VARIATION OF FISCHER ASSAY PYROLYSIS PRODUCTS WITH DEPTH GREEN RIVER FORMATION OIL SHALES 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/ft^3 in the MZ to 200-500 BTU/ft^3 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/cm^3) 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 stochiometries 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 stochiometry 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 asess variations in product yield and quality with depth in the MZ-R4 interval. The data are also used 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).

ANALYTICAL METHODS

Material balance Fischer Assays were made following standard techniques. Product gas compositions (H_2, CO, CO_2, H_2S, CH_4, C2-C5 hydrocarbon gases) were determined by GC. Standard microanalysis (Microanalysis Inc., Wilmington, DE) techniques were used analyze the product oils for wt% C, H, N, O, and S. HPLC was used to determine the wt% saturated, aromatics, polar, and in soluble compounds in the product oils. The wt% olefins in the product oils were also determined. Simulated distillation curves by GC were also obtained for the product oils. Retorted oil shales were analyzed for organic C and H and total N by standard techniques (Microanalysis Inc.).

The mineralogical composition of the oil shales were determined by a normative method in which whole rock chemical data are recalculated in terms of a set of normative or standard minerals with defined compositions (usually stochiometric). This procedure is described in detail by Meddaugh and Salotti (1983). The minerals included in the norm are quartz, albite, orthoclase, illite, analcite, pyrite, calcite, dolomite, ankerite (Fe/Mg=1), magnesite, Mg-siderite (Fe/Mg=1), dawsonite, and nahcolite. All samples were also analyzed by x-ray diffraction. Chemical data for the organic matter in the oil shale samples used in this study are given in Meddaugh et al (1984).

RESULTS

The material balance FA data (oil yield, oil gravity, gas yield, and water yield) and product gas composition data (H_2, CO, CO_2, H_2S, C1-C5 hydrocarbon gases) are reported in Table 1. Product oil data (wt% C, H, N, O, S, saturates, aromatics, polars, insolubles, and the saturate/olefin ratio) are reported in Table 2.

Organic C - Oil Shale Yield Correlation

Figure 1 is a plot of shale yield (gal/ton) vs wt% organic C for the 22 oil shale samples analyzed in this study. The least squares, best-fit line for the data shown in Figure 1 is

$$\text{Yield (in gal/ton)} = [(2.346)(\text{wt\% organic C})] - 0.7976 \qquad (1)$$

Equation (1) predicts, on the basis of wt% organic C, approximately 4% more oil than the correlation reported by Singleton et al. (1982) and about 8% more oil than the correlation reported by Cook (1973).

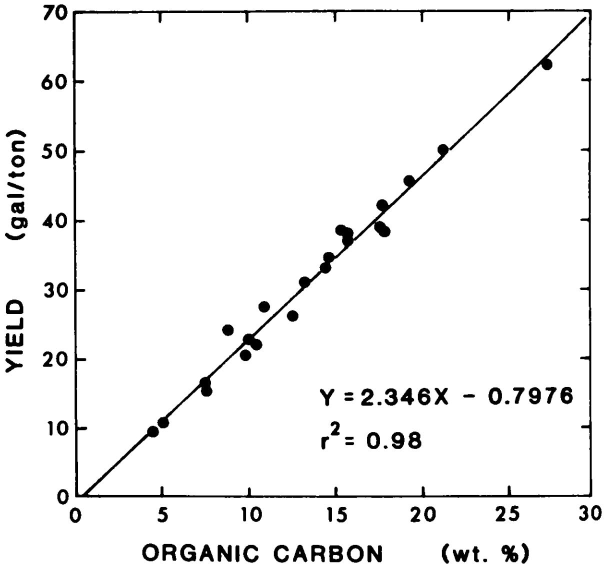

Figure 1 Plot of wt% organic C vs oil shale yield (gal/ton).

Product Gas - Variation With Depth

Figure 2 shows the variation of the FA product gas yield (1/100 g shale) and composition (mol% H_2, CO, CO_2, H_2S, and CH_4) with depth in the MZ-R4 interval studied. In the upper part of this interval (MZ-L5 interval) the gas yield is fairly uniform, about 2.5 1/100 g shale. In the lower part of the interval studied (R5-R4 interval) the gas yield is greater and varies considerably from sample to sample. The gas yield ranges from 1.8 to 6.8 1/100 g shale in the R5-R4 interval.

Table 1. Fischer Assay and Product Gas Data

#	Oil Yield gal/ton	Water Yield gal/ton	Oil Gravity g/cm³	Gas Yield (ℓ/100 g shale)	Gas Yield g/100 g shale	H_2	CO	CO_2	H_2S	CH_4	C_2H_4 Mole %	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	C_5H_{12}	
4	9.53	2.19	.9095	6.73	16.95	2.46	7.24	2.45	3.16	2.49	1.86	0.99					
5	49.80	5.60	.9095	5.78	6.06	24.45	14.61	16.63	7.11	14.69	2.24	5.77	2.43	3.03	1.89	1.55	0.66
8	16.43	3.89	.9116	1.77	1.92	26.21	9.95	25.52	6.05	16.78	2.74	8.50	2.79	3.64	2.64	2.07	0.97
9	41.96	3.91	.8980	3.33	3.42	29.28	4.91	19.60	4.11	18.18	2.59	9.13	3.06	4.53	2.51	1.97	1.13
12	34.56	2.60	.9061	2.37	2.37	30.10	5.60	17.08	20.71	12.56	2.18	5.66	1.99	4.24	2.03	1.85	0.75
18	20.50	3.28	.9077	2.65	3.10	20.58	6.35	21.10	10.62	12.83	2.06	6.03	2.56	3.57	2.16	1.64	1.18
19	22.50	3.59	.9026	1.83	2.04	24.01	12.39	20.97	7.27	18.75	2.43	8.63	2.48	3.48	2.56	1.89	1.35
24	38.18	2.92	.9149	3.03	2.42	31.92	4.95	14.29	10.10	14.80	2.37	7.02	2.93	8.00	2.42	1.82	1.13
25	24.12	2.63	.9158	2.55	3.00	21.33	5.23	22.87	10.45	15.19	2.51	7.23	3.29	6.62	2.43	2.21	1.04
29	33.02	2.70	.9196	2.26	2.74	16.61	11.63	20.80	27.24	9.27	1.71	4.11	2.40	2.38	1.73	1.23	0.60
32	10.68	2.63	.9253	1.81	1.45	19.16	4.65	25.55	1.61	17.36	3.52	8.89	4.04	4.85	3.21	2.42	0.99
42	38.33	5.37	.9023	3.11	3.54	22.76	6.81	23.56	8.36	14.68	2.33	6.65	2.84	3.70	2.64	2.09	1.34
43	38.17	4.03	.8991	3.61	2.64	23.45	8.11	23.82	3.45	11.77	2.17	6.33	2.43	2.89	2.25	1.71	1.40
46	61.93	2.80	.9029	6.81	8.28	21.38	9.91	34.33	2.13	11.06	1.82	4.80	2.39	3.11	1.97	1.41	0.85
48	37.28	4.55	.8969	4.83	6.27	16.28	13.06	41.12	4.07	4.99	0.80	1.93	1.18	1.08	0.98	0.56	0.38
51	15.24	6.65	.8933	6.42	7.746	14.59	4.10	65.33	1.51	5.13	1.46	3.03	1.21	1.26	1.11	0.75	0.53
55	22.90	5.47	.8976	6.18	8.85	14.22	8.81	60.99	0.44	10.22	2.39	5.19	1.96	2.21	1.24	1.15	0.64
58	22.24	4.81	.8929	1.85	2.45	17.76	5.41	50.90	1.41	9.60	1.22	3.08	1.79	1.42	1.70	1.38	0.60
60	26.22	5.86	.8993	2.57	3.41	16.80	11.19	49.82									
68	37.53	5.42	.8913														
69	31.03	4.03	.8801	3.07	4.00	20.26	3.88	48.12	5.99	8.60	1.73	4.29	1.56	1.88	1.74	1.24	0.72

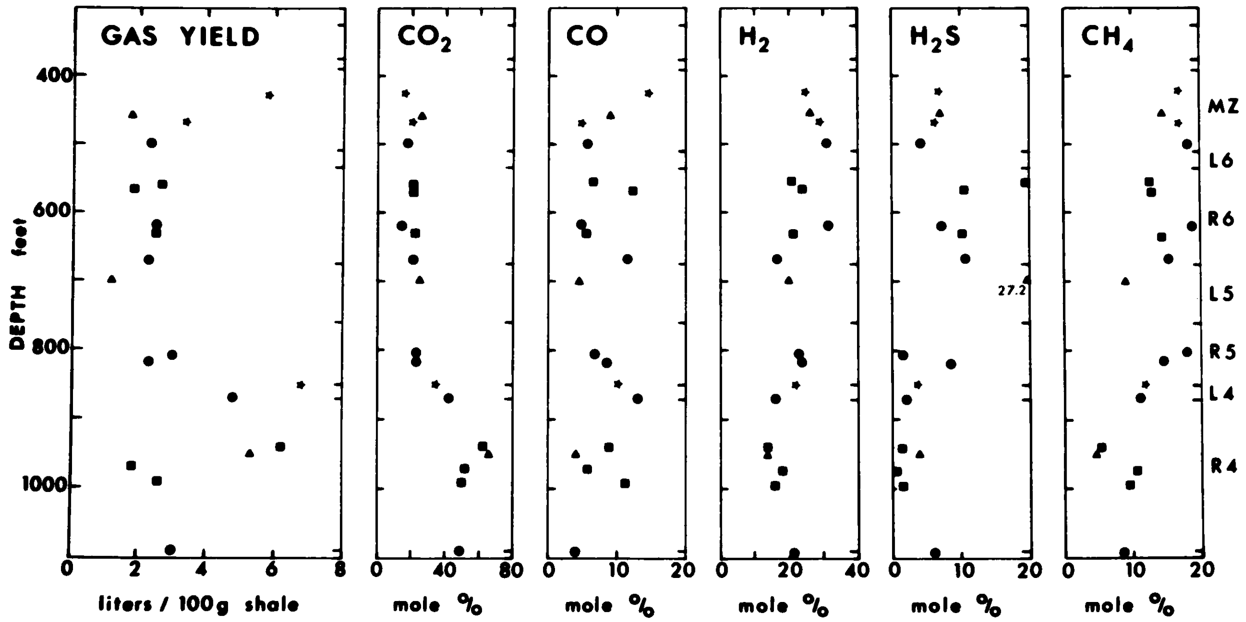

Figure 2 Variation of Fischer Assay pyrolysis gas composition (mol%) and yield (1/100 g shale) with depth. Symbols: (▲) shale grade < 15 gpt; (■) 15-30 gpt; (●) 30-40 gpt; (✱) > 40 gpt.

Table 2. Fischer Assay Product Oil Data (wt%)

Sample No.	C	H	N	O	S	Sat.*	Arom.**	Polars	Ins.+	Saturate/ Olefin
04	84.09	11.48	1.697	1.55	1.02	21.7	27.4	26.3	1.9	0.75
05	83.50	11.20	1.983	1.76	1.00	19.0	32.0	27.8	1.1	0.74
08	83.32	11.08	1.735	2.55	0.95	21.7	24.8	26.9	2.3	0.66
09	83.96	11.34	1.862	2.11	1.11	22.5	31.2	25.8	1.3	0.83
12	82.80	11.20	2.248	2.26	0.69	19.3	30.8	30.3	1.2	0.91
18	83.97	11.28	1.681	2.24	1.46	19.1	32.5	25.0	1.7	0.75
19	83.72	11.35	1.941	2.29	1.21	18.2	28.3	28.9	1.2	0.96
24	83.39	11.10	2.043	1.37	0.82	18.3	33.3	29.0	1.9	0.78
25	83.08	11.23	2.265	2.40	0.79	15.0	27.2	31.6	2.2	0.76
29	83.35	11.06	2.018	2.19	1.00	18.6	28.2	28.0	1.8	0.79
32	82.46	11.07	2.023	0.87	2.06					
42	83.95	11.05	1.942	2.50	0.75	14.4	30.6	30.3	1.1	0.87
43	83.42	11.04	1.606	1.95	1.13	23.5	25.0	28.5	1.1	0.88
46	82.48	11.12	1.761	2.43	1.14	17.3	32.7	26.3	0.9	0.90
48	83.25	11.39	1.799	1.57	0.96	22.2	29.4	26.6	1.1	0.64
51	84.47	11.87	1.318	0.40	1.14					
55	84.24	11.41	1.656	2.00	1.05	23.0	31.4	24.8	1.4	0.93
58	83.49	11.69	1.591	2.13	1.17	23.3	29.4	24.2	1.7	0.81
60	83.73	11.56	1.628	2.27	1.17	24.2	32.1	24.2	1.4	0.98
63	83.91	11.28	2.018	2.00	1.02	20.9	32.2	25.2	1.0	0.66
68	83.55	11.58	1.819	1.48	1.14	20.9	31.4	26.1	0.9	0.90
69	83.32	11.40	1.722	1.70	1.39	19.2	33.7	22.2	1.3	0.81

*Saturates
**Aromatics
+Insolubles

Gas composition also varies with depth. In the MZ-L5 interval mol% $H_2 > CO_2 > CH_4$. In the R5-R4 interval mol% $CO_2 \gg H_2 > CH_4$. Note that the CO_2 content of the product gas is about 20 mol% throughout the MZ-L5 interval. However, in the R5-R4 interval the product gas contains 35-65 mol% CO_2. The increased CO_2 content of the product gas in the R5-R4 interval reflects the presence of significant dawsonite and nahcolite in the R5-R4 interval. The samples obtained from the R5-R4 interval contain 2-15 wt% dawsonite and 0-5 wt% nahcolite (Meddaugh and Salotti, 1983).

Figure 3 shows the variation of the product gas yield and composition with depth on a constant organic C basis. Except for two samples containing > 15 wt% dawsonite, the gas yield is nearly constant, about 20 1/100 g organic C. Also, the mol% H_2, CH_4, and C2-C5 hydrocarbon is essentially uniform on a constant organic C basis throughout the interval studied. The decrease in the mol% H_2 and CH_4 with depth shown in Figure 2 is largely due to CO_2 dilution.

A significant consequence of the large increase in the CO_2 content of the product gas from the dawsonitic R5-R4 interval oil shales is a decrease in the thermal value of the product gas. Figure 4 shows the variation of the thermal value of the FA product gas with depth on a constant shale weight, a constant organic C, and a constant gas volume basis. The BTU value of the product gas varies between 50 and 150 BTU/100 g shale. The BTU value of the product gas varies from 4 to 7 BTU/g organic C. There is no significant correlation between the themal value of the product gas and depth on either a constant shale or constant organic C basis. On a constant gas volume basis, the BTU value of the product gas ranges from 700-900

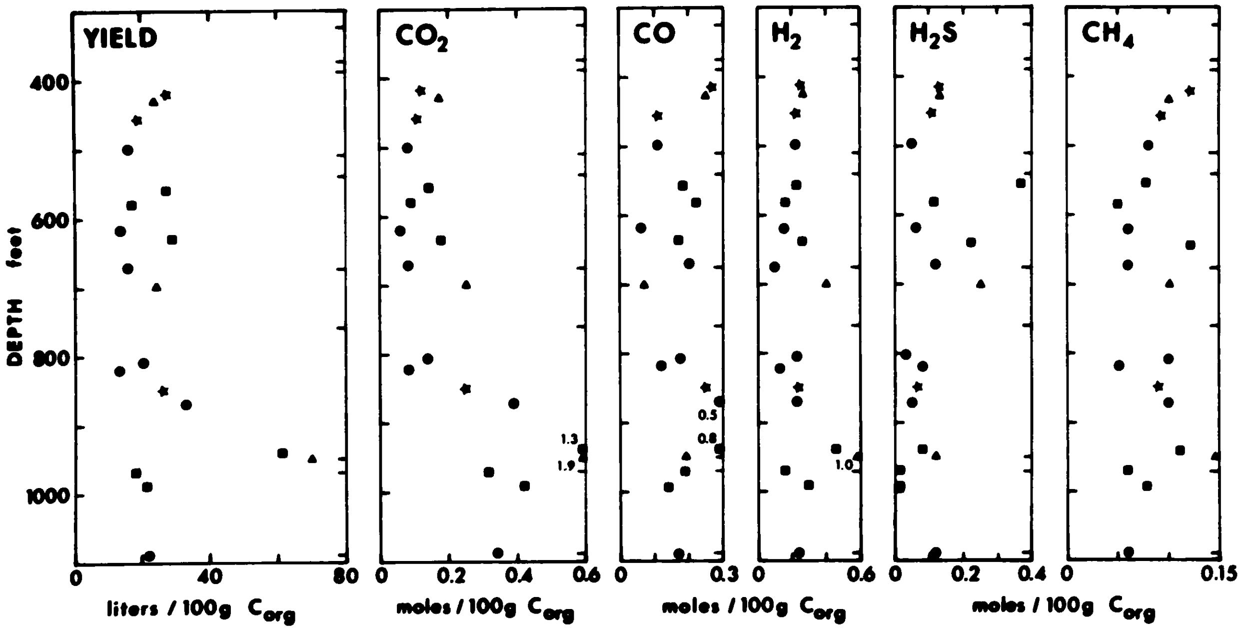

Figure 3 Variation of Fischer Assay pyrolysis gas composition (mol%) and yield (1/100 g organic C) on a constant organic C basis. Symbols given in Figure 2.

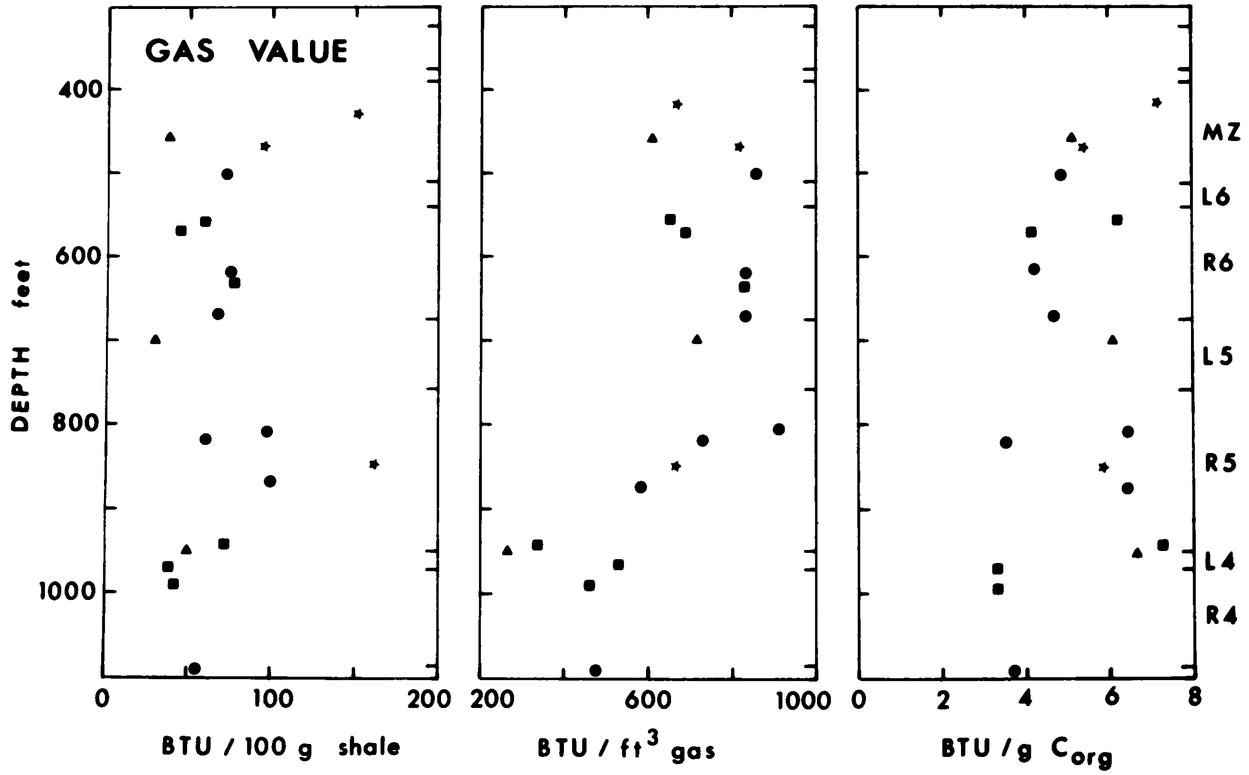

Figure 4 Variation of Fischer Assay product gas thermal value (BTU) on a constant shale weight, constant gas volume, and constant organic C basis. Symbols given in Figure 2.

BTU/ft^3 in the MZ-L5 interval to 200-700 BTU/ft^3 in the dawsonitic R5-R4 interval. In general, the greater the dawsonite content of the oil shale, the lower the BTU value of the product gas.

Product Gas - Variation with Shale Grade and Mineralogy

As shown in Figure 5 there is a positive correlation between gas yield and shale grade (gal/ton or wt% organic C). The least squares, best fit line for the data shown in Figure 5 is

$$\text{Gas Yield (1/100 g shale)} = (0.2332)(\text{wt\% organic C}) - 0.1766 \qquad (2)$$

Singleton et al. (1984) noted a direct relationship between CO, H_2, CH_4, and C2-C5 hydrocarbon gase and shale grade. Figure 6 shows a plot of produced H_2 and CH_4 (g/100 g shale) vs shale grade for the samples analyzed in this study. Note that the H_2 production from dawsonitic shales is generally greater than that from non-dawsonitic shales with similar organic C values. Samples containing more than 15 wt% dawsonite produce 2-5 times more H_2 than would be expected on the basis of their organic C content. The presence of dawsonite does not appear to significantly affect the amount of CH_4 or C2-C5 hydrocarbons produced during FA pyrolysis.

Figure 7 is a plot of produced CO_2 (g/100 g shale) vs wt% organic C. The absence of an overall corerlation between CO_2 production and shale grade, in contrast to the positive correlation reported by Singleton et al. (1982), reflects the fact that CO_2 production during FA pyrolysis is clearly dominated by the decomposition of dawsonite and nahcolite (as well as the other carbonate minerals). This is shown more clearly in Figure 8, a plot of CO_2 production vs wt% dawsonite. The CO_2 production from the non-dawsonitic MZ-L5 interval oil shales varies between 0.5-1.2 g CO_2/100 g shale. If the dawsonite-bearing shales are excluded, there is a slight positive correlation between CO_2 production and shale grade. This is probably due to the fact that there is a negative correlation between shale grade and wt% dolomite (the major carbonate mineral in the MZ-L5 interal, see Meddaugh and Salotti, 1983) in the MZ-L5 interval. The somewhat surprising negative correlation between CO_2 production and wt% total carbonate shown in Figure 9 (excluding dawsonitic oil shales) reflects the fact that calcite is proportionally more abundant in the high total carbonate samples in the MZ-L5 interval than dolomite and ankerite (both of which decompose at lower temperatures than calcite).

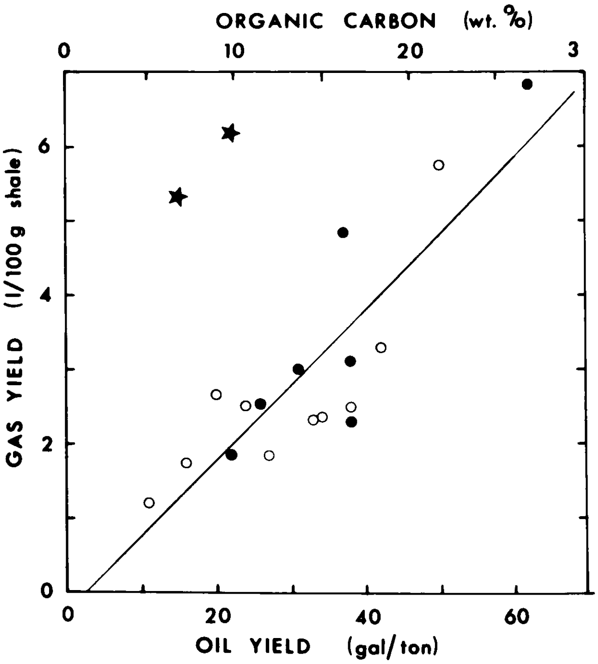

Figure 5 Plot of Fischer Assay product gas yield vs shale grade. (○) non-dawsonitic oil shales; (●) dawsonitic oil shales; (★) oil shales with > 15 wt% dawsonite.

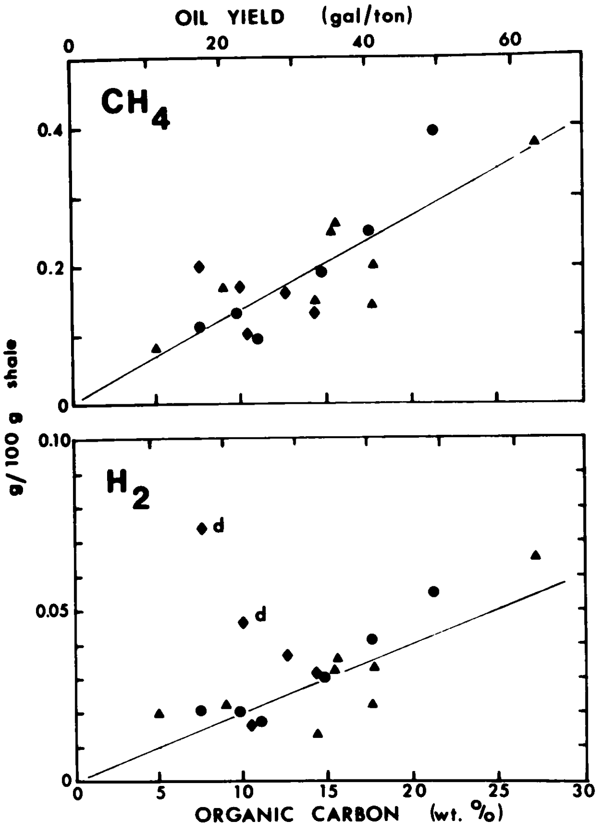

Figure 6 Plot of produced H_2 and CH_4 (g/100 g shale) vs shale grade. (●) non-dawsonitic oil shales; (▲) dawsonitic oil shales (d >15 wt% dawsonite).

There is no correlation between shale grade and H_2S production. H_2S production is clearly related to the wt% pyrite in the oil shale. This relationship has been discussed in detail by Burnham (1982) and will not be considered further.

Product Oil - Variation with Depth

Figure 10 shows the variation of the specific gravity (g/cm^3), and the H/C, N/C, O/C, and S/C ratios of the FA product oil with depth. The specific gravity of the product oil increases with depth from 0.89-0.90 in the MZ to about 0.92 in the L5 zone. Below the L5 zone the specific gravity of the product oil decreases with depth to about 0.86-0.88 in the

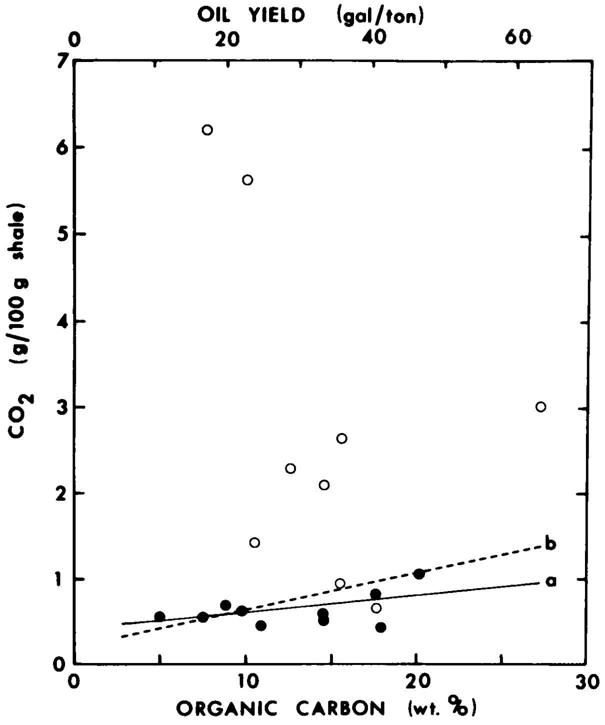

Figure 7 Plot of produced CO_2 vs wt% organic C. (●) non-dawsonitic oil shales; (○) dawsonitic oil shales.

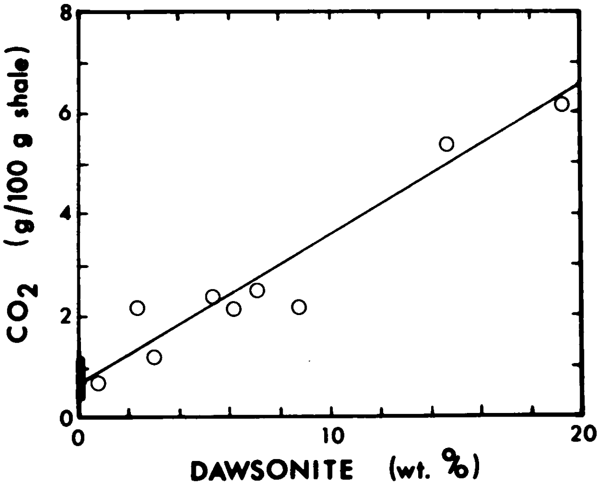

Figure 8 Plot of produced CO_2 vs wt% dawsonite. Heavy bar shows range for non-dawsonitic oil shales.

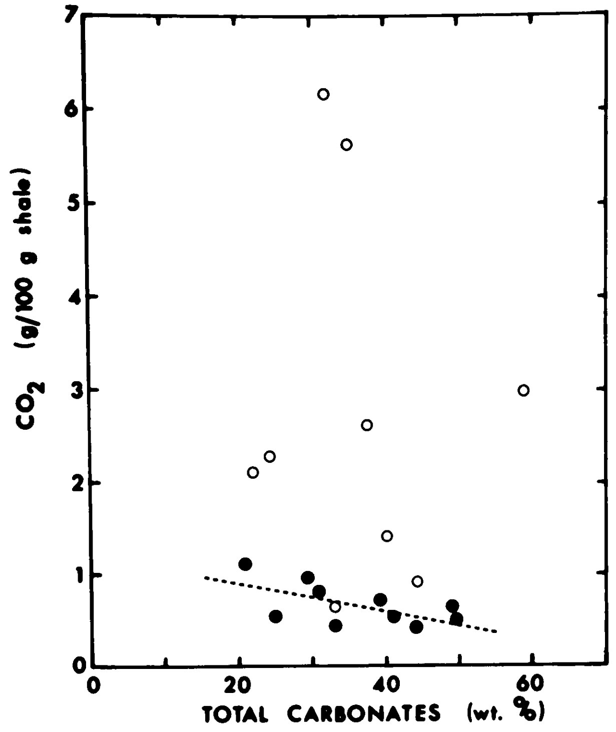

Figure 9 Plot of produced CO_2 vs wt% total carbonates. (●) non-dawsonitic oil shales; (○) dawsonitic oil shales.

R4 zone. The H/C ratio of the product oil decreases with depth from about 1.66 in the MZ to 1.60 in the L5 zone. Below the L5 zone the H/C of the product oil increases with depth to 1.64-1.68 in the R4 zone. The reversal of both the specific gravity and H/C ratio trend at the top of the R4 zone corresponds to the appearance of significant dawsonite in the oil shales. Within the R5-R4 interval wt% dawsonite and nahcolite increase with depth (Meddaugh and Salotti, 1983). The N/C, O/C, and S/C ratios of the product oil do not vary significantly with depth.

Smith (1963) reported that the specific gravity of oil reported from Green River Formation oil shales decreases uniformly with depth, in apparent contrast to the data shown in Figure 10. However, Smith's (1963) oil gravity data (see his Figure 2) shows many abrupt reversals, some of which may be related to changes in the mineralogical composition and/or changes in the composition of the organic fraction of the oil shale in addition to the decarboxylation reaction proposed by Smith (1963). This is discussed in greater detail below.

Figure 11 shows the variation of the wt% saturates, aromatics, polars, and insolubles (by HPLC) in the product oil with depth. In the MZ-L5 interval the wt% saturates and aromatics decrease and the wt% polars increase with depth. In the dawsonite-bearing R5-R4 interval these trends are reversed; wt% saturates and aromatics increase and the wt% polars decrease with depth. The saturate/olefin ratio and the simulated distillation curves show no significant variation with depth.

Product Oil - Variation with Shale Grade

Figure 12 shows the variation of the product oil H/C, N/C, O/C, and S/C ratios vs shale grade. Note the negative correlation between the product oil H/C ratio and shale grade. This is consistent with the negative correlation between the H/C ratio of the organic matter and shale grade reported by Meddaugh et al (1984) and a positive correlation between the H/C ratio of the product oil and the H/C ratio of the organic matter (see below). There is no correlation between the N/C, O/C, or S/C ratios of the product oil and shale grade. Also, there is no correlation between the wt% saturates, aromatics, polars, or insolubles in the product oil and shale grade.

Product Oil - Variation with Organic Matter Chemistry and Oil Shale Mineralogy

Figure 13 is a plot of the H/C ratio of the product oil vs the H/C ratio of the organic matter in the raw shale. There is a positive correlation between the H/C ratio of the product oil and the H/C ratio of the organic matter in the non-dawsonitic oil shales in the MZ-L5

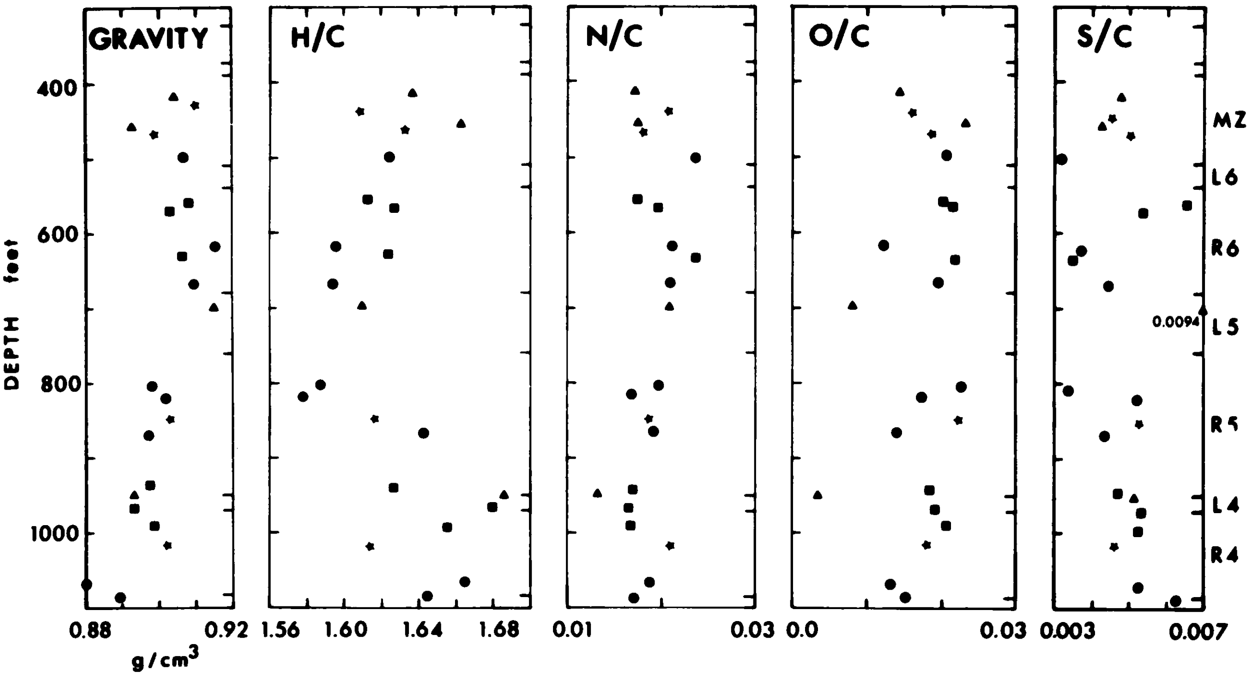

Figure 10 Variation of Fischer Assay product oil gravity (g/cm^3) and H/C, N/C, O/C, and S/C ratios with depth. Symbols given in Figure 2.

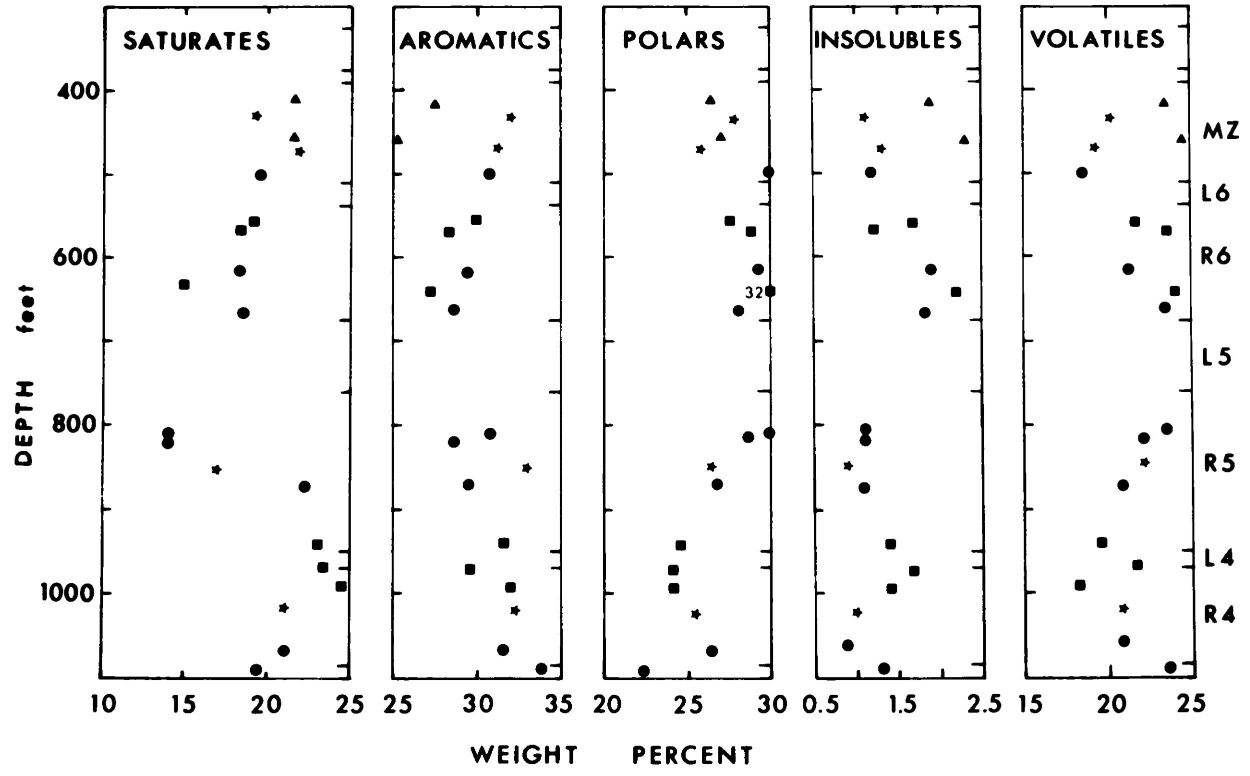

Figure 11 Variation of Fischer Assay product oil wt% saturates, aromatic, polars, insolubles, and volatiles (by HPLC) with depth. Symbols given in Figure 2.

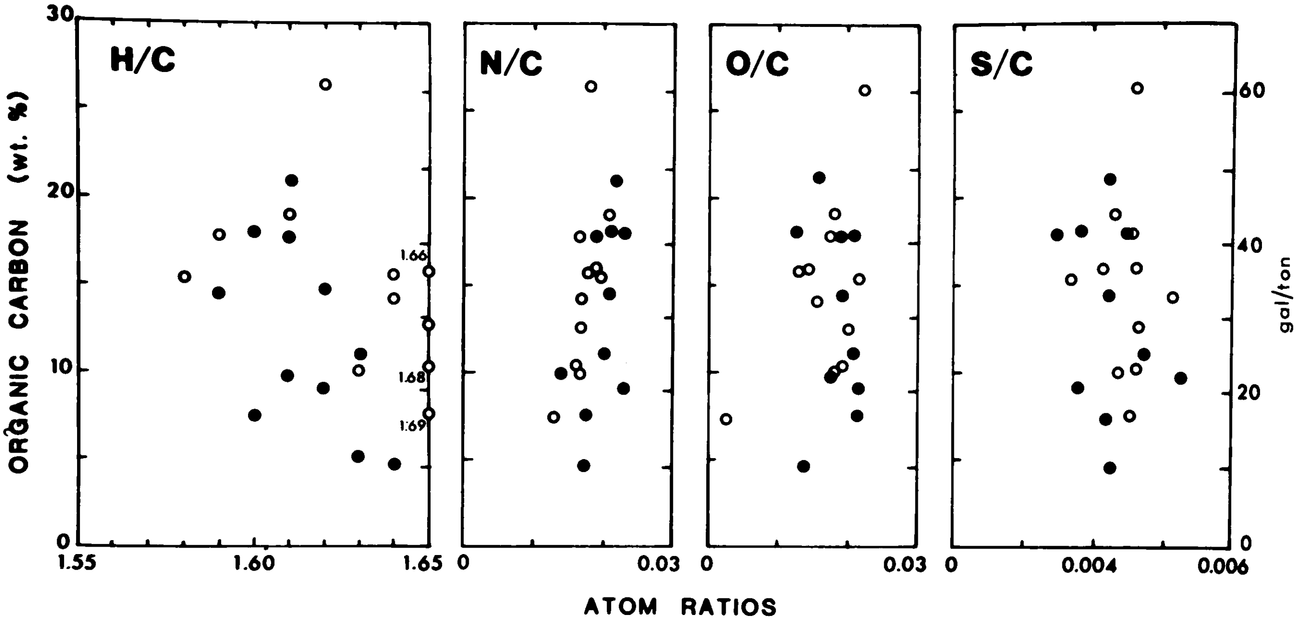

Figure 12 Variation of Fischer Assay product oil H/C, N/C, O/C, and S/C ratios with shale grade. Symbols given in Figure 9.

interval. The H/C of the product oil is less than the H/C ratio of the organic matter for non-dawsonitic oil shales. The relationship between the H/C ratio of the product oil is and the H/C ratio of the organic matter is given by

$$\text{oil H/C} = (0.1919)(\text{organic matter H/C}) + 1.2788 \qquad (3)$$

For dawsonitic shales this is no apparent correlation between the H/C ratio of the product oil and the H/C ratio of the organic matter. Note that the H/C ratio of the product oil obtained from dawsonitic oil shales is generally greater than the H/C ratio of the organic matter. The reversal of the product oil H/C ratio trend with depth shown in Figure 9 is more surprising in view of the observation that the H/C ratio of the organic matter decreases uniformly with depth over the entire MZ-R4 interval (Meddaugh et al., 1984).

There is a strong, positive correlation between the N/C ratio of the product oil and the N/C ratio of the organic matter. This is shown in Figure 14. The N/C ratio of the product oil is less than the N/C ratio of the organic matter. The N/C ratio data shown in Figure 13 can be described by the following:

$$\text{oil N/C} = (0.6294)(\text{organic matter N/C}) + 0.0018 \qquad (4)$$

Figure 14 also shows a plot of the O/C ratio of the product oil vs the O/C ratio of the organic matter. The O/C ratio of the product oil is considerably less than the O/C ratio of the organic matter. Note the considerable scatter of the O/C data shown in Figure 14.

Conversion Efficiency

Figure 15 shows the variation of the fraction of organic C and H converted to oil and gas during FA pyrolysis with depth. The fraction of organic C converted to gas during pyrolysis varies between 0.055 and 0.181. The fraction of organic C converted to oil during pyrolysis varies between 0.628 and 0.745. The

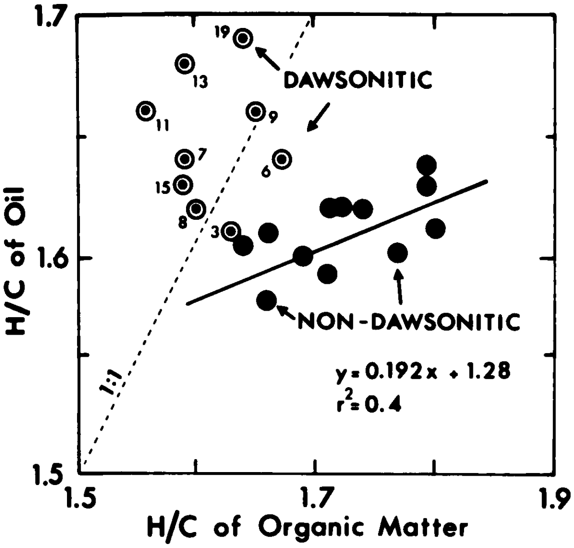

Figure 13 Plot of product oil H/C vs organic matter H/C (in raw oil shale). Numbers = wt% dawsonite.

total fraction (gas + oil) of organic C converted during pyrolysis varies between 0.733 and 0.898. Note that there is no significant variation of the fraction of organic C converted to either gas or oil with depth. The fraction of organic H converted to gas during pyrolysis ranges between 0.093 and 0.245. The fraction of organic H converted to oil during pyrolysis varies between 0.594 and 0.764. The total fraction of organic H converted during pyrolysis is generally greater than that for organic C. For H, the total fraction converted varies between 0.720 and 0.987. Note that there is no significant correlation between the fraction of organic H converted to either gas or oil with depth in the interval studied.

Figure 16 shows the expected correlation between the fraction of organic C and the fraction of organic H converted to gas and oil during FA pyrolysis. Interestingly, the fraction of organic H converted to oil is greater than the fraction of C converted to oil

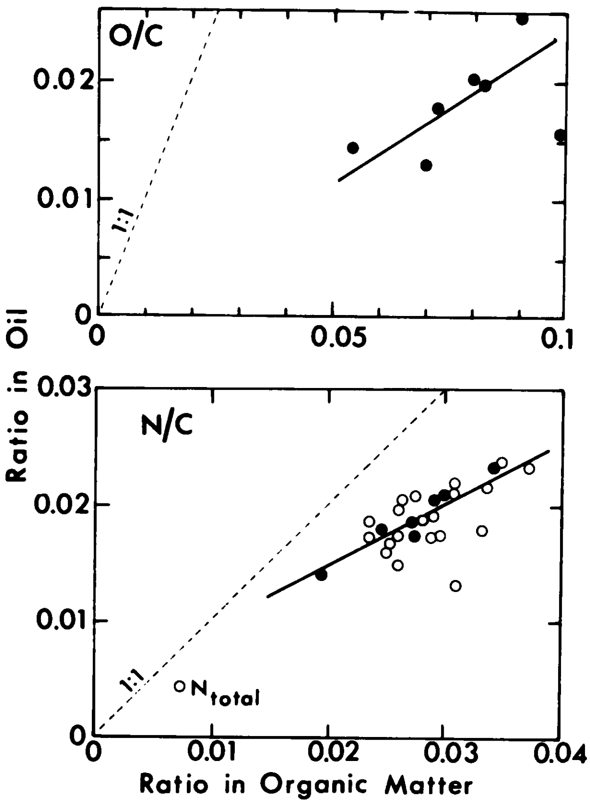

Figure 14 Plot of product oil N/C and O/C vs organic matter N/C and O/C ratios. Symbols given in Figure 9.

in dawsonitic oil shales. This is consistent with the fact that the H/C ratio of oil obtained from dawsonitic oil shales is greater than expected on the basis of the H/C ratio of the organic matter in the dawsonitic oil shales (Figure 13). There is no significant difference in the fraction of organic C and H converted to gas in dawsonitic or non-dawsonitic oil shales.

Figure 17 shows the variation of the fraction of total N converted to oil during FA pyrolysis with depth in the interval studied. No data are available for the N content of the product gas. The fraction of total N converted to oil during pyrolysis varies between 0.272 and 0.607. There is no correlation between the fraction of N converted to oil and depth.

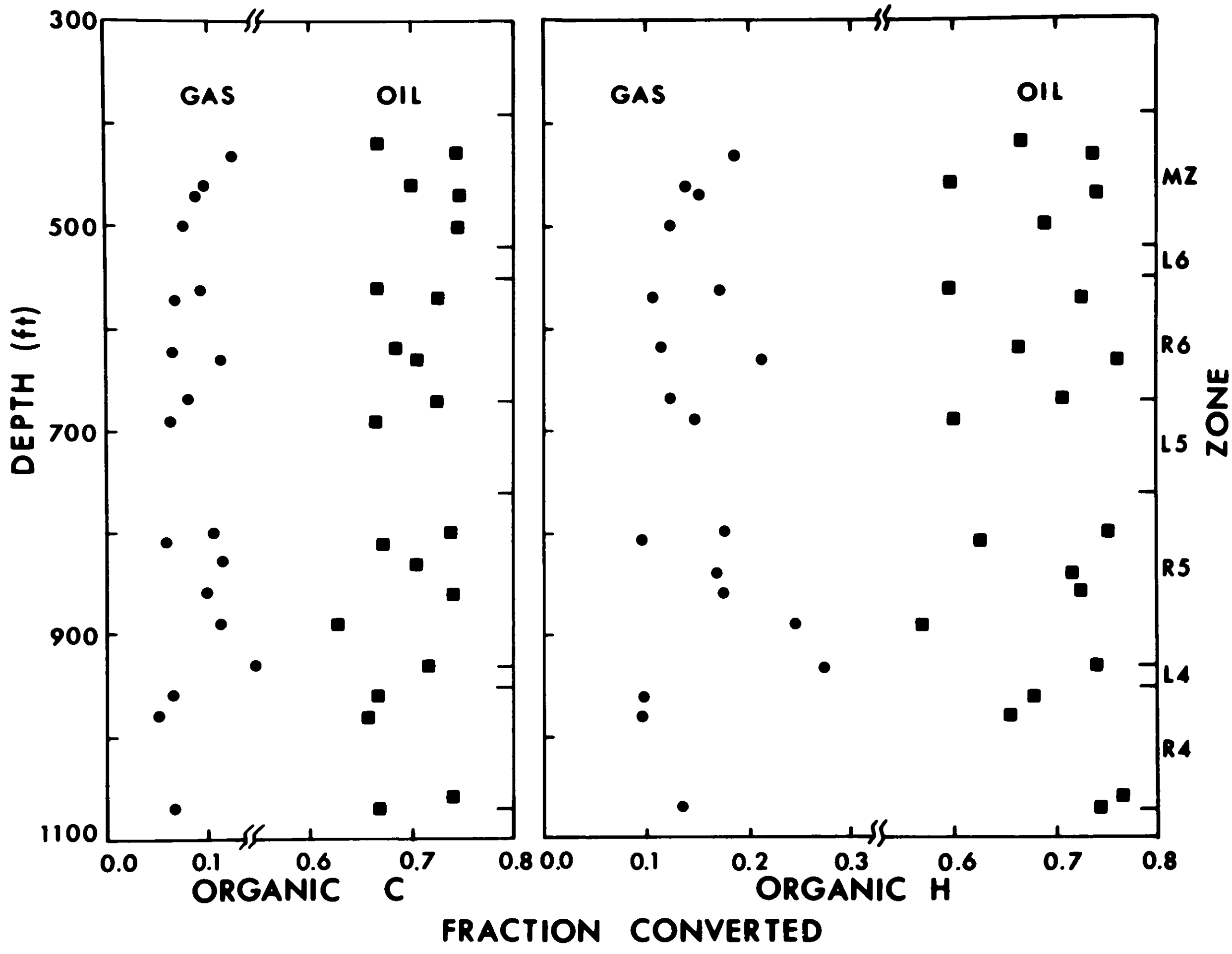

Figure 15 Variation of organic C and H converted to product gas and oil during pyrolysis with depth.

Some researchers (e.g. Jeong and Patzer, 1983) have noted a correlation between pyrolysis yield and the silicate/carbonate ratio of the oil shale. Figure 18 shows that there is little, if any, correlation between the silicate/carbonate ratio of the oil shale and the fraction of organic C converted to either oil or gas during pyrolysis. There is also no correlation between the silicate/carbonate ratio and the fraction of organic H converted to oil or gas. The absence of any correlation between the silicate/carbonate ratio is not surprising - if such a correlation was significant the published correlations between shale yield and wt% organic C (e.g. Cook, 1973; Singleton et al, 1982; this study) would show more scatter.

Pyrolysis Stoichiometry

Table 3 gives the average pyrolysis stochiometries for the MZ, R6, R5, and R4 zones. These stochiometries were calculated from the gas data shown in Table 1, the oil data shown in

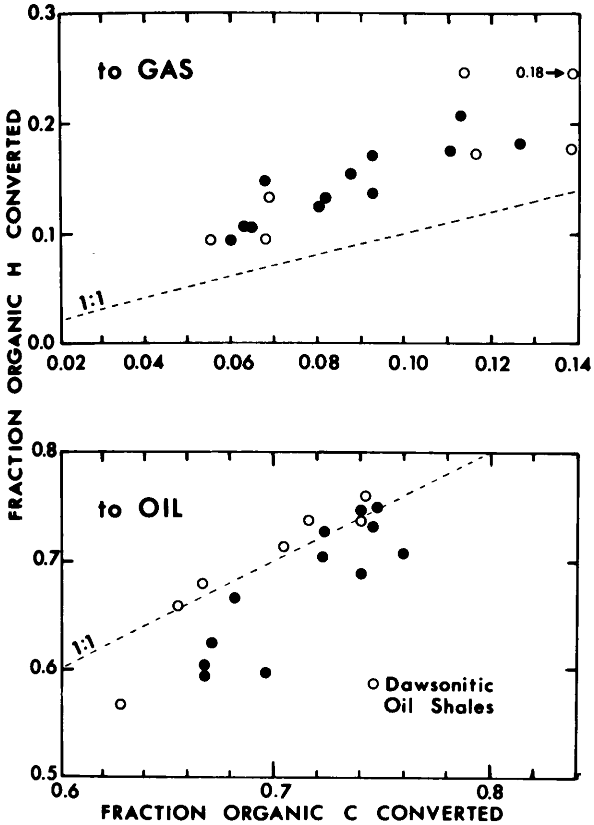

Figure 16 Plot of fraction of organic C converted to oil and gas and fraction of organic H converted to oil and gas, respectively, during pyrolysis.

Table 2, and the raw shale data reported by Meddaugh et al. (1984, see their Table 1). The average stochiometry reported by Singleton et al (1982) is shown in Table 3 for comparison. No values are given for CO_2 in this study because virtually all of the CO_2 produced during pyrolysis is due to carbonate mineral decomposition. Singleton et al. (1982) have reported that, on average, about 20% of the FA produced water is derived from the organics and 80% from inorganic phases such as illite or analcime. Figure 19 shows a plot of FA produced water vs wt% organic C and wt% analcite + illite + dawsonite. (Mineral data are from Meddaugh and Salotti, 1983). Note the absence of a strong correlation between the FA produced water and either wt% organic C or wt% analcite + illite + dawsonite + nahcolite. It is clear from Figure 17, however, that water yield is greater in dawsonitic oil shales with a given wt% organic C than in non-dawsonitic oil shales. Additional work is needed in order to accurately predict the FA water yield.

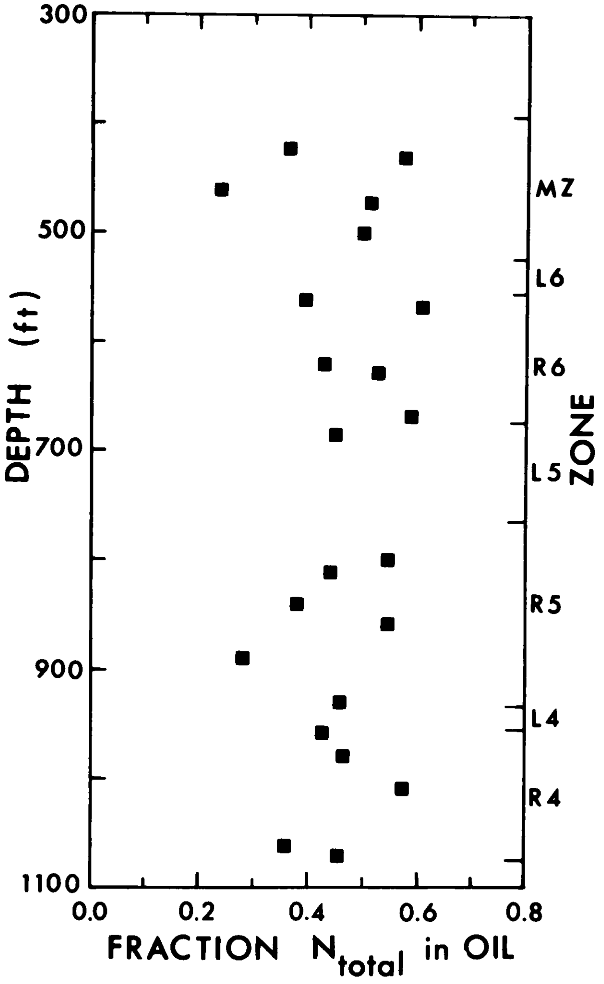

Figure 17 Variation of N converted to oil with depth.

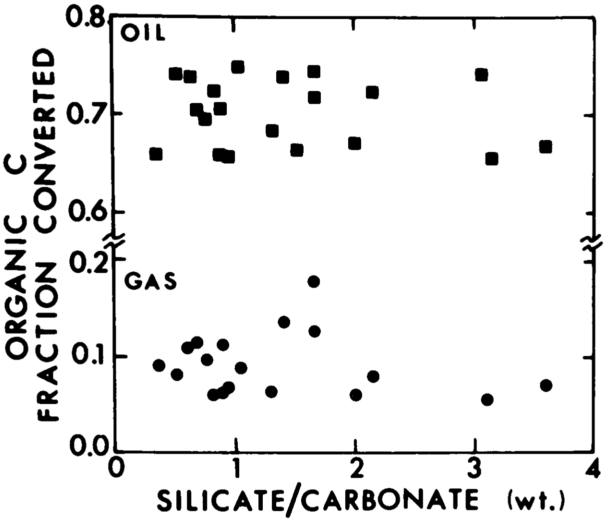

Figure 18. Plot of fraction of organic C converted to oil and gas vs silicate/carbonate ratio of raw oil shale.

Although the average organic compositions shown in Table 3 contain considerably more H than the stochiometry reported by Singleton et al. (1982), the abundance and composition of the pyrolysis products shown in Table 3 for the data reported in this study is quite similar to that reported by Singleton et al (1982). Note that the stoichiometries reported for the MZ, R6, R5, and R4 zones differ very little. There is a slight increase in the H/C ratio of the product oil with depth, a slight decrease in the N/C ratio with depth, and a slight decrease in the H/C ratio of the C2-C5 hydrocarbon fraction. Such average stochiometries do not reflect some of the significant variations in product quality described in the previous sections.

Table 3. Pyrolysis Stoichiometry

Mahogany Zone	
OM*	$CH_{1.73}N_{0.029}O_{0.089}$
oil	0.719 $CH_{1.62}N_{0.020}O_{0.018}$
H_2	0.034
CO	0.010
H_2S	0.011
CH_4	0.018
(C_2-C_5)	0.064 $C_{2.94}H_{7.23}$
char	0.188 $CH_{0.30}$
R6 Zone	
OM	$CH_{1.73}N_{0.019}O_{0.082}$
oil	0.701 $CH_{1.61}N_{0.070}O_{0.019}$
H_2	0.03
CO	0.008
H_2S	0.023
CH_4	0.017
(C_2-C_5)	0.075 $C_{3.02}H_{7.46}$
char	0.232 $CH_{0.33}$
R5 Zone	
OM	$CH_{1.65}N_{0.027}O_{0.055}$
oil	0.700 $CH_{1.63}N_{0.017}O_{0.016}$
H_2	0.041
CO	0.015
H_2S	0.011
CH_4	0.017
(C_2-C_5)	0.076 $C_{3.08}H_{7.47}$
char	0.193 $CH_{0.21}$
R4 Zone	
OM	$CH_{1.60}N_{0.028}O_{0.071}$
oil	0.683 $CH_{1.65}N_{0.018}O_{0.017}$
H_2	0.022
CO	0.007
H_2S	0.005
CH_4	0.009
(C_2-C_5)	0.037 $C_{3.04}H_{7.34}$
char	0.279 $CH_{0.21}$
Singleton et al (1982)	
OM	$CH_{1.50}N_{0.032}O_{0.046}$
oil	0.715 $CH_{1.63}O_{0.019}$
H_2	0.022
CO	0.003
H_2S	-----
CH_4	0.019
(C_2-C_5)	0.012 $C_{3.0}H_{7.1}$
char	0.222 $CH_{0.42}N_{0.070}$

*OM = organic matter.

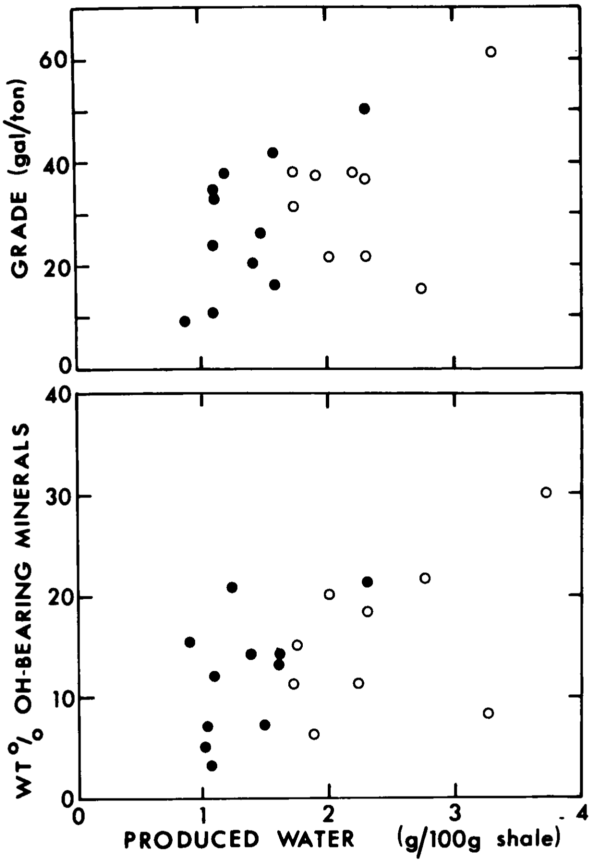

Figure 19 Plot of water yield (g/100 g shale) vs wt% organic C and wt% illite + analcite + dawsonite + nahcolite. Data from dawsonitic oil shales shown by open circles. Symbols given in Figure 9.

SUMMARY AND CONCLUSIONS

Significant variations in FA pyrolysis product composition (quality) exist in the MZ-R4 interval examined in this study. For the product gas, the most significant variations with depth is an increase in the mol% CO_2 and a related decrease in the thermal value (BTU/ft^3) of the product gas. These variations reflect the presence of abundant dawsonite (and nahcolite) in the R5-R4 interval. The production of H_2 during pyrolysis is enhanced by the presence of dawsonite. Some of the "excess" H may be due to H released during dawsonite decomposition, either directly or from cracking reactions catalyzed by Al_2O_3, a probable end product of dawsonite decomposition (Smith et al., 1978).

In the MZ-L5 interval the observed decrease in the oil H/C ratio, wt% saturates and wt% aromatics and an increase in the oil gravity (g/cm^3), wt% polar compounds and wt% insolubles with depth is consistent, overall, with the observed decrease in the H/C and O/C ratios of the organic matter with depth reported by Meddaugh et al. (1984). Strong correlations between the H/C and N/C ratios of the organic matter and the H/C and N/C ratios of the FA product oil, respectively, suggests that pyrolysis product composition may be eventually be predicted in the composition of the organic matter is known, at least in the non-dawsonitic MZ-L5 interval.

In the R5-R4 interval the observed increase in the oil H/C ratio, wt% saturates, and wt% aromatics and a decrease in the oil gravity and wt% polar compounds is probably related to the appearance of dawsonite, rather than the composition of the organic matter. Meddaugh et al. (1984) reported that the H/C and O/C ratios of the organic matter decrease uniformly throughout the MZ-R4 interval. Possibly, dawsonite decomposition products, particularly A1203, may act as catalysts. Prediction of pyprolysis products in the dawsonitic oil shales will require additional studies in order to determine the role of dawsonite (and its decomposition products) during pyrolysis. Such studies will require that the absolute abundance of dawsonite (instead of a normative wt% as used in this study) be known. The development of a quantitative x-ray diffraction analysis technique is in progress (Smith, D. K., et al., 1983).

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