

VARIATIONS IN ORGANIC GEOCHEMISTRY AND PETROGRAPHY
WITH DEPTH OF BURIAL, GREEN RIVER FORMATION OIL SHALES
PICEANCE CREEK BASIN, COLORADO

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ABSTRACT

Chemical analysis, ¹³C NMR, and IR spectroscopy were used to characterize organic matter concentrates (HCl/HF dissolution) and carbonate mineral-free (HCl dissolution) oil shale samples from a 213 m (700 ft) interval between the top of the Mahogany Zone and the base of the R4 zone, C-a Tract, Colorado. The H/C, O/C, and N/C ratios and the fraction of aliphatic C of the organic matter decrease with depth. The aliphatic/aromatic ratio also with depth. Organic petrography data, both qualitative and quantitative, were obtained by reflected white-light and reflected blue-light fluorescence microscopy. Qualitative petrographic parameters, such as overall fluorescence color, show regular and systematic trends with depth. Vitrinite reflectance increases slightly with depth. The observed chemical and petrographic variations are consistent with increasing thermal maturation with depth.

INTRODUCTION

Efficient extraction of any natural resource requires a detailed understanding of the resource. In the case of the Eocene-age Green River Formation oil shales of Colorado,

Utah, and Wyoming a detailed understanding of the variability of the organic and inorganic fraction is required. Unfortunately, our knowledge of such variability is limited. The few studies on the variability of the organic fraction that have been published are somewhat contradictory. Smith (1961, 1963, 1983) reported that the only significant variation in the composition of the organic matter is a decrease in the O/C ratio with depth; lateral variability, at least in the Mahogany zone, was reported to be minimal. Robison and Cook (1971, 1973) reported significant differences in the properties of kerogen taken from different stratigraphic and geographic locations. In the Colorado No. 1 core, for example, the H/C ratio of the kerogen varied between 0.92 and 1.77. Robinson (1978) noted that there appeared to be no correlation between the H/C ratio (or other measured properties) and depth of burial.

In the present study a variety of analytical techniques have been used to characterize the variation of the total organic fraction with depth in a single core from the C-a Tract, Piceance Creek Basin, Colorado. Techniques used include elemental analysis (C, H, N, O, S, and ash), ¹³C NMR, and IR spectroscopy. Quantitative petrographic data for the organic fraction were also obtained.

METHODS AND PROCEDURES

The samples used in the present study were obtained at irregular intervals from a single core obtained from near the center of the C-a Tract. The location of the C-a Tract is shown in Figure 1. The 25 samples used in the present study were obtained from the interval between the top of the Mahogany Zone (MZ) and the base of the R4 Zone (Figure 2), a stratigraphic interval of 213 m (700 ft). The samples range in grade from 4.8-27.5 wt% organic C (10-62 gal/ton). Mass balance Fischer Assay data for these samples are given in Meddaugh (1984). Mineralogical data for this interval were reported by Meddaugh and Salotti (1983).

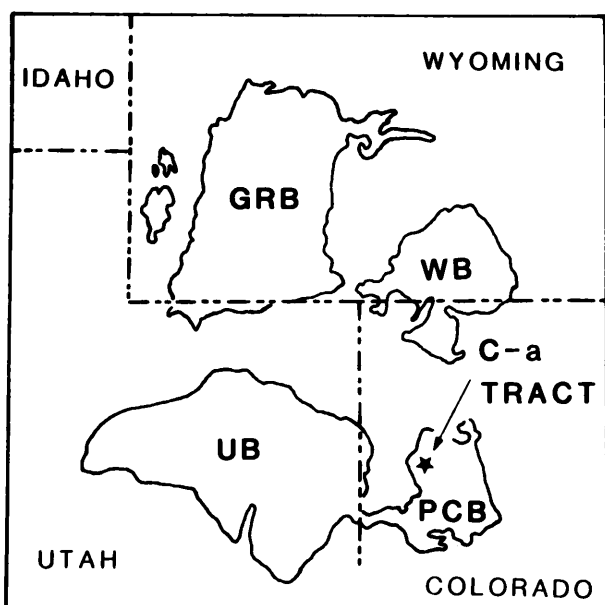


Figure 1 Map showing the distribution of the Green River formation and location of a C-a tract (star). PCB=Piceance Creek basin; UB=Unita basin; GRB=Green River basin; WB=Washakie basin.

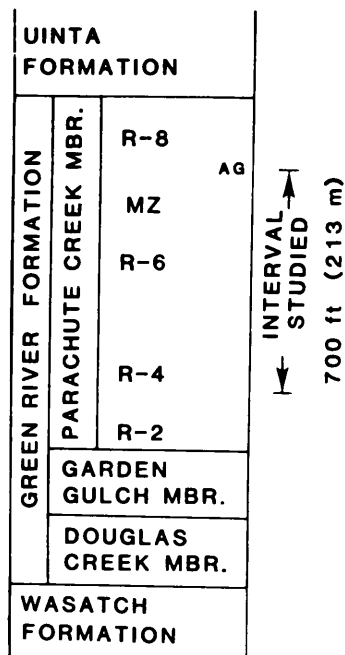


Figure 2 Stratigraphic column showing interval studied. After Desborough (1978).

Organic Fraction Concentrates

Organic fraction concentrates were prepared from eight selected samples by HCl/HF dissolution. No extraction of the soluble portion of the organic matter was made prior to elemental analyses. The amount of benzene-methanol (7:3) soluble organic matter (bitumen) was determined on a separate split before initial HCl dissolution and before and after HF dissolution. Elemental compositions (C, H, N, O, and S) of the organic fraction were determined using standard techniques by Microanalysis Inc. (Wilmington, DE); oxygen was determined directly using a modified Unterzaucher technique. Duplicate analyses (C, H) were obtained for four concentrates. IR spectra were recorded on a Digilab Model 15C interferometer using KBr pellets. ¹³C cp-mas NMR spectra were recorded on a Varian XL-200.

Carbonate-Free (HCl-leached) Samples

Organic H and C and total N were determined for 25 samples by standard techniques (Micro-analysis Inc.) following removal of carbonates and analcite by HCl dissolution. Organic H values obtained from the HCl-leached samples have been corrected for H₂ released from illite during analysis (high temperature combustion). Figure 3 shows the excellent correlation between the organic H/C values obtained from the organic matter concentrates and the corrected organic H/C values obtained from the HCl-leached samples.

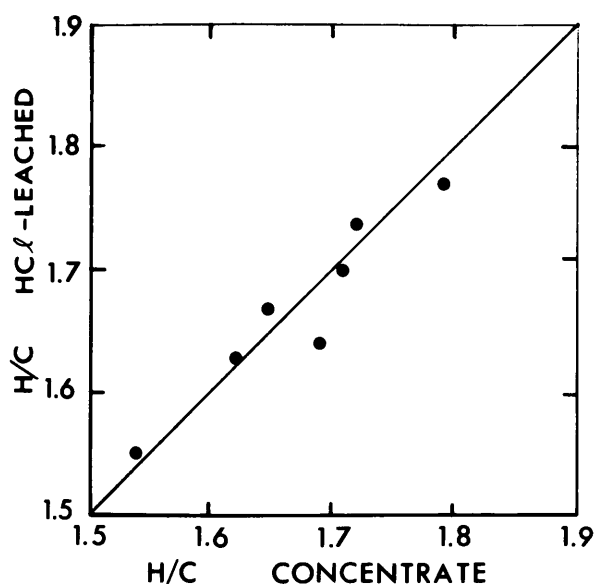


Figure 3 Plot of H/C ratio determined on organic concentrates and H/C ratio obtained on carbonate mineral-free (HCl-leached) samples (corrected for water released from illite during analysis).

Organic Petrography

Polished blocks were prepared for 19 samples and examined in reflected white-light and reflected blue-light fluorescence at 400X magnification. After initial examination of the sample suite a set of petrographic parameters suspected of changing with depth (or shale grade) were qualitatively described and quanti-

tatively measured. Quantitative data were obtained by point counting (500 points) in the fluorescent mode to obtain the volume percent of various organic constituents (see Table 3). Vitrinite reflectance data were also obtained.

RESULTS

Organic Geochemistry

Chemical data for the organic matter concentrates are reported in Table 1. Figure 4 shows the variation of the H/C, N/C, and O/C ratios of the organic matter in the oil shale with depth. Note that there is a strong decrease in the O/C ratio with depth, from about 0.11 in the Mahogany Zone (MZ) to about 0.05 at the base of the R4 Zone. This is consistent with the observations of Smith (1963, 1983).

Figure 4 also shows a significant decrease in the H/C ratio of the organic matter, from about 1.7-1.8 in the MZ to 1.55-1.68 in the R4 zone. The trend of decreasing H/C ratio with depth is partially obscured by an apparent negative correlation between the H/C ratio of the organic matter and the oil shale grade (wt% organic C). This is shown in Figure 5. Note that for a given shale grade there is a decrease in the H/C ratio of the organic matter with increasing depth. This is particularly obvious for oil shales with less than 15 wt% organic C (about 35 gal/ton). The relationship between shale grade and organic matter H/C ratio suggests that there may be some fundamental difference in the "type" of organic matter in rich and lean oil shales. Superimposition of the apparent decrease in the H/C ratio of the organic matter with increasing shale grade and the decrease in the H/C ratio with increasing depth of burial may explain why previous workers have not reported any systematic variation in the H/C ratio of the organic matter.

Figure 6 is a plot of H/C vs O/C for the organic matter concentrates. Note the clear decrease in both H/C and O/C ratios with increasing depth.

Table 1. Chemical Data for Organic Matter in Green River Formation Oil Shales (wt%)

Sample	Organic Concentrates					Whole Rock		
	C	H	N	O	S	C	H	N
4						4.57	0.68	0.157
5	59.49	8.37	2.019	8.39	3.70	21.18	2.89	0.649
8	58.44	8.71	1.661	6.95	4.87	7.48	1.10	0.225
9						17.65	2.53	0.573
12	59.63	8.54	2.369	6.32	2.70	14.60	2.12	0.583
18						9.79	1.47	0.328
19						10.96	1.63	0.331
24						17.83	2.51	0.695
25	65.32	9.30	1.418	7.11	4.28	8.94	1.27	0.392
29						14.42	1.97	0.508
30						5.05	0.70	0.182
42						15.41	2.13	0.513
43						17.75	2.53	0.519
46						27.28	3.63	1.056
48	61.76	8.50	1.944	4.50	2.20	14.71	2.05	0.427
55						10.07	1.33	0.306
56						7.62	1.04	0.276
58						10.40	1.38	0.305
60						12.53	1.72	0.343
63	69.34	9.35	2.396	6.73	5.15	19.40	2.63	0.622
68	61.05	7.83	1.966	5.63	3.76	15.72	2.04	0.429
69						14.20	1.88	0.449

Note sample depth (in feet) = 390 + (10) (sample number).

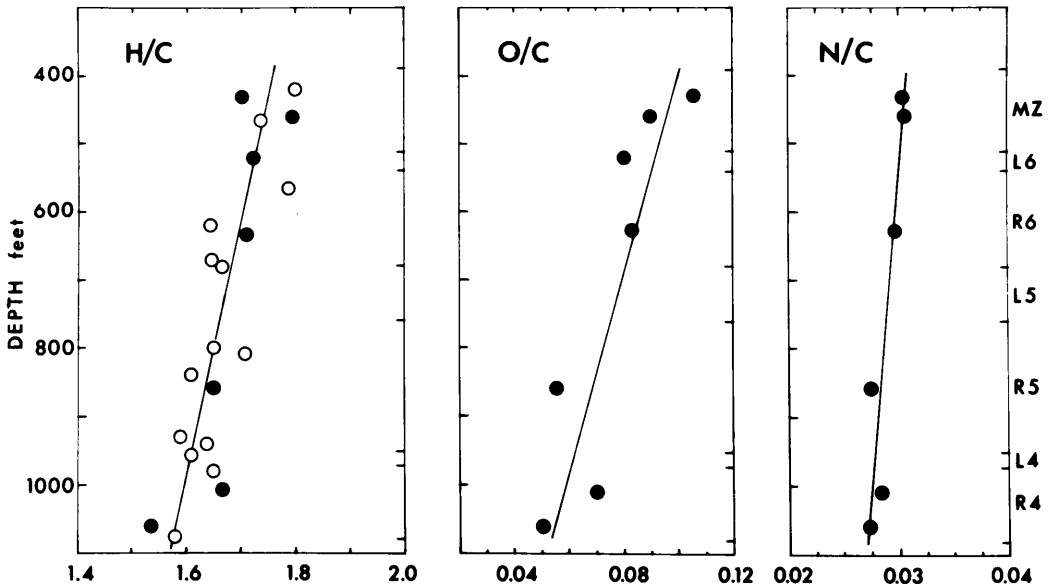


Figure 4 Variation of H/C, O/C, and N/C ratios with depth of burial. Solid circles=data obtained from organic concentrates; open circles=data obtained from HCl-leached samples.

Figure 4 shows a slight decrease in the N/C ratio of the organic matter concentrates with depth, from about 0.030 in the MZ to about 0.029 in the R4 Zone. Such a variation is probably within the analytical error of the analyses, however. There is no variation of the total N/organic C ratio with depth of burial. Recent workers (Cooper et al, 1983) have suggested that the N in the Green River oil shales is largely present in the inorganic fraction, particularly as NH_4 substituting for K in illite and/or K-feldspar. However, there is no correlation between wt% total N and wt% normative illite and K-feldspar (orthoclase). There is a strong correlation between wt% total N and wt% organic C (Figure 7). This suggests that inorganic N is relatively unimportant in the samples studied.

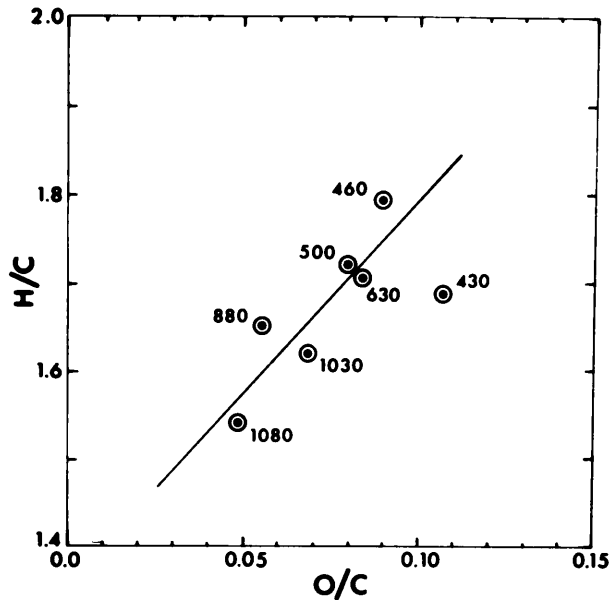


Figure 6 Plot of H/C vs O/C for organic matter concentrates. Numbers=sample depths.

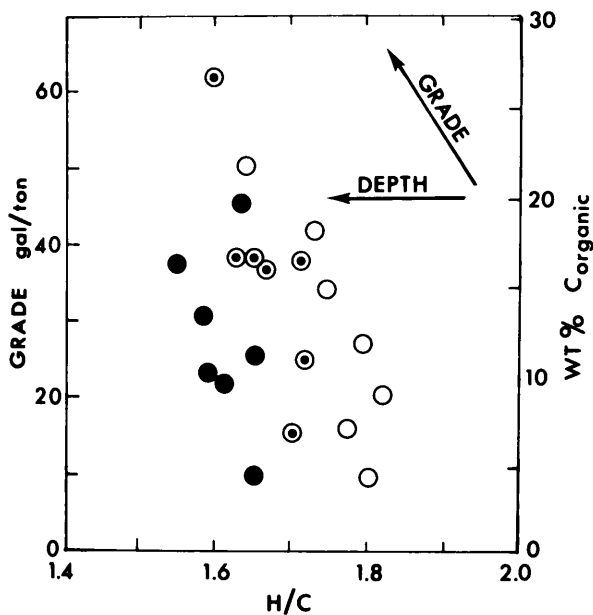


Figure 5 Variation of H/C ratio with shale grade. Open circles=data obtained from shallow samples (core depth 390-600 ft; partially filled circles-data obtained from intermediate depths (core depths 600-900 ft); solid circles=data obtained from deep samples (core depth 900-1200 ft).

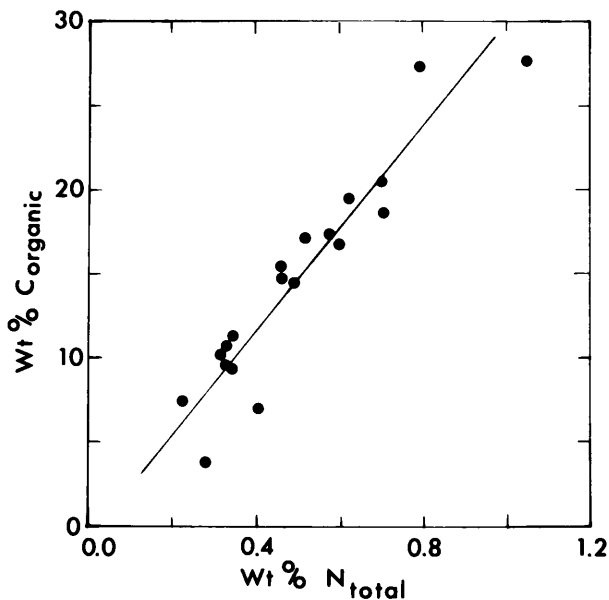


Figure 7 Plot of wt% total N vs wt% organic C.

^{13}C NMR data for six organic matter concentrates are shown in Figure 8. Note that while there are no major differences in the NMR spectra, there is a clear decrease in the aliphatic/aromatic ratio with depth, from about 3 in the MZ to 2.5-2.6 in the R4 Zone; the aromatic C content of the concentrates increases from about 23% in the MZ to 26-27% in the R4

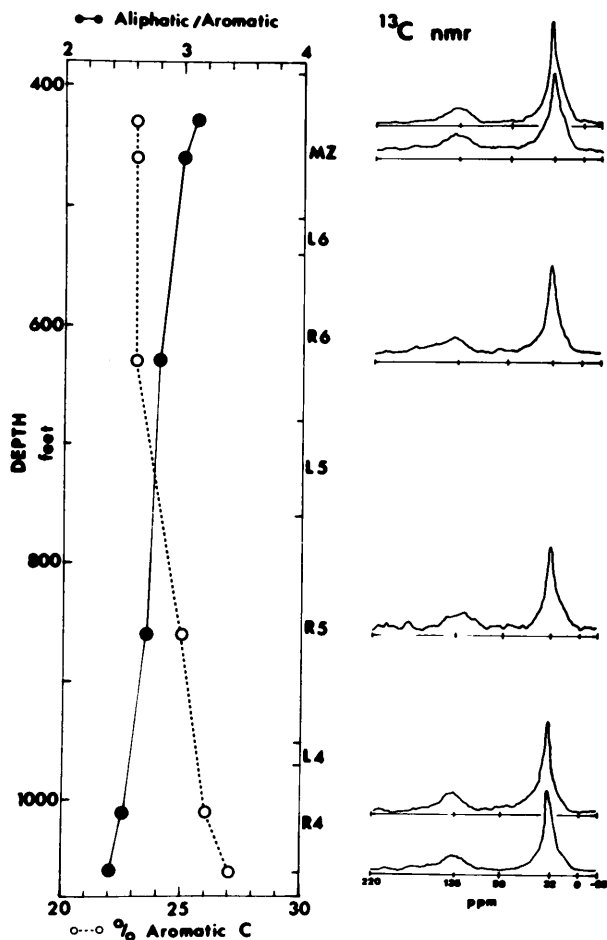


Figure 8 Summary of ^{13}C NMR data showing variation of aliphatic/aromatic ratio and fraction of aromatic C with depth. Individual spectra are also shown. Note the overall similarity of the NMR spectra.

Zone. The decrease in the aliphatic/aromatic ratio and the increase in percent aromatic C with depth is consistent with the decrease in the H/C ratio with depth shown in Figure 4.

IR spectra for organic matter concentrates are shown in Figure 9. Note that there are no major differences in the IR spectra of concentrates obtained from the top and bottom of the interval studied. Table 2 shows the variation of the relative importance of selected absorbance bands with depth of burial. Note that there is little change in the absorbance at 2920 cm^{-1} (aliphatic CH) or at 1640 cm^{-1} (aromatic C=C) with depth. There is a slight decrease in the 1705 cm^{-1} band (due to C=O), consistent with the observed decrease in the C/O ratio with depth. There is also a slight decrease in the absorbance at 1375 cm^{-1} (aliphatic CH₃).

Figure 10 shows a decrease in the percent extractable organic C with depth: three samples from the MZ contain 8-9.5% extractable organic C; two samples from the R4 Zone contain about 5% extractable organic C.

Organic Petrography

Bradley (1929) provided early descriptions of Green River formation oil shales from thin section studies. He found that the most common type of varve is comprised of a pair of distinctly segregated dark and light laminae possessing sharp and regular contacts with each other and with neighboring varves. The organic matter in dark laminae is most often light to dark orange. Black, light, and dark shades of gray, and brown occur less frequently. Mineral-free concentrations of organic matter are usually dark orange or brown whereas organic concentrations rich in clay minerals are generally gray or black. Light laminae generally have yellow or orange colored interstitial spaces but may appear as a pure, almost brilliant white.

Table 2. IR Absorbance for Selected Peaks (Relative Units)

Sample	2920 cm-1 CH	1705 cm-1 C=O	1640 cm-1 C=C	1460 cm-1 CH2 + CH3	1375 cm-1 CH3
5	0.82	0.19	0.12	0.16	0.06
8	0.87	0.17	0.12	0.17	0.07
12	0.90	0.21	0.13	0.18	0.07
48	0.94	0.18	0.14	0.20	0.06
63	0.84	0.16	0.12	0.19	0.05
68	0.83	0.16	0.12	0.18	0.04

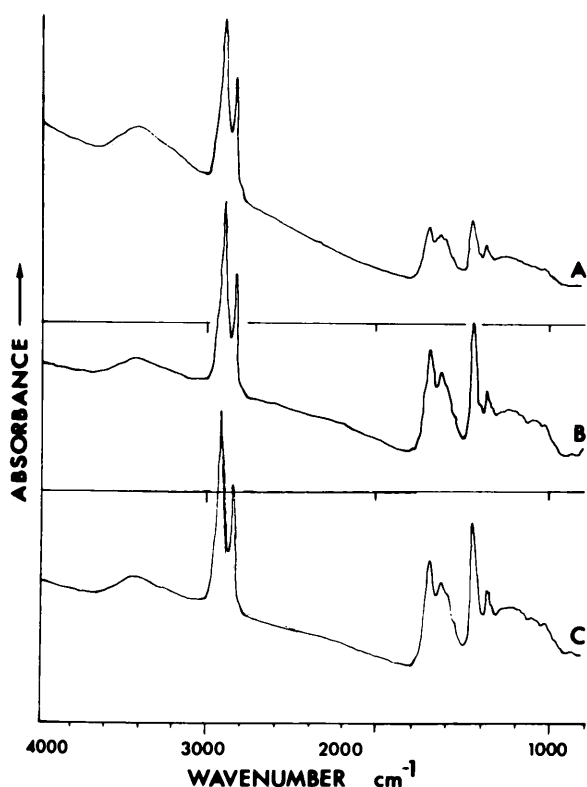


Figure 9 Typical IR spectra for organic matter concentrates. Sample A from core depth=430 ft; sample B from core depth=870 ft; sample C from core depth 1180 ft.

In addition to the amorphous organic matter found concentrated or dispersed in the dark or light bands, respectively, vitrinite is also visible in reflected light. Vitrinite (huminite) occurs most commonly in thin, continuous bands (0.001-0.007 mm wide), as dispersed, elongate particles (0.007-0.6 mm in diameter). Figure 11 shows the variation of mean vitrinite reflectance with depth in the interval studied; samples from the MZ have vitrinite reflectances of about 0.18 (excluding very low grade samples which appear to have anomalously high vitrinite reflectances; see below); samples from the R4 Zone have reflectance near 0.27. Although vitrinite reflectances increase systematically with depth (especially if samples of similar grade are compared), several factors limit the significance of the trend shown in Figure 11. First, there is some question as to the precision and accuracy of vitrinite reflectance measurements for $R_m\%$ < 0.3. Second, in samples with comparatively low vitrinite abundances, re-worked organic matter may appreciably "skew" the reflectance histograms. (Re-worked vitrinite probably accounts for the flat histograms and comparatively high mean reflectances for the very low grade oil shale samples.) Thirdly, some samples with very uniform petrography do

not have a "normal" distribution of reflectance data. Finally, vitrinite reflectance can be "influenced" by alginite content (Hutton and Cook, 1981).

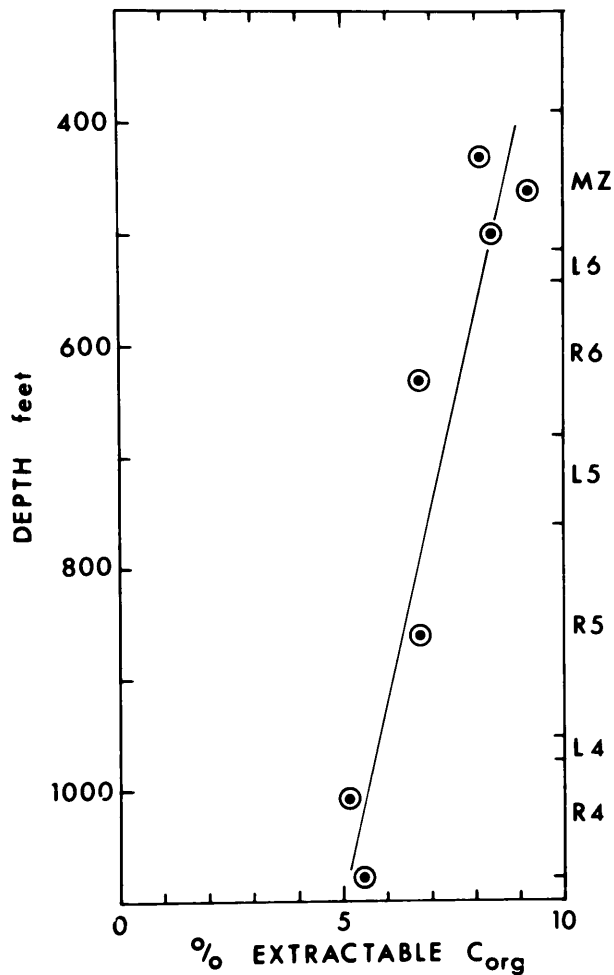


Figure 10 Plot of % extractable organic C (benzene-methanol) vs depth.

Further elucidation of the nature of the organic matter in the oil shales was accomplished using blue-light fluorescence microscopy. Although descriptive petrography under fluorescent excitation is more definitive than white-light examination, it is still not possible to discuss with certainty the

biological or depositional origin of the amorphous organic matter. The overall appearance of an oil shale sample in blue-light fluorescence can be described as either dull yellow green or bright yellow green. The dull or bright fluorescing organic matter concentrations at least 0.24 mm in length were arbitrarily designated as bands; samples with either dispersed organic matter or with concentrations less than 0.24 mm in length were designated as dispersed. Bright and dull dispersed organic matter comprise the bulk of the organic material in the samples studied. Other types of organic matter, usually present in only trace amounts, were discernable in blue-light fluorescence. Palynomorphs (fossil pollen and spores) of several shapes, sizes, and fluorescent color were noted in nearly all samples. Cutinite (waxy coatings on some woody tissues or leaves) is occasionally associated with vitrinite. Fragments of alginite A and organic remains of microorganisms were rarely seen.

Table 3 summarizes the quantitative organic petrography data for the 19 oil shale samples studied. Note the overall abundance of the dispersed organic matter (bright and dull fluorescent). No significant correlations exist between the data shown in Table 3 and depth of burial. However, several qualitative and semi-quantitative trends with depth were noted. The most significant change with depth is the fluorescent character of the amorphous organic matter. Bands and dispersed particles change from thin, well defined, brilliant yellow-green fluorescent entities in the shallow samples to poorly defined and less brilliant yellow and green fluorescent entities in the deep samples. In many of the deeper samples, bands and some dispersed particles appear to engulf mineral grains. Dull fluorescent dispersed organic matter shows little variation in texture with depth but changes from predominantly green to a more yellow or orange fluorescence with depth. Relative fluorescent intensities of palynomorphs showed no correlation with depth.

Table 3. Quantitative Petrographic Data (Vol%)

Sample	Bright Banded	Dull	Bright Dispersed	Dull	Vit.	Palyn.	Other
4	0.0	0.2	4.8	33.6	2.0	0.8	1.8 (1)
5	3.8	1.2	10.0	24.2	4.8	0.0	1.4 (1)
8	0.0	0.0	1.8	38.4	0.0	0.0	0.4 (2)
9	0.0	0.0	13.6	26.8	0.0	0.0	1.4 (3)
18	0.2	0.0	7.8	32.6	0.0	0.2	2.6 (4)
19	0.2	0.0	9.5	32.3	1.0	0.0	1.0 (5)
24	0.0	0.6	1.2	25.0	0.0	0.0	16.0 (1)
25	0.0	0.0	21.2	26.6	0.8	0.0	0.0
29	0.0	0.0	0.6	41.8	0.2	0.0	0.4 (7)
42	0.0	0.0	35.4	8.8	0.0	0.0	0.0
43	2.2	0.0	18.4	32.0	0.2	0.0	0.2 (6)
46	0.0	0.6	39.2	8.4	0.4	0.0	0.6 (7)
48	3.8	0.8	13.0	33.0	0.6	0.0	10.1 (7)
55	1.2	1.2	5.2	35.2	0.0	0.2	2.2 (7)
58	0.0	0.0	2.2	39.6	0.0	0.2	41.4 (7)
60	0.2	0.2	3.8	36.4	0.4	0.0	27.3 (7)
63	2.2	1.8	13.8	34.8	1.0	0.0	0.0
68	3.6	0.6	20.2	24.3	0.4	0.0	0.4 (7)
69	0.0	0.0	4.0	36.0	0.2	0.2	0.0

*minimum 500 points counted, organic density assumed = 1.0

(1) dark black fluorescing matter, (2) alginite, (3) bituminite, (4) fluorescent porosity fill, (5) microfossils, (6) solid hydrocarbon, (7) voids (excluded from point count total)

DISCUSSIONS AND CONCLUSIONS

The change in the chemical composition of the organic matter with depth in the Green River Formation oil shales studied almost certainly reflects increasing organic maturation with depth. The observed decrease in both the H/C and O/C ratios of the organic matter is consistent with the maturation pathway given by Tissot and Welte (1978) for Type I organic matter. This is shown in Figure 12. Note that the organic matter concentrates analyzed in this study all plot slightly above the "mean" Type I maturation pathway. The apparently high H/C ratios of the concentrates analyzed in this study (although well within the overall range reported by other workers; i.e. Robinson and Cook, 1971, 1973) may reflect the fact that the total organic fraction in the shales was analyzed instead of only the kerogen (or non-soluble) fraction. The decrease in the aliphatic/aromatic ratio of the organic matter and the

increase in the percent aromatic C (NMR data) is also consistent with increasing organic maturation with depth. Recently, Miknis et al. (1982), showed a significant decrease in the fraction of aliphatic C with depth in the Permian Phosphoria Formation organic rich shale units using NMR techniques. The IR data reported in this study are consistent with the decrease in the O/C ratio of the organic matter with depth of burial.

The correlation between the H/C ratio of the organic matter and oil shale grade (wt% organic C or gal/ton) suggests that there may be a difference in the type of organic matter in organic-rich and organic-poor shales. Minor petrographic differences exist between organic-rich and organic-poor laminae: organic matter in dark (=organic-rich) laminae are typically light or dark orange colored while organic matter in light laminae are typically yellow or orange. Recall, also, that the vitrinite reflectances of organic-poor oil shales appear

anomalously high. (Unfortunately, not enough high-grade low-grade sample pairs from similar depths were analyzed.) The limited NMR and IR data, however, show no clear relationship with oil shale grade. Clearly, additional studies are needed in order to determine if such differences actually exist.

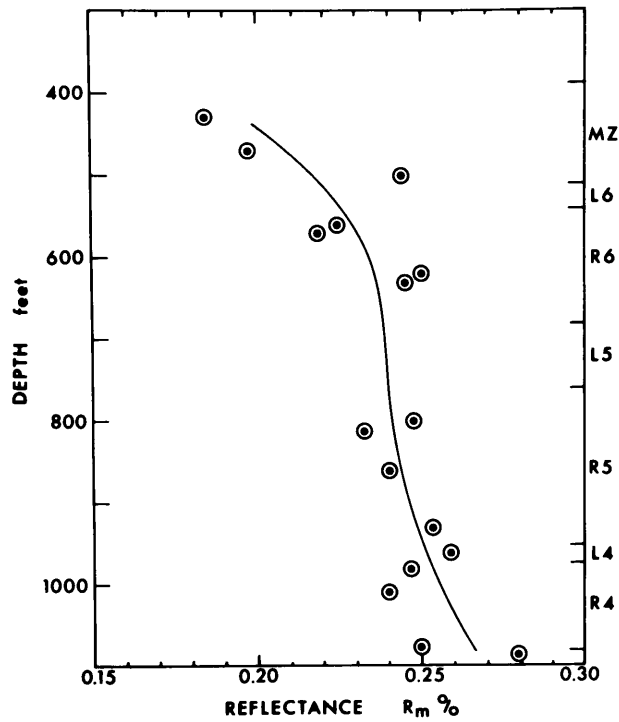


Figure 11 Variation of vitrinite reflectance with depth. Stars=samples with less than 5 wt% organic C.

Changes in the appearance of the organic matter with depth in the oil shales are difficult to detect because of non-uniform distribution of organic matter, varying organic-inorganic associations, and the relatively small stratigraphic separation between shallow and deep samples in the section studied. The significance of the changes actually observed with depth depends on the relative influence of changing depositional environment vs thermal maturation. Several workers (i.e. Robinson,

1976; Cane, 1976; Bradley, 1976) believe that a variety of source materials, depositional environments, and microbial degradation processes occurred throughout deposition of the Green River formation. Although such changes may affect the appearance of the amorphous organic matter in the shales, some of the qualitative and semi-quantitative changes observed with depth are so systematic that explanations involving thermal maturation are necessary. The most convincing petrographic evidence for increased thermal maturation with depth in the interval studied is the fluorescent character of the organic matter. The absence of thin, sharply defined individual bands in the deeper samples and the corresponding lack of diffuse bands in the shallow samples suggest that some thermal threshold must have been reached by the near the middle of the sequence studied (R5 zone). Overall, the fluorescent color of the organic matter shifts from green to yellow with depth (provided mineral interferences are minimal). Although the authors are not aware of literature documenting substantial changes in the fluorescent character of the organic matter with depth in the Green River formation, the variation reported in this study is consistent with changes reported for low rank coals (i.e. Stach, 1975), particularly the shift in fluorescence maxima (green to yellow). Vitrinite reflectance is the only quantitative parameter that showed significant variation with depth. The observed increase in vitrinite reflectance is consistent with increased thermal maturation with depth. As noted earlier, several factors limit the usefulness of the vitrinite data as a thermal maturation indicator.

Considered together, the organic geochemistry data and the organic petrography data reported in this study indicate that significant differences in the nature of the organic fraction with depth of burial exist in the oil shales of the Green River formation. The observed changes largely reflect increasing thermal maturation of the organic matter with

depth. Changes due to differences in depositional environments are minor in the interval studied. Depth-related variations in the composition of the organic matter need to be considered in process design, particularly the decrease in the H/C and O/C ratios and the increase in the aromatic/aliphatic ratio of the organic matter. The relationship between the composition of Green River formation oil shale, both the organic and inorganic fraction, and pyrolysis products in this interval are discussed by Meddaugh (1984).

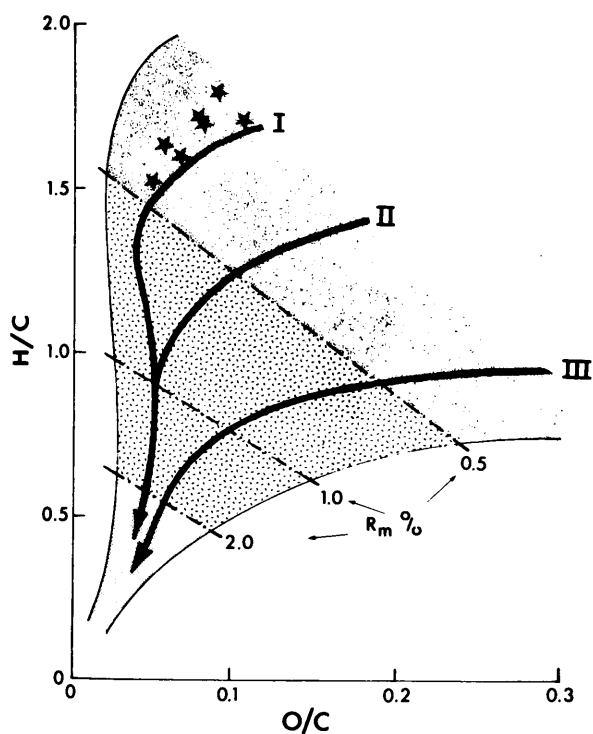


Figure 12 Van Krevelen diagram showing the relationship between the oil shale samples analyzed in this study and the various maturation pathways (I, II, III) of Tissot and Welte (1978).

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VARIATION OF FISCHER ASSAY PYROLYSIS PRODUCTS WITH DEPTH
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PICEANCE CREEK BASIN, COLORADO

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ABSTRACT

Material-balance Fischer Assay data have been obtained for 22 samples (10-62 gal/ton) in the 213 m (700 ft) interval between the top of the Mahogany Zone (MZ) and the base of the R4 zone. Significant variations in product yield and composition exist in the interval studied. In the MZ-L5 interval the product gas composition is (mol%) $H_2 > CO_2 > CH_4$. In the R5-R4 interval the product gas composition is $CO_2 \gg H_2 > CH_4$. The increased CO_2 content of the product gas, due largely to dawsonite decomposition, significantly lowers the thermal value of the product gas from about 900 BTU/ft³ in the MZ to 200-500 BTU/ft³ in the R5-R4 interval. Product oil composition also varies with depth. In the MZ-L5 interval the most important changes are a decrease in the H/C ratio and an increase in oil gravity (g/cm³) with depth. These changes are related to changes in the composition of the organic matter. In the dawsonitic R5-R4 zone the principal change is an increase in the H/C ratio and a decrease in the oil gravity with depth. This apparent reversal probably reflects some catalytic action of dawsonite (and/or nacholite) or its decomposition products (such as Al_2O_3). Average pyrolysis stoichiometries obtained for the MZ, R6, R5, and R4 zones are similar.

INTRODUCTION

The Fischer Assay (FA) pyrolysis technique is widely used to determine the oil yield (oil volume/shale weight) of oil shales. The assay products (oil, gas, and water) are often subjected to additional analyses in order to obtain an understanding of the pyrolysis stoichiometry as well as the nature and quality of the products.

In this study material-balance FA data were obtained from 22 oil shales samples from a core from near the center of the C-a Tract, Piceance Creek Basin, Colorado. The samples were obtained at irregular intervals from the 213 m (700 ft) interval between the top of the Mahogany Zone (MZ) and the base of the R4 zone. The material-balance FA data are used to assess variations in product yield and quality with depth in the MZ-R4 interval. The data are also used to assess correlations between product yield and quality and the in place nature of oil shale. The mineralogy of the oil shales within the MZ-R4 interval has been reported by Meddaugh and Salotti (1983). The organic geochemistry and petrography of this interval is discussed by Meddaugh et al. (1984).