do.............	1182	.80	.16	-19.76
Do................	......do.............	1186	.68	.63	10.49
Do................	......do.............	1190	.61	.11	-10.21
Do................	......do.............	1193	.63	.12	-10.76
Do................	......do.............	1210	.71	.12	-14.74
Do................	......do.............	1214	.65	.10	-10.83
Do................	......do.............	1217	.65	.10	-13.50

6

Table 2.--<u>Sample data</u>--continued

Well[1]	Formation	Depth	%C_{org}	%S	$\delta^{34}S$
Do...................	.......do.............	1152	.75	.23	-34.58
Do...................	.......do.............	1274	.73	.55	13.97
Do...................	.......do.............	1282	.79	.12	-12.71
Do...................	.......do.............	1269	.78	.13	-16.28
Do...................	.......do.............	1292	.71	.05	-11.90
Do...................	.......do.............	1293	.60	.23	-9.52
Berthoud State No. 3	Niobrara Formation	2914	2.86	2.26	
Do...................	.......do.............	2915	3.44	2.32	
Do...................	.......do.............	2916	2.28	2.08	
Do...................	.......do.............	2918	3.29	3.00	
1-32 Whomble	Sharon Springs Member Pierre Shale	1466	5.34	4.52	-30.85
Do...................	.......do.............	1470	6.76	4.81	-33.16
Do...................	.......do.............	1475	10.66	7.90	-34.42
Do...................	.......do.............	1475	9.54	7.05	-33.96
Do...................	.......do.............	1479	9.30	7.76	-34.03
Do...................	.......do.............	1480	7.00	6.00	-34.68

L Samples, Data

Well	Formation	Depth	%C_{org}	%S	$\delta^{34}S$
Berthoud State No. 3	Niobrara Formation	2914	2.86	2.26	
Do...................	.......do.............	2915	3.44	2.32	
Do...................	.......do.............	2916	2.23	2.08	
Do...................	.......do.............	2918	3.29	3.00	
1-32 Whomble	Sharon Springs Member Pierre Shale	1466	5.34	4.52	
Do...................	.......do.............	1470	6.76	4.81	
Do...................	.......do.............	1475	10.66	7.90	
Do...................	.......do.............	1475	9.54	7.05	
Do...................	.......do.............	1479	9.30	7.76	
Do...................	.......do.............	1480	7.00	6.00	
Heil No. 1	Pierre Shale	6205	2.46	1.34	
Do...................	.......do.............	6209	1.82	1.35	
Do...................	.......do.............	6211	2.43	1.50	
Do...................	.......do.............	6214	1.57	1.12	
Guy Holland No. 1	Sharon Springs Member & Niobrara Formation	15	4.70	5.40	
Do...................	.......do.............	20	9.60	7.35	
Do...................	.......do.............	30	3.10	3.40	
Do...................	.......do.............	50	5.00	3.80	
Do...................	.......do.............	65	5.20	3.80	

Table 2.--<u>Sample data</u>--continued

Well[1]	Formation	Depth	%C_{org}	%S	$\delta^{34}S$
Do..................	......do..............	80	4.10	2.70	
Do..................	......do..............	95	4.10	2.50	
Do..................	......do..............	112	4.20	2.25	
Do..................	......do..............	128	4.40	2.10	
Do..................	......do..............	144	4.60	2.00	
Do..................	......do..............	152	3.80	2.20	
Do..................	......do..............	168	4.30	2.05	
Do..................	......do..............	184	3.50	2.55	
Do..................	......do..............	200	3.00	1.65	
Do..................	......do..............	216	3.00	1.65	
Do..................	......do..............	232	4.30	2.80	
Do..................	......do..............	248	4.00	3.35	
Hayes No. 2	Pierre Shale	62	1.24	0.89	
Do..................	......do..............	77	1.19	.54	
Do..................	......do..............	102	0.82	.67	
Do..................	......do..............	115	1.59	2.62	
Do..................	......do..............	140	.73	.85	
Do..................	......do..............	160	.85	.87	
Do..................	......do..............	177	1.36	.57	
Do..................	......do..............	212	1.36	.85	
Do..................	......do..............	240	.80	.42	
Do..................	......do..............	249	1.06	.46	
Do..................	......do..............	270	1.29	.78	
Do..................	......do..............	302	1.34	.41	
Do..................	......do..............	319	1.22	.37	
Do..................	......do..............	362	.95	.74	
Do..................	......do..............	382	1.10	.46	
Do..................	......do..............	493	.70	.28	
Do..................	......do..............	507	.39	.25	
Turner No. 1	......do..............	78	1.25	.53	
Do..................	......do..............	107	.85	.35	
Do..................	......do..............	140	.53	.22	
Do..................	......do..............	195	1.20	.27	
Do..................	......do..............	250	.57	.10	
Do..................	......do..............	281	.98	.42	
Do..................	......do..............	305	.98	.60	
Do..................	......do..............	335	.64	.20	
Do..................	......do..............	380	.31	.13	
Do..................	......do..............	390	.65	.06	
Do..................	......do..............	417	.25	.17	
Do..................	......do..............	425	.48	.11	

Table 2.--<u>Sample data</u>--continued

Well[1]	Formation	Depth	$\%C_{org}$	$\%S$	$\delta^{34}S$
Do....................	......do..............	440	.66	.39	
Do....................	......do..............	450	.45	3.25	
Do....................	......do..............	460	1.24	.74	
Do....................	......do..............	475	1.33	2.28	
Do....................	......do..............	479	.65	.12	
Do....................	......do..............	500	1.21	1.50	
Do....................	......do..............	505	.79	1.45	
Do....................	......do..............	520	5.40	2.47	
Do....................	......do..............	521	4.40	2.59	
Do....................	......do..............	525	4.96	2.68	
Do....................	......do..............	540	8.21	3.50	
Do....................	......do..............	545	8.52	3.46	
Do....................	......do..............	545	2.65	2.36	

[1]Locations of wells provided in table 1.

9
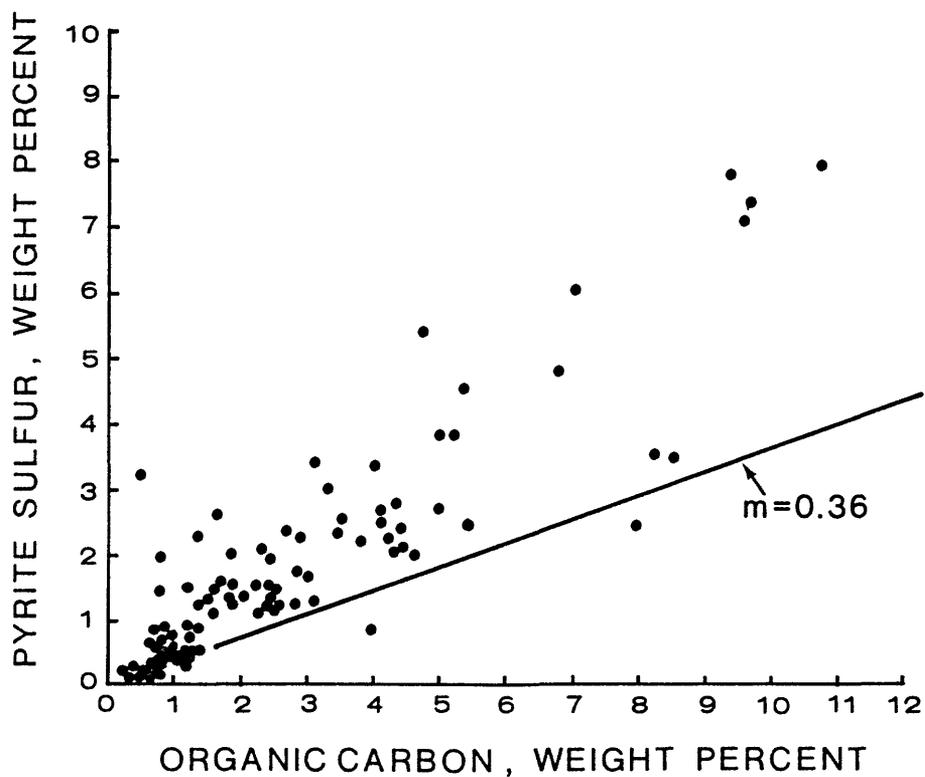
Figure 2.—Weight percent pyrite sulfur plotted against weight percent organic
carbon for all samples of marine shale of Late Cretaceous Age included in
this study. Data are listed in table 2. Line is best fit (M=0.36) for
correlation of sulfide sulfur vs. organic carbon of normal marine
sediments (Sweeney, 1972; Goldhaber and Kaplan, 1974).

INTERPRETATION OF S/C VALUES

A positive correlation between organic carbon and sulfide sulfur is typical of noneuxinic marine sediments (Berner, 1970; Sweeney, 1972, Goldhaber and Kaplan, 1974; Sweeney and Kaplan, 1980; Berner, 1982; Leventhal, 1983). This relationship derives from the processes of sulfate reduction during early diagenesis (e.g. Berner, 1970). In recent noneuxinic marine sediments, the average S/C ratio is approximately 0.36, but with considerable variation of the data (Sweeney and Kaplan, 1973). This variation probably reflects the wide variety of environments sampled and the sampling procedures used in determining the relationship of sulfur to carbon (Berner, 1970; Goldhaber and Kaplan, 1974). Generally, the more narrowly defined the environment, the better the observed correlation between sulfide sulfur and organic carbon (Berner, 1970). A perfect S^{2-}/C_{org} correlation would imply use of a constant proportion of organic matter by sulfate-reducing bacteria (Goldhaber and Kaplan, 1975).

The two data sets considered here display somewhat different average S/C ratios but evidence similarly high degrees of correlation. Ratios of S^{2-} to C_{org} are the slope for best fit lines resulting from linear regression on the data sets. The G data display a slope (S/C) of M=0.563, whereas the L data yield a slope of M=0.75.

Regardless of which data set is used, the Cretaceous shales yield S/C ratios that are significantly larger than the ratio reported for modern marine environments by Sweeney and Kaplan (1973) (M=0.36 for recent sediments vs. an average of M=0.67 for the Cretaceous sediments), and much larger than the inverse of the C/S ratio calculated by Berner and Raiswell for the global Cretaceous (1983; their fig. 5). Considering the probability that circulation was restricted in the epeiric sea of the Western Interior during the Cretaceous, poor ventilation as a cause of higher S/C ratios seems an obvious possibility. However, the situation may be more complex. Goldhaber and Kaplan (1975) showed that in sulfur/carbon plots of recent marine sediments the slope is dependent upon the fraction of carbon oxidized during sulfate reduction and upon the fraction of sulfide reoxidized and lost from the sediment. But unlike in modern sediments, the fraction of organic carbon lost subsequent to the cessation of sulfate reduction in ancient sediments may not be trivial. The slope (S/C) may thus be dependent upon variables whose values are not known with certainty. Three cases seem plausible:

(Case 1) The amount of organic carbon lost following sulfate reduction is small and the fraction of organic carbon consumed during sulfate reduction has remained approximately constant through time. This case implies that the higher S/C ratios in the Cretaceous samples result from systematic variation in the amount of sulfide reoxidized and lost from the sediment. Because significant variations in sulfide oxidation would likely result principally from changes in intensity of bioturbation (mixing) and sedimentation rate, the effects would be mainly local and (or) temporary and thus should result in a scattering of the S/C relationship rather than in a systematic change.

(Case 2) The fraction of organic carbon consumed during sulfate reduction
is essentially constant through time, and the effects of changes in the
fraction of sulfide reoxidized and lost have been random. This case implies
that a significant amount of organic carbon has been consumed by diagenetic
processes following the cessation of sulfate reduction. Although the
selection of samples that are thermally immature with respect to oil and
thermal-gas generation probably eliminates the large-scale loss of fluid
hydrocarbons by petroleum generation, significant loss of carbon may have
occurred during methanogenesis (Claypool and Kvenvolden, 1983) and (or) during
shallow-burial decarboxylation of kerogen (Carothers and Kharaka, 1978;
Lundegard and Land, in press). In this case the principal cause of the
variation in S/C ratio is diagenetic, and variations in S/C ratios of
sediments of different ages do not reflect temporal changes in global S/C but
rather in the local diagenetic history.

(Case 3) The fraction of organic carbon lost during post sulfate
reduction processes is small, and the fraction of sulfide reoxidized and lost
has remained approximately constant. In this case the implied cause of the
variation in S/C is a temporal change in the efficiency of the sulfate
reducers, as expressed by the fraction of organic carbon consumed per unit
sulfate reduced. It seems unlikely that the metabolic processes of this
ancient and conservative group of anaerobic bacteria has changed much in the
past 100 million years or so, but the type of organic matter being delivered
to the ocean floor may have been somewhat different in the environments of the
Cretaceous Interior seaway than in recent marine environments or in other
Cretaceous marine environments. This may be the case particularly with
respect to the relative importance of the most reactive components of the
organic matter. Moreover, it is likely that bottom waters were periodically
depleted in free oxygen, owing to restricted circulation during much of
Cretaceous time (Pratt, 1984) and thus inhibiting the effectiveness of aerobic
oxidation and providing more suitable (reactive) organic substrata for the
sulfate-reducing bacteria. This, I believe, best explains higher S/C in
Cretaceous Western Interior shales, as compared with modern marine sediments
or calculated values for other Cretaceous marine sedimentary rocks.

ISOTOPIC COMPOSITION OF SULFIDE SULFUR

Sulfur isotope compositions, determined for the G samples only, range
from $\delta^{34}S$ = +16.7^o/oo to $\delta^{34}S$ =-34.7^o/oo CDT, with the vast majority of
results between -8 and -36°/oo (table 2). The mean $\delta^{34}S$ value for 50 G
samples is -19.7^o/oo. However, the average value does not reflect the
systematic variations in $\delta^{34}S$ within the sample set. Sulfur isotope values
fall into three populations closely related to depositional environment and
organic carbon concentration, as illustrated in figure 3.
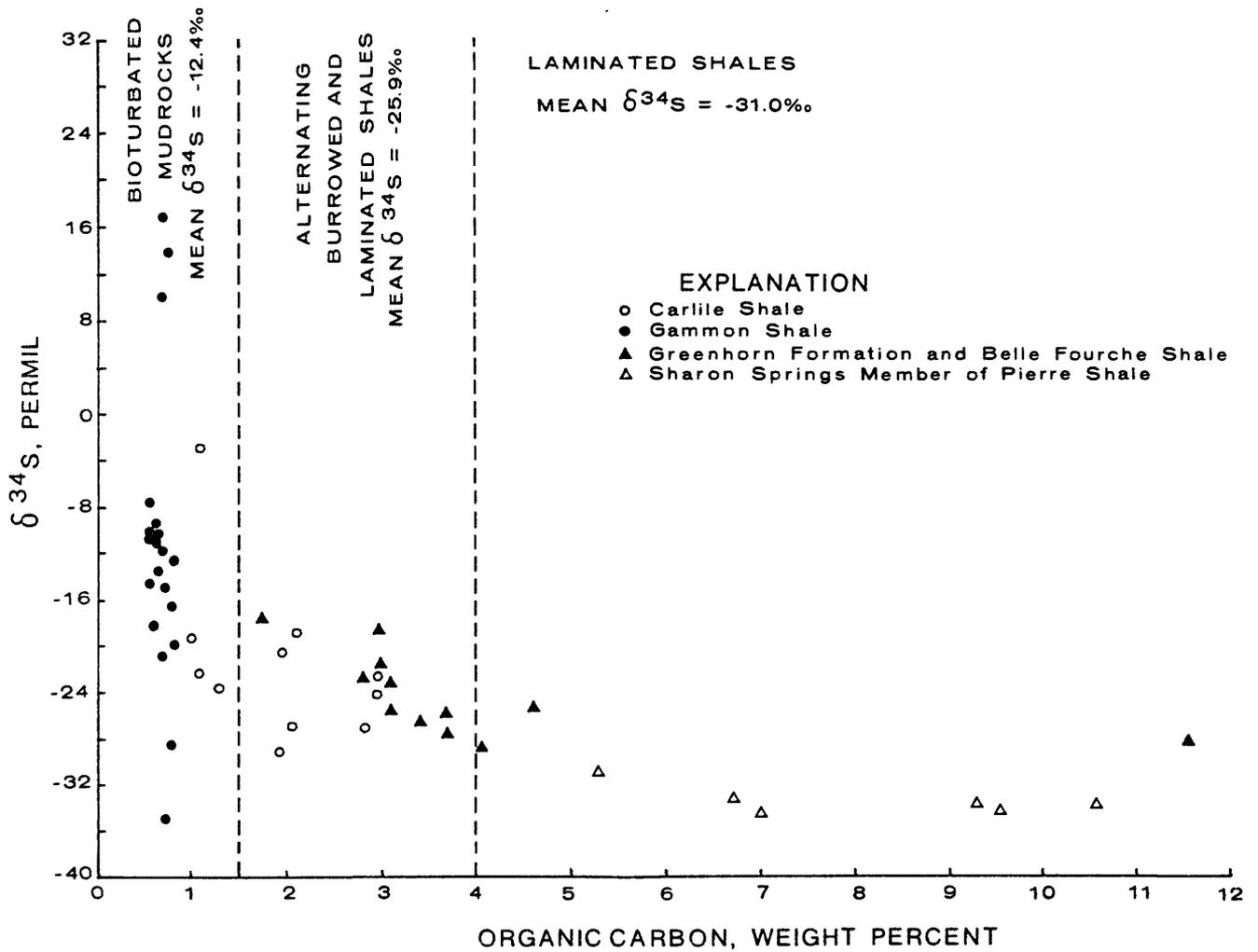
Figure 3.--Sulfur isotopic composition, expressed in standard delta notation, plotted against weight percent organic carbon for the "G" samples. Data are listed in table 2.

13

Generally, samples with organic carbon in excess of 4 percent contain disseminated pyrite which is extremely depleted in ^{34}S (δ^{34}S = -25 to -36°/oo). The mean δ^{34}S for all samples containing at least 4 percent organic carbon is -31°/oo. These samples represent black shales from the Sharon Springs Member of the Pierre Shale and from Greenhorn Formation north-central Montana (fig. 3). These organic carbon-rich rocks are laminated and contain hydrogen-rich (type II) organic matter presumably derived in large part from marine phytoplankton (fig. 4), a depauperate fossil fauna, and abundant sulfide sulfur generally exceeding 1.75 percent by weight. These shales were deposited at rates of less than 10 cm/10^3 yr beneath anoxic and probably sulfidic bottom waters in the deeper parts of the seaway (Gautier et al., 1984).

In contrast to the organic carbon-rich shales, samples with less than about 1.5 percent organic carbon display a wide range of δ^{34}S values (δ^{34}S = -34.58 to δ^{34}S = +16.75 with a mean of -12.4°/oo). These samples represent silty mudstones of the Gammon Shale from North Dakota and the Carlile Shale from north-central Montana (fig. 3). The rocks are characteristically burrowed or intensely bioturbated, contain hydrogen-poor (Type III) organic matter (fig. 4), and have relatively small amounts of S^{2-}. Sedimentation rates during deposition of the bioturbated samples exceeded 100 cm/10^3 yr (Gautier, 1981; 1982) and therefore the bioturbated mudstones accumulated more rapidly by an order of magnitude than the organic carbon-rich shales. The bioturbated mudstones were deposited under oxygenated bottom waters at relatively shallow depths on a current-swept shelf (Gautier, 1981; Gautier and Rice, 1982).

Samples containing intermediate amounts of organic carbon (C$_{org}$= 1.5 to 4 percent) contain disseminated pyrite with δ^{34}S values ranging from -16°/oo to almost -30°/oo with a mean of -25.9°/oo. These samples display neither the isotopically "lightest" nor "heaviest" pyrite in this sample set (fig. 3). The intermediate samples are derived from shales of the Greenhorn Formation, Carlile Shale, and Belle Fourche Shale. The lithology of the rocks is characterized by alternating sequences of burrowed mudrock and laminated shale, containing mainly but not exclusively Type III terrigenous (hydrogen-poor) organic matter (fig. 4). These shales were probably deposited at intermediate rates of from 10 to 100 cm/10^{3}yr (D. L. Gautier, unpublished data), generally beneath bottom waters episodically dysaerobic to anoxic.
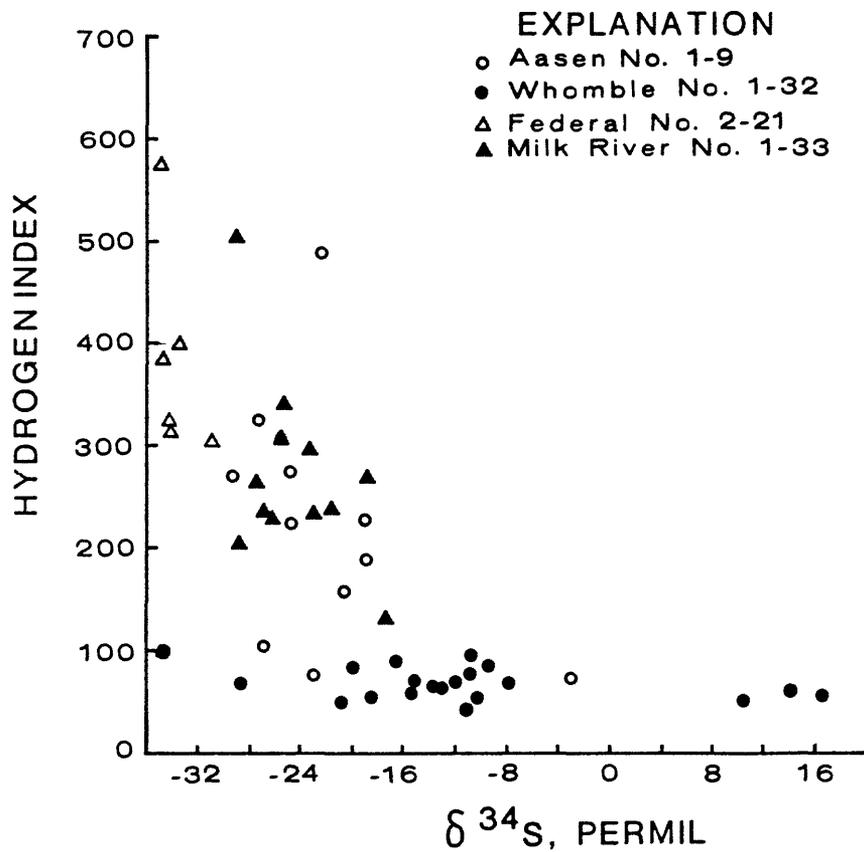
Figure 4.--Plot of hydrogen indices for organic matter vs. $\delta^{34}S$ of sulfide sulfur in "G" samples. Data are listed in table 2. Well information in table 1A.

INTERPRETATION OF SULFUR ISOTOPE DATA

Disseminated pyrite framboids and tiny crystals, such as those analyzed for this study, are early diagenetic features derived from the bacterial reduction of dissolved sulfate in marine waters. From Cenomanian to Campanian time, sulfur isotope values of global seawater sulfate were similar but not identical to modern seawater sulfur values (Claypool and others, 1980). As in most marine sediments, pyrite sulfur in the Cretaceous shale samples is present in amounts greatly exceeding the amounts originally included in the sediment as pore water sulfate (Kaplan et al., 1963; Berner, 1964; Goldhaber and Kaplan, 1980). Whereas a simple burial of pore water sulfate and a closed-system reduction to sulfide might be expected to yield about 0.1 percent $S^=$ by weight with a $\delta^{34}S$ identical to seawater sulfate (+20°/oo), the Cretaceous samples contain from 0.05 percent to almost 8.0 percent sulfide sulfur, most of which is severely depleted in ^{34}S. Generally, in Cretaceous samples where sulfur is present in excess of 1 percent of the sample by weight, isotopic separations between solid sulfide and initial seawater sulfate are 40 to 50°/oo.

Recent analogs to the Cretaceous marine rocks in the Western Interior are not present in the Gulf of California, nor in other Pacific Coast basins that have been intensively studied with respect to sulfur isotope geochemistry (Kaplan et al., 1963; Goldhaber and Kaplan, 1974; 1980). The relationships among sulfate reduction rate, sulfide sulfur accumulation, and organic carbon content so carefully documented in Quaternary sediments sampled during the DSDP and other ocean drilling are not strictly applicable to the marine Cretaceous rocks from the Western Interior. The Cretaceous samples that contain the greatest amount of organic carbon and therefore the greatest amount of sulfide sulfur (figure 2) also display the greatest depletion in ^{34}S (figure 3). In recent marine sediments accumulating beneath oxic bottom waters, total organic carbon and total sulfide directly correlate with sedimentation rate (Berner, 1972). Rapid burial tends to preserve the readily metabolizable organic matter from the metazoans and aerobic bacteria in the oxygenated environment. In the Cretaceous samples, however, the most hydrogen-rich (and hence most reactive) organic matter, occurs in those sediments that accumulated most slowly.

The Cretaceous samples with the most organic carbon and sulfide sulfur, as well as the "lightest" sulfur isotopic composition, are those that accumulated very slowly in anoxic and sulfidic depositional environments. Similar relationships were observed in Devonian shales by Maynard (1980). For example, the samples from the 1-32 Whomble cores (tables 1 and 2) are from the Sharon Springs Member of the Pierre Shale. The Sharon Springs shales in the Whomble cores contain between 5 and 11 percent organic carbon, perhaps one half of which was derived from marine phytoplankton (Gautier et al., 1984). The Sharon Springs samples also contain 1.8 to 3.9 percent sulfide sulfur, with $\delta^{34}S$ values ranging from -30.8 to -34.7°/oo, suggesting isotopic separation from starting seawater sulfate of more than 50°/oo. The Sharon

Springs samples accumulated at a rate of less than a few tens of centimeters per thousand years. The Sharon Springs is a laminated rock, containing few fossils (e.g. Gilbert, 1897). What fossils are present include remains of vertebrates (fish, and large marine reptiles) and pelagic cephalopods. The laminated character of the sediment, the paucity of fossils of bottom-dwelling organisms, and the preservation of hydrogen-rich organic matter at low rates of sedimentation are strong evidence that the Western Interior epeiric seaway was stratified with anoxic and sulfidic bottom waters during deposition of the organic-carbon-rich portions of the Sharon Springs Member (Gautier et al., 1984). Similar arguments have been made for the most organic-rich claystones of the Greenhorn Formation in the vicinity of Rock Canyon anticline near Pueblo, Colorado (Pratt, 1984) and such interpretations probably also apply to the organic-carbon-rich, laminated samples of Greenhorn Formation from north-central Montana analyzed for this study (tables 1 and 2). Thus, in these laminated, organic-carbon-rich, slowly deposited rocks, the sulfur isotope composition may not reflect the rate of sulfate reduction; rather, the composition may reflect the formation of isotopically light sulfide in the water column as well as the formation of iron sulfides in the presence of an "infinite" reservoir of seawater sulfur in a manner analogous to that observed in modern sediments of the Black Sea (Sweeney and Kaplan, 1980).

Samples analyzed during this study which were deposited rapidly include those from cores of the Gammon Shale and from the Carlile Shale. The Gammon mudstones accumulated at a rate of more than 100 cm/1000 years (Gautier, 1982). However, this represents the integrated rate over millions of years, as interpreted from K/Ar dating of bentonites and ammonite biostratigraphy (Obradovich and Cobban, 1975), and does not necessarily reflect the "instantaneous" sedimentation rate that may have been much higher or zero.

The Gammon Shale samples are relatively low in organic carbon and in total sulfide sulfur. The rocks are burrowed to intensely bioturbated. These samples of Gammon Shale are principally silty mudstones, clearly deposited beneath oxygenated bottom waters. Organic matter in the Gammon is mainly hydrogen-poor Type III (fig. 4). The pyrite sulfur in the Gammon displays $\delta^{34}S$ values ranging from -34.58 to +16.75, and thus covers the entire range of values measured. Most samples have isotopic compositions ranging from -8 to -20°/oo, with an average sulfide sulfur content of 0.14 percent. The depletion of 34S in samples with such low amounts of sulfide sulfur probably reflects the degree to which chemical micro-environments dominate early diagenetic processes in sediments irrigated by a significant burrowing infauna. Because of the range and magnitude of values for sulfide sulfur concentration and isotopic composition, it would appear that most sulfide was formed within the range of effect of the burrowing organisms and within the lower part of the mixing zone. In such environments today, sulfate reduction can occur in undisturbed sediment immediately adjacent to burrows containing aerobic organisms (e.g. Rhoads, 1974; Howard and Frey, 1973).

17

In contrast to the Devonian Shales of the Appalachian basin, where isotopically heavy sulfides are relatively common (Maynard, 1981) only three samples, all from the Gammon Shale (samples AA 1173, AA 1186, and AA 1273.5), display isotopically positive composition (table 2, fig. 3). Average sulfur content for these three samples is about 0.55 percent, thus exceeding the sulfur content for the rest of the Gammon samples by a factor of three. These samples contain comparatively large amounts of euhedral (octahedral) pyrite (in contrast to framboids). Such euhedral crystals are believed to form somewhat later in sulfate reduction than framboids and are expected to display larger amounts of ^{34}S (Raiswell, 1982). This relatively high sulfur content (for the Gammon) suggests that the positive values result from the addition of isotopically heavy sulfur to the isotopically "light" sulfur incorporated in all of the other Gammon samples. A mechanism by which such "heavy" sulfur would be incorporated would entail the formation, for example, of about 0.15 percent pyrite sulfur in the mixing zone, resulting in an isotopic composition similar to other samples from the Gammon (e.g. $-15^o/oo$), and, in addition, fortuitously isolating an aliquot of seawater sulfate ($\delta^{34}S= +18^o/oo$) which would add an additional 0.34 percent pyrite sulfur when completely reduced. Because of the isolation of the buried portion of seawater sulfate, the resulting total S^{2-} composition is approximated by adding the two portions of sulfur together-- (0.15 percent) x ($-15^o/oo$) + (.35 percent) x (+18$^o/oo$)--to yield 0.5 percent S^{2-}, with $\delta^{34}S$ = +8.1 percent.

Many samples from the Carlile and Belle Fourche Shales that were used in this study display isotopic values for sulfide ($\delta^{34}S$ = $-25.9^o/oo$) that are intermediate between the extremely "light" values of the Sharon Springs Member ($\delta^{34}S$ = $-31.8^o/oo$) and the "heavier sulfur" in the intensely bioturbated mudrocks of the Gammon Shale ($\delta^{34}S$ = $-12.4^o/oo$). The cores of the Carlile and Belle Fourche range from burrowed to laminated, display intermediate values of organic carbon, and show a mixed suite of Type III and Type II organic matter. Thus the Carlile and Belle Fourche samples are intermediate in most respects. It is likely that they accumulated under generally dysaerobic or oscillating dysaerobic/anaerobic conditions.

Sulfur isotope values are thus related not only to sedimentation rate, but also to the abundance of sulfide sulfur and organic carbon and also to the level of oxygenation of bottom waters. A principal interpretation of this paper is that the isotopic composition is directly related to the depositional environment. The waters of the Cretaceous epeiric seaway in the Western Interior of North America were probably chemically inhospitable to many sediment-dwelling organisms (e.g. Frush and Eicher, 1975; Pratt, 1984), and it is thus reasonable to suppose that the level of habitation intensity of sediments was directly related to the availability of particularly reactive components of organic matter to the sulfate reducing bacteria. In those sediments where oxygen was absent and sulfide was present in bottom waters, hydrogen-rich organic matter accumulated on the bottom and was not consumed by aerobic infauna. In sediments where oxygen was available, most hydrogen-rich organic matter were consumed during aerobic oxidation. Thus the level of

consumption of reactive organic matter by aerobic organisns probably
determined to a large extent the degree of preservation of organic matter, it
also thus determined the effectiveness of sulfate reducing bacteria, the
ultimate content of sulfide sulfur in the sediment, and the sulfur isotopic
composition.

SUMMARY AND CONCLUSIONS

The samples for which data are presented in this study display
significantly higher S/C ratios, on average, than those generally observed in
recent marine sediments. To the extent that these samples are representative
of the Cretaceous marine sediments of the epeiric seaway, the Cretaceous rocks
of the Western Interior also have a higher S/C than has been calculated for
the Cretaceous worldwide (Berner and Raiswell, 1983).

The large observed S/C ratio may have resulted from (1) the consumption
of organic matter subsequent to the cessation of sulfate reduction during
early diagenesis, or (2) the greater loss of sulfide from the Cretaceous rocks
because they were deposited, on average, more slowly than recent marine
sediments included in the tabulation by Sweeney and Kaplan (1973). In
Cretaceous rocks of the Western Interior , higher organic carbon contents and
preservation of hydrogen-rich, reactive organic matter are generally
correlative with relatively slow sedimentation.

This is in contrast to recent marine sediments, in which the abundance of
organic carbon is generally correlative with the sedimentation rate due to the
rapid burial of reactive organic matter (Heath et al., 1977). The slow
sedimentation of Cretaceous rocks implies that the principal mechanism for the
preservation of reactive organic matter was the low level of aerobic activity
in the sediment due to restricted ventilation of bottom waters in the
seaway. The greater availability of metabolizable organic matter may have led
to more efficient sulfate reduction and to generally larger S/C ratios in the
Cretaceous System of the Western Interior.

The sulfur isotope composition of the rocks is strongly tied to the
organic matter type and to the abundance of organic carbon. More negative
$\delta^{34}S$ values are observed in samples containing a large amount of organic
carbon, in which hydrogen-rich organic matter of probable marine origin is
abundant and in which the content of sulfide sulfur is high. These same
samples were deposited relatively slowly beneath anoxic and sulfidic bottom
waters. Positive values of $\delta^{34}S$ are observed only in Cretaceous rocks
containing low amounts of organic matter, interpreted to be principally of
terrestrial origin. These isotopically "heavier" samples contain much less
sulfide sulfur, and accumulated beneath oxygenated bottom waters at relatively
high sedimentation rates.

It appears that percent organic carbon and $\delta^{34}S$ data may provide a
sensitive indicator of early diagenetic or depositional facies of fine-
grained, organic-carbon-rich rocks in the Western Interior (fig. 3). The

results of these studies suggest that those samples that are rich in organic carbon (more than about 4 percent) and contain isotopically "light" sulfur in pyrite (with δ^{34}S $<-30^{o}$/oo) accumulated beneath anoxic and perhaps sulfidic bottom waters. Samples with intermediate organic matter content (from about 4 percent to around 1.25 percent C_{org}) have intermediate δ^{34}S values and probably accumulated under principally dysaerobic bottom waters. Those samples with relatively low amounts of organic carbon (<1.5 percent C_{org}) have wide-ranging but generally less negative δ^{34}S values in pyrite and probably accumulated beneath oxygenated bottom waters.

These boundaries should not, of course, be used rigidly, as they probably only represent the maximum values for those facies below each limit, not the minimum value for facies above the limit. These data suggest that although organic carbon-poor sediments may have accumulated beneath anoxic and sulfidic waters in the epeiric sea, anoxia may have been required in the slowly deposited sediments of the Western Interior for the accumulation of a high concentration of organic carbon.

REFERENCES CITED

Arthur, M. A., Dean, W. E., and Claypool, G. E., in press, Anomalous [13]C Enrichment in Modern Marine Organic Carbon: Nature.

Arthur, M. A., Dean, W. E., and Schlanger, S. O., in press, Variations in the Global Carbon Cycle During the Cretaceous Related to Climate, Volcanism and Changes in Atmospheric CO_2.

Berner, R. A., 1964, Distribution and Diagenesis of Sulfur in some Sediments from the Gulf of California: Marine Geology, v. 1, p. 117-140.

Berner, R. A., 1970, Sedimentary Pyrite Formation: American Journal of Science, v. 268, p. 1-23.

Berner, R. A., 1982, Burial of Organic Carbon and Pyrite Sulfur in the Modern Ocean: Its Geochemical and Environmental Significance: American Journal of Science, v. 278, p. 257-275.

Berner, R. A., and Raiswell, Robert, 1983, Burial of Organic Carbon and Pyrite Sulfur in Sediments Over Phanerozoic Time: A New Theory: Geochimica et Cosmochimica Acta, v. 47, p. 855-862.

Caldwell, W. G. E., ed., 1975, The Cretaceous System in the Western Interior of North America: Geological Association of Canada Special Paper No. 13, 666 p.

Claypool, G. E.,, Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I., 1980, The Age Curves of Sulfur and Oxygen Isotopes in Marine Sulfate and Their Mutual Interpretation: Chemical Geology, v. 28, p. 199-260.

Dean, W. E., Arthur, M. A., and Claypool, G. E., in press, ^{13}C/^{12}C of Organic Carbon in Cretaceous Deep-Sea Black Shales: Influence of Source, Diagenesis, and Environmental Factors: Marine Geology.

Espitalie´, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefou, A., 1977, Me´thode rapide de caracte´risation des roches me´res, de leur pe´trolier et de leur degre´ d´evolution: Reune de l´Institute Francais du Petrole, v. 32, p. 23-42.

Frush, M. P., and Eicher, D. L., 1975, Cenomanian and Turonian Foraminifera and Paleoenvironments in the Big Bend Region of Texas and Mexico, in W. G. E. Caldwell, ed., The Cretaceous System in the Western Interior of North America: The Geological Association of Canada Special Paper Number 13, p. 277-301.

Gautier, D. L., 1982, Siderite Concretions: Indicators of Early Diagenesis in the Gammon Shale (Cretaceous): Journal of Sedimentary Petrology, v. 52, p. 859-871.

Gautier, D. L., Clayton, J. L., Leventhal, J. S., and Reddin, N. J., 1984, Origin and Source-Rock Potential of the Sharon Springs Member of the Pierre Shale, Colorado and Kansas, in Woodward, Jane, Meissner, F. F., and Clayton, J. L., eds., Hydrocarbon Source Rocks of the Greater Rocky Mountain Region: Rocky Mountain Association of Geologists 1984 Symposium Volume, p. 369-385.

Gautier, D. L., and Rice, D. D., 1982, Conventional and Low-Permeability Reservoirs of Shallow Gas in the Northern Great Plains: Journal of Petroleum Technology, July, 1982, p. 1600-1608.

Gilbert, G. K., 1897, Description of the Pueblo Quadrangle (Colorado): U.S. Geological Survey Atlas Folio 36, 9 p.

Goldhaber, M. B., and Kaplan, I. R., 1974, The Sulfur Cycle, in Goldberg, E. D., ed., The Sea: New York, John Wiley, v. 5, p. 569-655.

Goldhaber, M. B., and Kaplan, I. R., 1975, Controls and Consequences of Sulfate Reduction Rates in recent Marine Sediments: Soil Science, v. 119, p. 42-55.

Goldhaber, M. B., and Kaplan, I. R., 1980, Mechanisms of sulfur incorporation and isotope fractionation during early diagenesis in sediments of the Gulf of California: Marine Chemistry, v. 9, p. 95-143.

Howard, J. D., and Frey, R. W., 1973, Characteristic Physical and Biogenic Structures in Georgia Estuaries: American Association of Petroleum Geologists Bulletin, v. 57, p. 1169-1184.

Kaplan, I. R., 1983, Stable Isotopes of Sulfur, Nitrogen, and Deuterium in Recent Marine Environments, in Arthur, M. A., Anderson, T. F., Kaplan, I. R., Veizer, Jan, and Land, L. S., eds., Stable isotopes in sedimentary geology: Society of Economic Paleontologists and Mineralogists Short Course Notes No. 10, p. 2-1 to 2-108.

Kaplan, I. R., Emery, K. O., and Rittenberg, S. C., 1963, The distribution and isotopic abundance of sulfur in recent marine sediments off southern California: Geochimica et Cosmochimica Acta, v. 27, p. 297-331.

Leventhal, J. S., 1983, An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition: Geochimica et Cosmochimica Acta, v. 47, p. 133-138.

Maynard, J. B., 1980, Sulfur isotopes of iron sulfides in Devonian-Mississippian shales of the Appalachian basin--Control by rate of sedimentation: American Journal of Science, v. 280, p. 772-786.

Obradovich, J. D., and Cobban, W. A., 19755, A time-scale for the Late Cretaceous of the Western Interior of North America, in Caldwell, W. G. E., ed., The Cretaceous system in the Western Interior of North America: Geological Association of Canada Special Paper No. 13, p. 31-54.

Pratt, L. M., Influence of paleoenvironmental factors on preservation of
    organic matter in Middle Cretaceous Greenhorn Formation, Pueblo,
    Colorado: American Association of Petroleum Geologists Bulletin, v. 68,
    p. 1146-1159.

Raiswell, R., 1982, Pyrite texture, isotopic composition and the availability
    of iron: American Journal of Science, v. 282, p. 1244-12633.

Rhoads, D. C., 1974, Organism-sediment relations on the muddy seafloor:
    Oceanogr. Mar. Biol., Annu. Rev., v. 12, p. 263-300.

Rice, D. D. and Gautier, D. L., 1983, Patterns of Sedimentation, Diagenesis
    and Hydrocarbon Accumulation in Cretaceous Rocks of the Rocky Mountains:
    Society of Economic Paleontologists and Mineralogists Short Course Note
    No. 11.

Schultz, L. G., Tourtelot, H. A., Gill, J. R., and Boerngen, J. G., 1980,
    Composition and properties of the Pierre Shale and equivalent rocks,
    northern Great Plains region: U.S. Geological Survey Professional Paper
    1064-B, 114 pages.

Sweeney, R. E., 1972, Pyritization during diagenesis of marine sediments: Los
    Angeles, University of California, Unpub. Ph.D. thesis, 184 pages.

Sweeney, R. E., and Kaplan, I. R., 1980, Diagenetic sulfate reduction in
    marine sediments: Mar. Chem., v. 9, p. 165-174.

Sweeney, R. E., and Kaplan, I. R., 1980, Stable isotope composition of
    dissolved sulfate and hydrogen sulfide in the Black Sea: Mar. Chem., v.
    9, p. 145-152.