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Hydrocarbon generation and migration from Type III
kerogen as related to the oil window

by

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ABSTRACT

$R_o = 0.6$ has been documented, from numerous organic-geochemical studies of rocks with oxygen-rich organic matter (OM), as the maturation rank at which the threshold of intense hydrocarbon (HC) generation occurs. $R_o = 0.6$ has also come to be identified as the lowest maturation rank at which rocks generate oil deposits. However, close examination reveals that the threshold of intense HC generation spans a rather wide maturation rank range ($R_o = 0.6$ to 0.8 , and higher in some cases), before strong HC generation actually begins. In rocks with oxygen-rich OM, the commencement of intense HC generation and intense primary petroleum migration commonly coincide at $R_o = 0.8$, with the migration mechanism hypothesized to be gaseous solution. The apparent synchronization of these events probably is due to the initial generation of substantial quantities of HC gases. Except in atypical cases in which the same rock is both a source and reservoir, accumulation of oil deposits cannot occur until HC's move from their generation sites. Thus, $R_o =$ at least 0.8 (and probably higher) is suggested as, more likely than $R_o = 0.6$, the rank at which oxygen-rich (Type III) OM has the first possibility of yielding oil deposits.

In many studies of rocks with oxygen-rich OM, precipitous decreases of C_{15+} HC concentrations occur over the maturation-rank range $R_o = 0.9$ to 1.35 , with zero or near zero HC concentrations reached by $R_o = 1.35$. These decreases are probably due to primary migration by gaseous solution. However, in past studies, these decreases have been attributed to the thermal destruction of C_{15+} HC's (and, therefore, the deadline for oil deposits by $R_o = 1.35$). Evidence suggests that this attribution is erroneous: 1) In rocks containing oxygen-rich OM and near zero values of C_{15+} HC's (at $R_o = 1.35$), the kerogen of these rocks still retains significant C_{15+} HC generation capacity. In fact, oxygen-rich OM does not completely lose its capacity to generate C_{15+} HC's until $R_o = 1.8$ to 2.0 . 2) Where primary migration apparently has been impeded or arrested, moderate to high concentrations of C_{15+} HC's remain in fine-grained rocks with oxygen-rich OM to at least $R_o = 2.00$. 3) Moderate to high concentrations of C_{15+} HC's, and moderate (remnant) C_{15+} HC generation capacity, remain in fine-grained rocks with hydrogen-rich OM to maturation ranks far in excess of $R_o = 1.35$, or even $R_o = 2.00$. 4) In some rocks, if the decreases in C_{15+} HC's from $R_o = 0.9$ to 1.35 were due to their thermal destruction and conversion to lighter HC's, then an increase in the concentrations of C_{15-} (and especially C_1-C_7) HC's should occur over this maturation rank, instead of the concentration decreases of C_{15-} HC's which do occur.

Whether or not fine-grained rocks with oxygen-rich OM can be source rocks for oil deposits is an important and unanswered question. The three principal reasons usually cited for coals not being possible source rocks can be shown to be invalid. Although hydrous-pyrolysis experiments suggest that coals with low hydrogen indices (20-40 mg/g O.C.) are unlikely oil source rocks, by conventional source rock criteria, coals with hydrogen indices of 150-300 mg/g O.C. would be premier source rocks. Mass balance considerations dim the likelihood that shales with: 1) oxygen-rich OM, 2) T.O.C. contents of 0.3-1.0 percent, and 3) hydrogen indices of 30-100 mg/g O.C., could serve as oil source rocks.

Primary migration of C_{15+} HC's by aqueous solution is not considered significant from rocks with oxygen-rich OM for two reasons. First, primary migration by gaseous solution usually removes most or all the indigenous and generated HC's from such rocks before aqueous solution can become effective

(burial temperatures $>275^{\circ}\text{C}$, $R_o = 1.95$). Second, oxygen-rich OM completely loses its generation potential from thermal burnout by $R_o = 1.8$ to 2.0 .

INTRODUCTION

The vitrinite reflectance (R_o) values of 0.6 and 1.35 have become perhaps the most important numbers in petroleum organic geochemistry. $R_o = 0.6$ represents the threshold of intense hydrocarbon (HC) generation and therefore this maturation rank has come to be considered the lowest rank at which rocks generate oil deposits. $R_o = 1.35$ has been cited as the rank where the thermal destruction of both C_{15+} HC's and oil deposits occurs; i.e. - the "oil deadline". In frontier exploration, recommendations or condemnations of oil potential, based on organic-geochemical parameters, often depend on the determination of these maturation values. State, federal, and energy company resource appraisal groups model the potential of HC deposits on both worldwide and local scope, often with the major or the only organic-geochemical input being organic richness and/or the expected burial depths where the R_o values of 0.6 and 1.35 will be encountered. Current national and world energy policies are often guided by such assessments. Huge rock volumes, in both frontier and maturely-explored petroleum basins, have been condemned for commercial oil because these rocks are at maturation ranks of $R_o > 1.35$; however, examples exist of oil deposits in rocks at maturation ranks of $R_o > 1.35$. Many examples exist of oil deposits having not been found in prospective sedimentary basins where adequate source rocks have been exposed to maturation ranks of at least $R_o = 0.6$. The absence of oil in such cases has usually been attributed to timing problems between HC generation and migration and trap formation. Because of the pivotal roles that the R_o values of 0.6 and 1.35 play, this paper reexamines the validity of the interpretations assigned to these numbers. In this paper, the following abbreviations will be used: hydrocarbon (HC, HC's); organic matter (OM); threshold of intense HC generation (TIHG), and total organic carbon (T.O.C.). Vitrinite reflectance data in some of the publications quoted in this paper were originally expressed as mean maximum vitrinite reflectance (R_m). R_m values were converted to mean random vitrinite reflectance (R_o) using the formula $R_o = 1.066 (R_m)$. All vitrinite reflectance values in this paper carry an unwritten percent symbol. HC concentrations in some of the publications quoted in this paper were plotted against R_m or the temperature at the maximum of the S_2 ROCK EVAL pyrolysis peak (hereafter identified as T_{max}). T_{max} values were converted to corresponding R_o values from a curve generated from the data of table 1. ROCK EVAL pyrolysis data are extensively referred to in this paper. The S_1 pyrolysis peak, normalized to organic carbon (mg/g O.C.) has been found to approximate the C_{15+} HC coefficient as determined by solvent extraction. The S_2 pyrolysis peak, normalized to organic carbon (mg/g O.C., also called the hydrogen index), is equated to a measure of the HC generation potential in kerogen. The terms hydrogen index and S_2 pyrolysis peak are used interchangeably in this paper. The transformation ratio (hereafter termed T.R.) is equal to $S_1/(S_1+S_2)$ and is also known as the production index or P.I. Throughout this paper, the term organic matter (OM) is used interchangeably with kerogen. Oxygen-rich (Type III) OM in this paper refers to OM with hydrogen index values of $0-350$ mg/g O.C., irrespective of oxygen index values. Hydrogen-rich OM refers to OM with hydrogen index values greater than 450 mg/g O.C. Type I and II OM are undifferentiated in this paper. All coals are assumed to be oxygen-rich OM, although it is recognized that great variability can exist in the maceral composition and geochemical characteristics of different coals. Indeed, hydrogen indices of immature coals can vary from below 30 mg/g O.C. to above 350 mg/g O.C.

TABLE 1

Equivalent T_{\max} , R_m , and R_o values. These data were derived from figure 3 of Tissot (1984), by drawing a bisecting line between the two dashed lines of that figure. Corresponding R_m values were determined for given T_{\max} values by drawing perpendicular lines which intersected this bisectrix. R_m values were converted to R_o values by the formula $R_o = 1.066 (R_m)$. These data apply only to coals and rocks with Type III (oxygen-rich) kerogen.

T_{\max} °C	R_m	R_o
400	.22	.21
410	.31	.29
420	.41	.38
430	.54	.51
435	.62	.58
440	.77	.72
445	.81	.76
450	.95	.89
455	1.10	1.03
460	1.25	1.17
470	1.41	1.32
480	1.59	1.50
490	1.72	1.62
500	1.88	1.76
510	2.03	1.90
520	2.17	2.03
530	2.32	2.18
540	2.47	2.31
550	2.63	2.47
560	2.77	2.60
570	2.92	2.74
580	3.07	2.88

$R_o = 1.35$ AND THE OIL DEADLINE

The significance of $R_o = 1.35$ probably originated with the French studies of the Upper Cretaceous Shale of the Logbaba Formation of the Douala basin (Albrecht and others, 1976; Durand and Espitalié, 1976; and Vandenbroucke and others, 1976). Referring to the $C_{15} + HC$ data of these studies (Albrecht and others, 1976, p. 792) noted, "Deeper than 2200 m the chloroform extract decreases rapidly, reaching very small values below 3000 m. This decrease is mainly due to thermal cracking, leading to light material which is not analyzed by our procedure." This is a pivotal point. Albrecht and others (1976) assumed that the concentration decrease of $C_{15} + HC$'s in figure 1 at $R_o > 0.9$ was due to their thermal destruction by carbon-carbon bond breakage. However, this assumption was not based on direct evidence. Albrecht and others (1976) did not consider an alternate hypothesis, that the decrease of $C_{15} + HC$'s could have been due to primary migration. Other organic-geochemical studies on rocks from other areas with oxygen-rich OM have reported results similar to those of the Douala

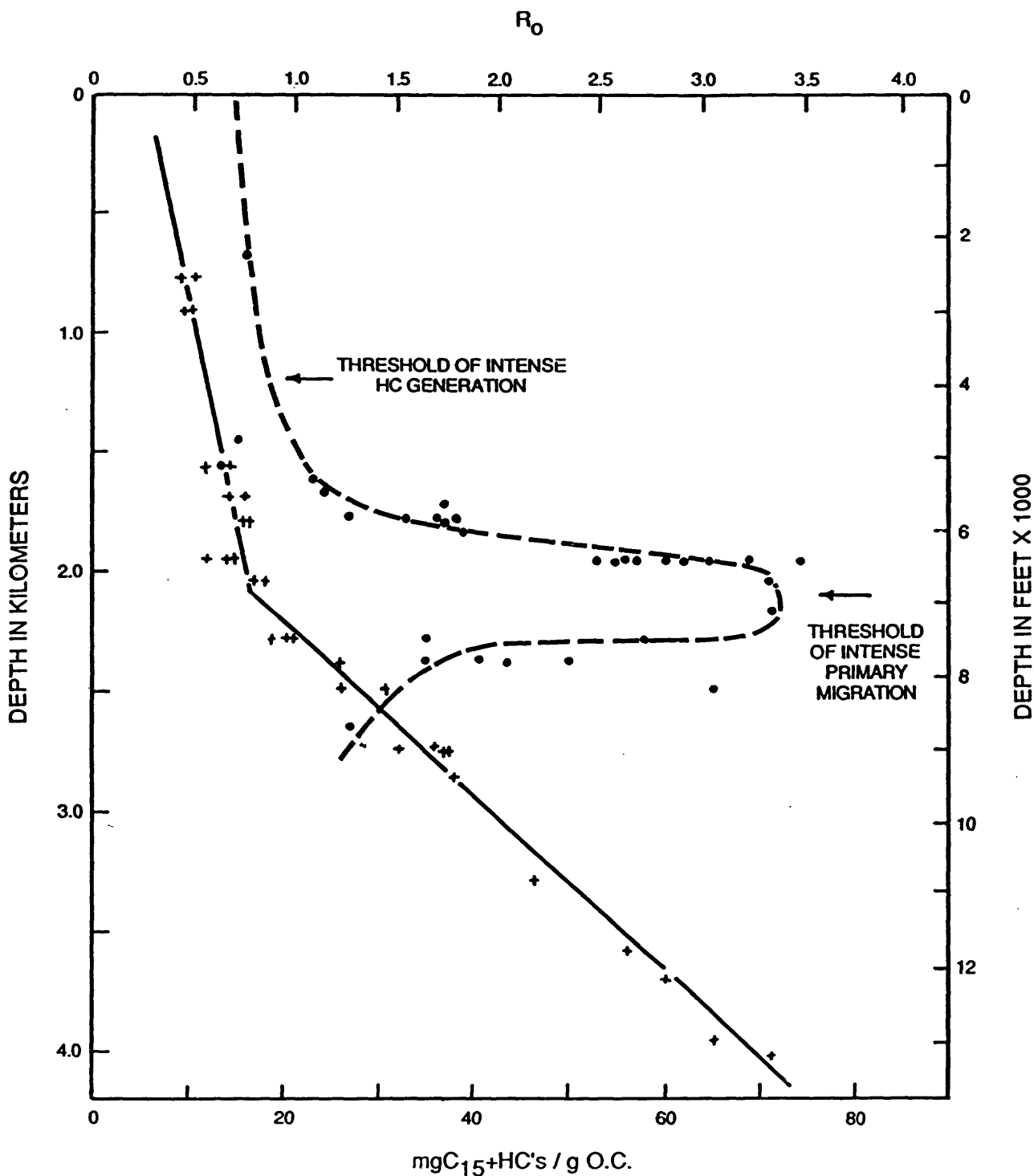


Figure 1. Plot of the $\text{C}_{15}+\text{HC}$ coefficient (dashed line, $\text{mg C}_{15}+\text{HC's} / \text{g O.C.}$) and R_o (solid line) versus depth for Upper Cretaceous shales of the Logbaba Formation, Douala, Cameroon. The arrow at 1200 m (3940 ft) denotes the first detectable increase in $\text{C}_{15}+\text{HC's}$. The arrow at 2050 m (6726 ft) denotes the threshold of intense primary petroleum migration. Data from Albrecht and others (1976) and Durand and Espitalié (1976). It is assumed that the vitrinite reflectance data given by Durand and Espitalié (1976) were R_m values. These R_m values were converted to mean random vitrinite reflectance (R_o) by the formula $R_m = 1.066 (R_o)$.

study. These other studies sustained the conclusion that $C_{15}+$ HC's are thermally destroyed by a maturation rank of $R_o = 1.35$. For example, figure 2 from data of Hood and Castaño (1974) shows R_o versus the ratio of $C_{15}+$ HC's to T.O.C. (the $C_{15}+$ HC coefficient) for a suite of coals from the U.S. Bureau of Mines. As is typical for oxygen-rich OM: 1) the threshold of intense HC generation (TIHG) occurs at $R_o = 0.50$ to 0.60 , 2) the maximum in the HC coefficient occurs at $R_o = 0.80$ to 0.90 , and 3) very low to zero values of the HC coefficient occur by R_o values of 1.5 and greater. Similar data (Teichmüller and Durand, 1983), for Paleozoic to Tertiary coals from different worldwide localities, is shown in a plot (Fig. 3) of vitrinite reflectance and T_{max} versus the S_1 ROCK EVAL pyrolysis peak normalized to T.O.C. (mg/g O.C.). As discussed, the S_1 pyrolysis peak, when normalized to T.O.C., is taken here as an indirect approximation of the $C_{15}+$ HC coefficient. In figure 3: 1) the TIHG occurs at the usual value of $R_o = 0.5$ to 0.6 , 2) the $C_{15}+$ HC coefficient peaks at a maximum at $R_o = 0.81$, and 3) the $C_{15}+$ HC coefficient has low to zero values by $R_o > 1.35$. Similar relationships of R_o versus $C_{15}+$ HC concentrations exist in rocks with oxygen-rich OM from deep wells that I have studied (discussed below), and many other investigators have also observed these same relationships in other studies. Jones (1978, p. A-22 discussing the thermal stability of $C_{15}+$ HC's at high burial temperatures or high maturation ranks noted, ".....innumerable temperature (depth) versus weight percent bitumen/TOC plots exist in the literature which show severe, abrupt, and permanent drops in the weight percent bitumen/TOC ratio at maximum paleotemperatures well below 200°C . Many company geologists also have made their own unpublished plots of a similar nature.....".

Ample documentation certainly exists of $C_{15}+$ HC's disappearing in rocks with oxygen-rich OM at ranks of $R_o = 0.9$ to 1.35 . Yet, other organic-geochemical data suggest that this well-documented disappearance of $C_{15}+$ HC's may not be due to their thermal destruction but instead could be due to primary petroleum migration

Teichmüller and Durand (1983) also published S_2 pyrolysis peak values (normalized to T.O.C.-mg/g O.C, Fig. 3) versus R_m (here converted to R_o) and T_{max} for the coals that they studied. These coals retain significant HC generation potential at $R_o > 1.35$, and small amounts of HC generation potential at R_o as high as 1.7 . Activation energies for carbon-carbon bond breakage in HC's clearly are greater than those required for HC generation in the first place from any OM type. Thus, the thermal destruction of $C_{15}+$ HC's cannot have taken place in a rock whose kerogen still retains significant HC generation capacity, such as the coals of figure 3, at maturation ranks of $R_o > 1.35$. This HC generation capacity of coals and kerogen at ranks of $R_o > 1.35$ is not for methane only. Teichmüller and Durand (1983) also examined, by thermal vaporization (ROCK EVAL pyrolysis, product trapping, and gas chromatography), the carbon-number distribution of the generation products of some of their coal samples (Fig. 4). Even at maturation ranks of $R_o > 1.75$, a significant percentage of the generation products are $C_{15}+$ HC's. I also obtained a significant percentage of $C_{15}+$ HC's in the total generation product when I subjected a coal with an R_o value of 1.57 to hydrous pyrolysis (Fig. 5). Teichmüller and Durand (1983, p. 226) concluded that the laboratory demonstration of the generation potential of $C_{15}+$ HC's from coals at high maturation ranks, when considered with the low S_1 values of high-rank coals, implied that $C_{15}+$ HC's were migrating from coals in Nature as soon as they were generated, at ranks of $R_o > 0.9$. They also concluded that this explained the low

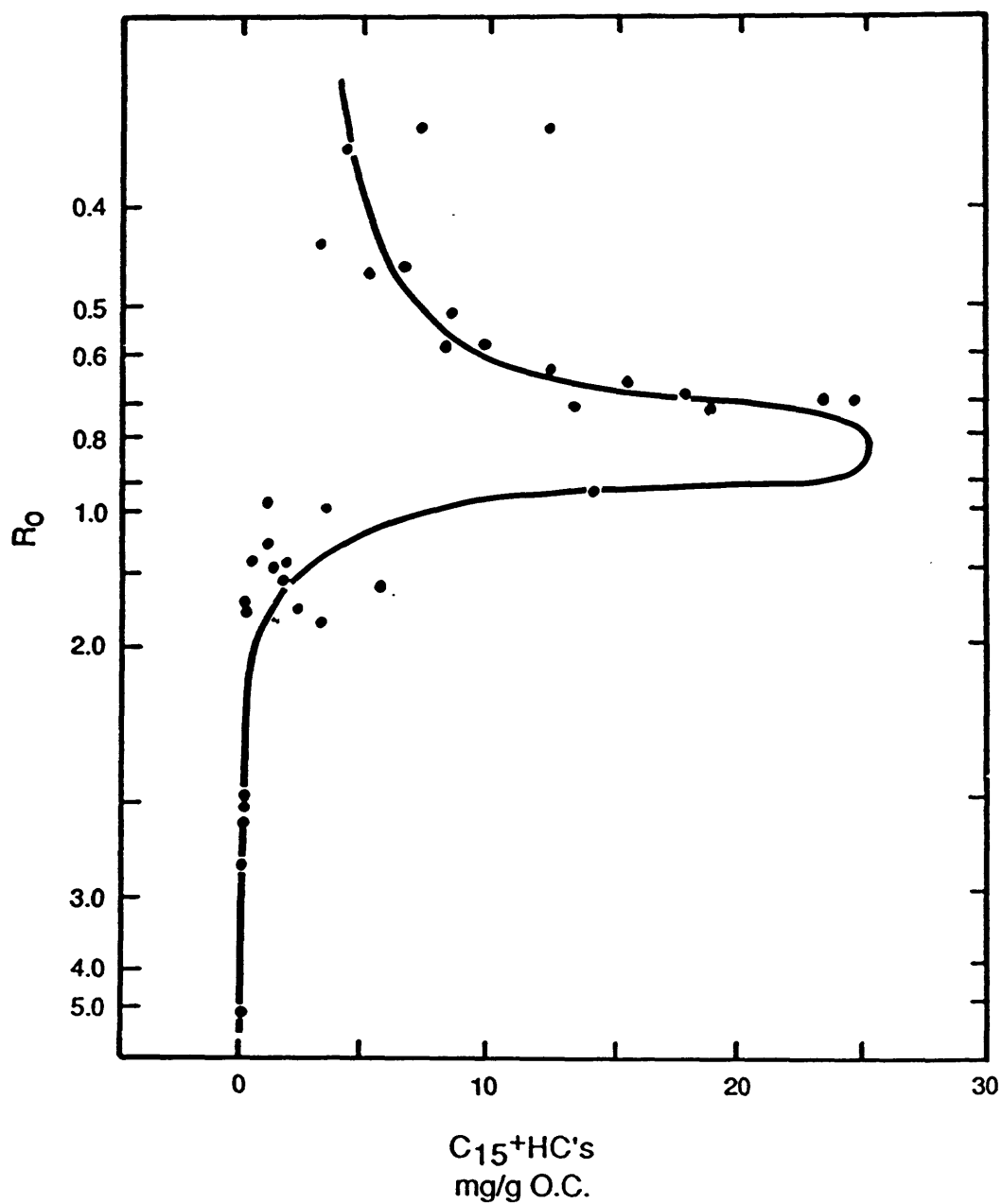


Figure 2. Plot of the $C_{15}+HC$ coefficient (mg $C_{15}+HC$'s/g O.C.) versus R_0 . Data from Hood and Castaño (1974). R_0 values were derived by converting volatile matter and rank scales from Hood and Castaño (1974) to R_m , using cross plots of these parameters and R_m from Stach and others (1982). R_m was converted to R_0 by $R_m = 1.066 (R_0)$.

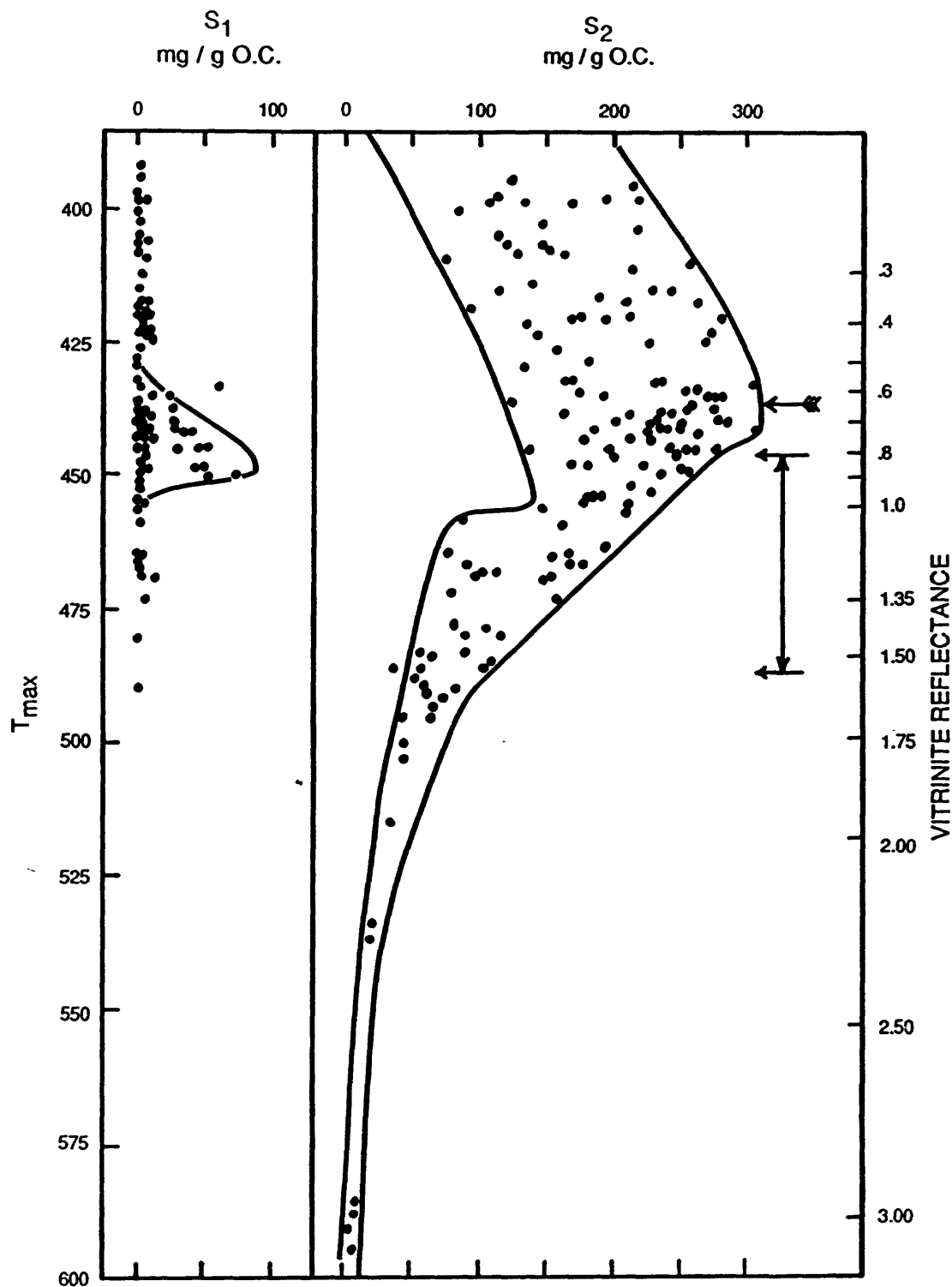


Figure 3. Plot of T_{\max} and R_o versus the S_1 and S_2 pyrolysis peaks (normalized to organic carbon-mg/g O.C.) for Paleozoic to Tertiary coals. The feathered arrow indicates the maximum in the hydrogen index data. T_{\max} was converted to R_o by the use of table 1. Data from Teichmüller and Durand (1983). The original vitrinite reflectance data of those authors was given in R_m values; R_m was converted to R_o by $R_m = 1.066 (R_o)$.

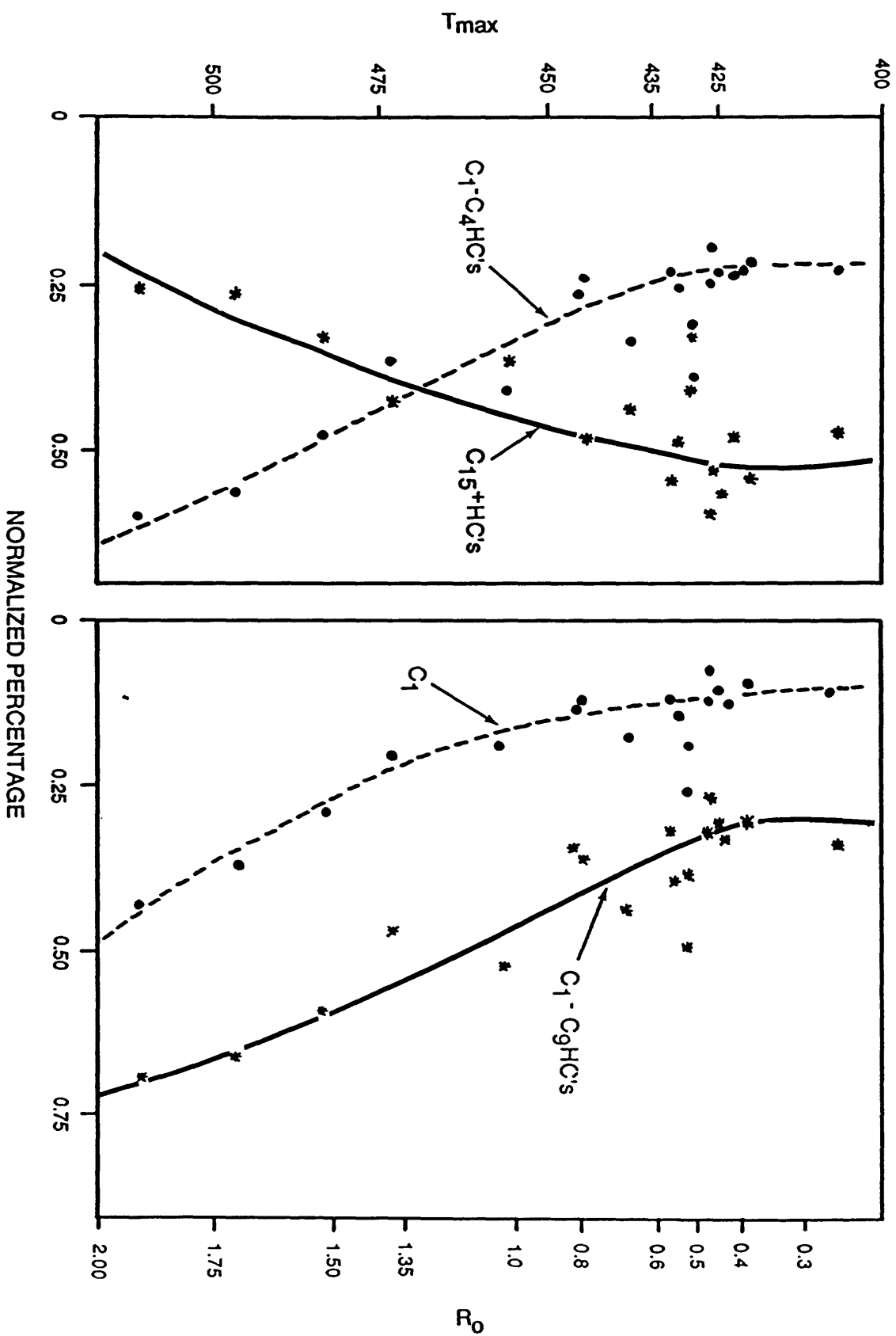


Figure 4.

Composition of products from thermal vaporization of coals (ROCK EVAL pyrolysis, product trapping, and gas chromatography). R_o values derived from T_{max} values by use of table 1. Data from Teichmüller and Durand (1983). The original vitrinite reflectance data of those authors was given in R_m values; R_m was converted to R_o by $R_m = 1.066 (R_o)$.

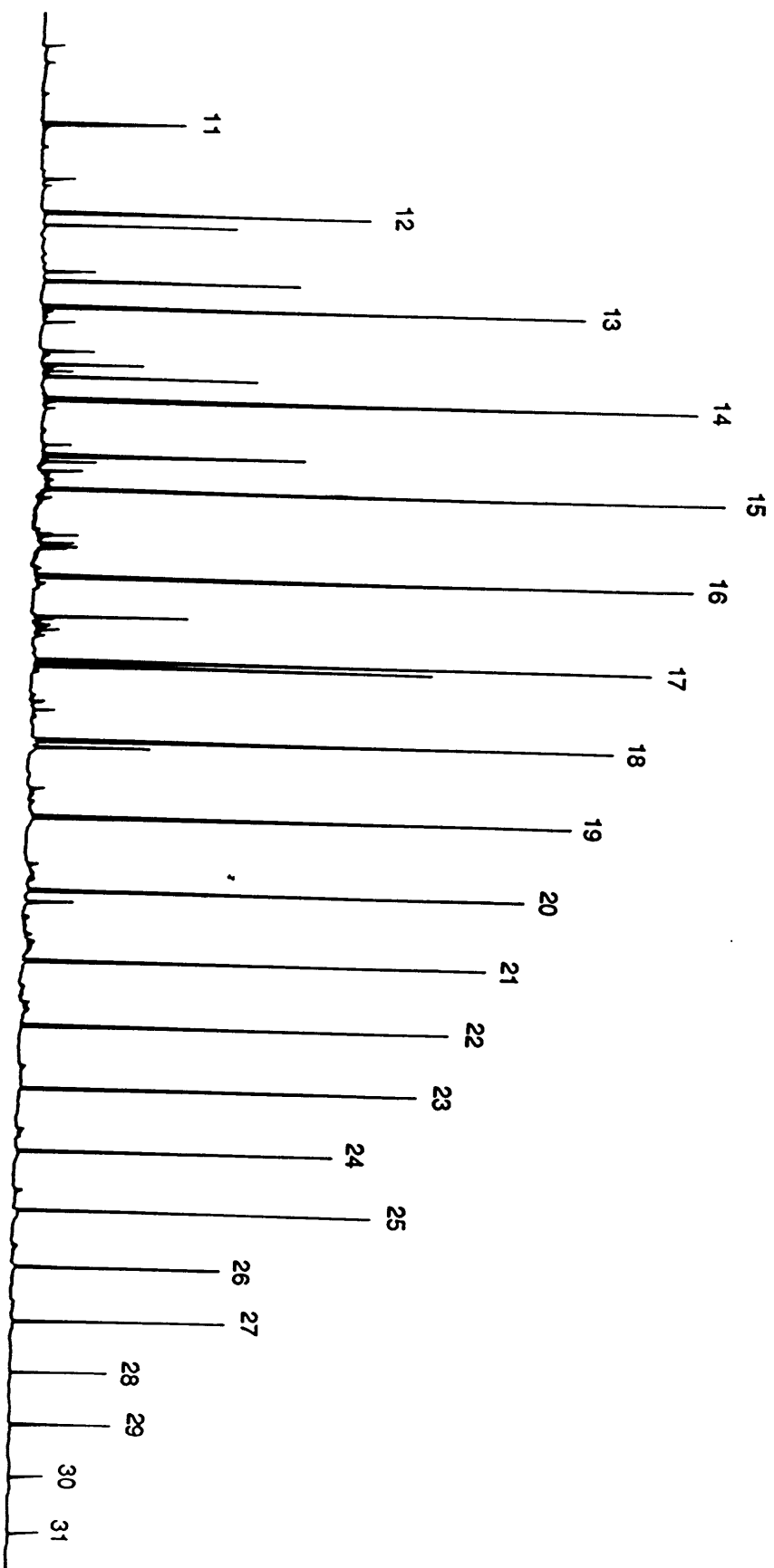


Figure 5. Gas chromatogram of C_{15}^{+} saturated HC's generated by hydrous pyrolysis of a coal with a maturation rank of $R_o = 1.57$. Carbon numbers of n-paraffins are shown.

S_1 pyrolysis peak values found in high-rank coals, better than an in situ thermal destruction of $C_{15}+$ HC's.

Durand and Oudin (1979), and Vandenbroucke and others (1983) reported on HC generation and migration from Miocene to Pliocene coals in a 4000 m (13,124 ft) clastic section in the Mahakam Delta, Indonesia. The samples for that study originated from two wells drilled on the flanks of two producing oil fields (Handil and Nilam) and from two wells drilled on the crest of the Handil field. Vandenbroucke and others (1983) plotted HC concentrations, as determined by thermal vaporization analysis, versus T_{max} , and noted that coals from the crestal Handil wells at depths corresponding to T_{max} values of 420°, 427°, and 440° to 443°C were impregnated with migrated oil. As we are concerned here only with indigenous HC's, I have excluded those samples from figures 6 and 7. The TIHG for all three sets of HC's of figure 6 occurs by $R_o = 0.50$. Maxima occur in the HC concentration curves between $R_o = 0.80$ to 0.85 for all three sets of HC's, and sharp decreases in HC concentrations occur for all three sets of HC's at $R_o > 0.85$.

By conventional interpretation, the strong decrease in the concentration of C_{25} to C_{35} HC's at $R_o > 0.85$ would be ascribed to their thermal conversion to lower molecular weight HC's by carbon-carbon bond breakage. However, if this were the case, one would expect concurrent large concentration increases in the C_{10} to C_{14} , and especially in the C_6 to C_9 HC's, when, in actuality, these HC's also show large concentration decreases. Vandenbroucke and others (1983, p. 152) recognized this logic, and regarding the concentration decreases of $C_{25}+$ HC's at $R_o > 0.85$, they stated, "This cannot, therefore, be the result of a cracking phenomenon. Consequently, this phenomenon will be interpreted as a depletion of hydrocarbons resulting from their departure by migration. As was seen previously, this phenomenon is much more appreciable for light hydrocarbons which migrate more easily."

This conclusion of Vandenbroucke and others (1983) is supported by data of Durand and Oudin (1979) for the same area (fig. 7). The TIHG for the C_1 to C_{35} HC's occurs at $R_o = 0.58$; a maximum in the HC concentration occurs at $R_o = 0.81$; and a pronounced decrease in HC concentrations occurs at $R_o > 0.81$. The thermal distillation profiles from the three most mature samples again show that this HC concentration decrease is due to primary migration, and not thermal cracking, as the C_1 to C_{14} , and especially the C_1 to C_9 HC's, exhibit even greater concentration decreases than the $C_{15}+$ HC's. The primary migration mechanism responsible for this HC movement from coals and/or from rocks with oxygen-rich OM has been hypothesized as mainly gaseous solution (Price, 1988a).

As discussed in Price (1988a), an obvious concentration buildup in $C_{14}-$, and especially C_1 to C_9 , HC's with increase in maturation rank from $R_o = 0.40$ to 0.75 (Fig. 7) is due to early generation of C_1 to C_{14} , and especially C_1 to C_7 , HC's. Once intense primary migration begins in rocks with oxygen-rich OM (in figure 7, at $R_o = 0.81$), the percentage of the solvent-extractable HC's made up by the $C_{14}-$ HC's sharply decreases and remains low at all higher maturation ranks. This is because primary migration by gaseous solution shows a marked preference for $C_{14}-$ HC's (Price and others, 1983). Also, the data of Price (1981a) show that at the burial temperatures equivalent to $R_o = 0.81$ (approximately 160°C), primary migration by aqueous solution would have a marked preference for $C_{10}-$ HC's, and only a limited carrying capacity for $C_{15}+$ HC's. Once intense primary migration begins from some rocks with oxygen-rich OM (R_o

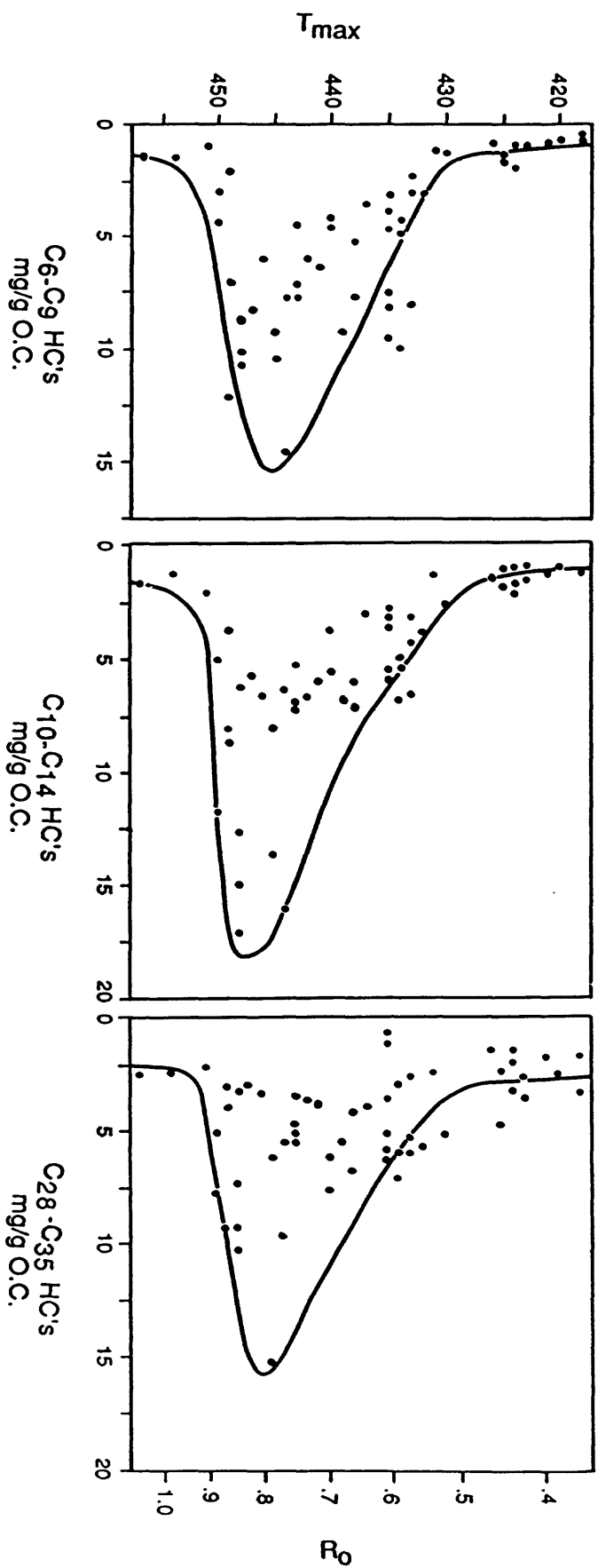


Figure 6. Plots of the amounts of C_6-C_9 , $C_{10}-C_{14}$, and $C_{28}-C_{35}$ HC's normalized to organic carbon (mg/g O.C.) versus T_{max} and R_0 for thermovaporization of coals from the Mahakam Delta, Indonesia. Solid lines are visual best fits to the data. Data from Vandenbroucke and others (1983). T_{max} values converted to R_0 values by use of table 1.

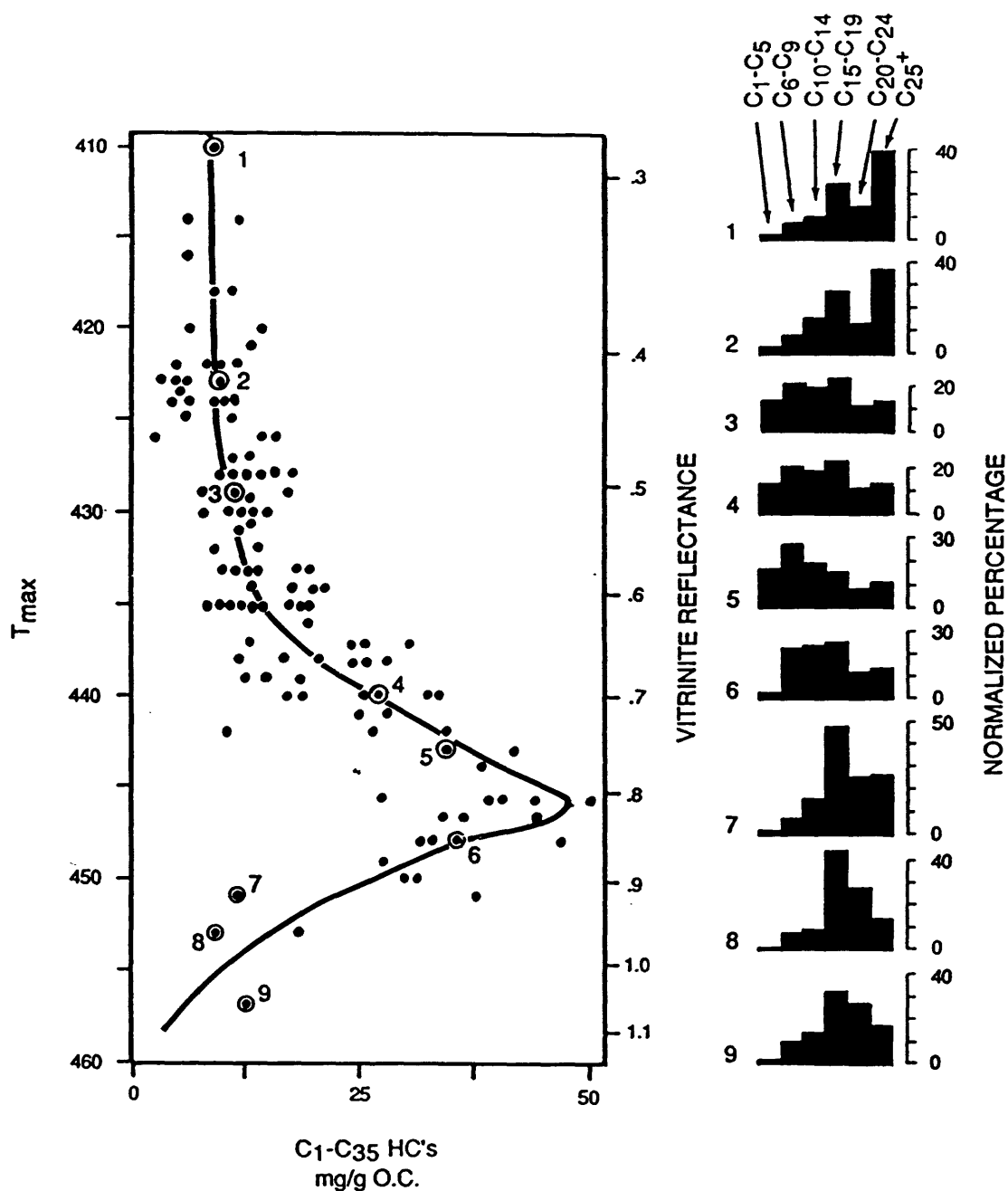


Figure 7. Plot of C_1 - C_{35} HC's normalized to organic carbon (mg/g O.C.) versus T_{max} and R_0 for thermovaporization of coals from wells in the Handil field, Mahakam Delta, Indonesia. Circled dots with numbers refer to samples whose carbon-number distribution, in percent of total product, is given to the right of the plot for the various carbon-number ranges indicated. Data after Durand and Oudin (1979). T_{max} values converted to R_0 by use of table 1. Samples designated by Durand and Oudin (1979) as contaminated by migrated HC's were excluded from plot.

≈ 0.80), the absolute concentration of C_{15}^+ HC's decreases and approaches zero with further increase in maturation rank (Figs. 1, 2, 3, 6 and 7). This efficiency of primary migration is hypothesized as due to the fact that the ratio of generated C_5^+ products to generated methane and carbon dioxide is much lower in rocks with oxygen-rich OM than in rocks with hydrogen-rich OM, at all maturation ranks (Fig. 8). Because rocks with oxygen-rich OM generate much greater relative amounts of methane and carbon dioxide than C_5^+ products, once intense primary migration by gaseous solution begins in some of these rocks, it is so efficient that it strips C_5^+ HC's from the rocks as fast as they are generated.

Huc and Hunt (1980) carried out organic-geochemical analyses of Miocene to Pleistocene shales with oxygen-rich OM from the offshore Texas (Padre Island) COST #1 well (Fig. 9). Huc and Hunt (1980, p. 1083) found that, "The ratio of C_{15}^+ bitumen to total organic carbon is about 10-20 mg/g C for samples down to 3050 m (10,000 ft). Beyond this depth, the ratio increases to a maximum of 100 mg/g C at 4115-4420 m (13,500-14,500 ft) in the South Padre Island well, then decreases with further burial due to exhaustion of the generating capability of the kerogen and cracking of previously generated products. An alternative or complementary explanation of this depletion may be a loss of hydrocarbons due to migration. In South Padre Island, the bitumen curve is peaking at 0.80-0.90 percent vitrinite reflectance, that is, in the usual range. This suggests that further cracking of previously generated products rather than a migration process is the principal factor of the decrease observed in the deeper part of the well." The trends in the Huc and Hunt (1980) C_{15}^+ HC data conform to trends in C_{15}^+ HC data from other areas (Figs. 1, 2, 3, 6, and 7) for rocks with oxygen-rich OM: 1) The THG for C_{15}^+ HC's occurs at $R_o = 0.50$ to 0.60 . 2) The maximum C_{15}^+ HC concentration occurs at $R_o = 0.80$ to 0.90 . 3) At $R_o > 0.8-0.9$, the concentration of C_{15}^+ HC's decreases, a decrease attributed to their thermal destruction. However, other HC data from Huc and Hunt (1980) contradict their proposed thermal destruction of C_{15}^+ HC's at $R_o > 0.8-0.9$. If the decrease in C_{15}^+ HC's at $R_o > 0.9$ in figure 9 was due to the thermal conversion of C_{15}^+ HC's to lower molecular weight HC's, a concurrent increase in the concentration of C_{14}^- HC's would take place with the decrease in C_{15}^+ HC's, which is not the case. Huc and Hunt (1980) recognized that a postulated decrease in C_{15}^+ HC's, due to their thermal conversion to C_{14}^- HC's, contradicted the decrease in the concentration of C_{14}^- HC's over the same depth interval. As such, they attributed the maxima in the C_2-C_8 , C_7-C_{10} , and $C_{11}-C_{14}$ HC's (Fig. 9, arrows) to HC migration into these shales from rocks much deeper in the section. As discussed in Price (1988a), their hypothesis on this point can be debated from both geochemical and geological viewpoints. However, whatever scenario one subscribes to regarding the maxima in HC concentrations, the lack of an increase of C_{14}^- HC's over the depths where C_{15}^+ HC's are decreasing, suggests that this decrease in C_{15}^+ HC's is not due to the thermal conversion of C_{15}^+ HC's to C_{14}^- HC's. Instead, the concurrent decrease of C_2-C_{14} HC's over the same depth range where the C_{15}^+ HC's are decreasing, suggests that the loss of all HC's from the rocks is due to the primary migration of these HC's.

Figure 10 is a plot, after data by Law (1984), of T.O.C., different ROCK EVAL measurements and R_o , all versus depth, for Upper Cretaceous to Lower Tertiary rocks with oxygen-rich OM from the Greater Green River basin. The R_o and T_{max} data exhibit tight, continuous increases, with depth, reaching values of $R_o^{max} = 2.0$, and $T_{max} = 500^\circ C$ by 5.49 km (18,000 ft). In contrast to the data of figures 1-3, 6, 7 and 9, the S_1 pyrolysis peak in figure 10 exhibits neither

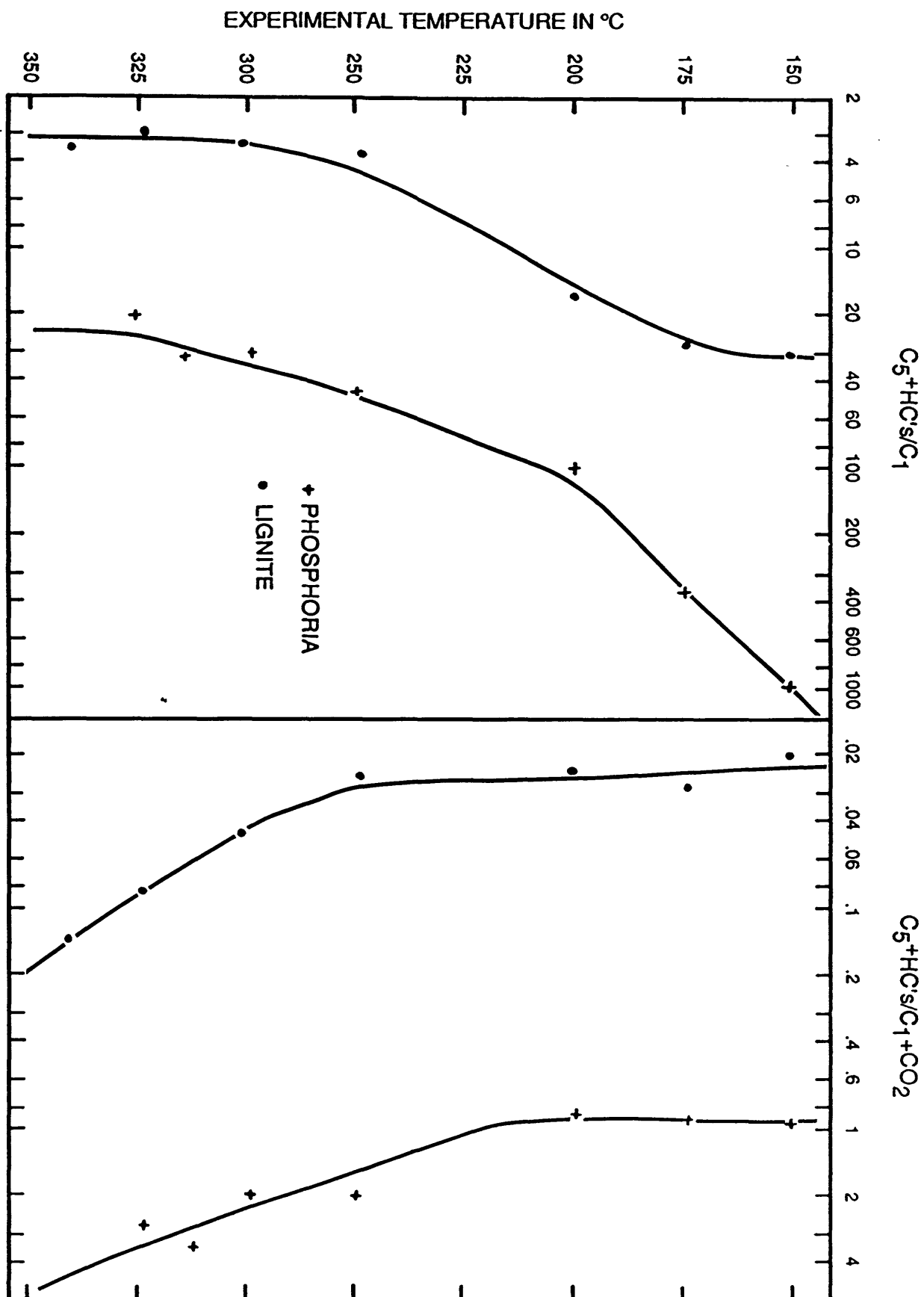


Figure 8.

Ratios of C_5+ generated products to generated methane and of C_5+ generated products to generated methane plus carbon dioxide for hydrous pyrolysis of the Paleocene Rattlesnake Butte lignite and shales of the Permian Phosphoria Formation. Hydrous pyrolysis reaction temperatures are plotted on an arithmetic scale and reaction product ratios are plotted on a logarithmic scale.

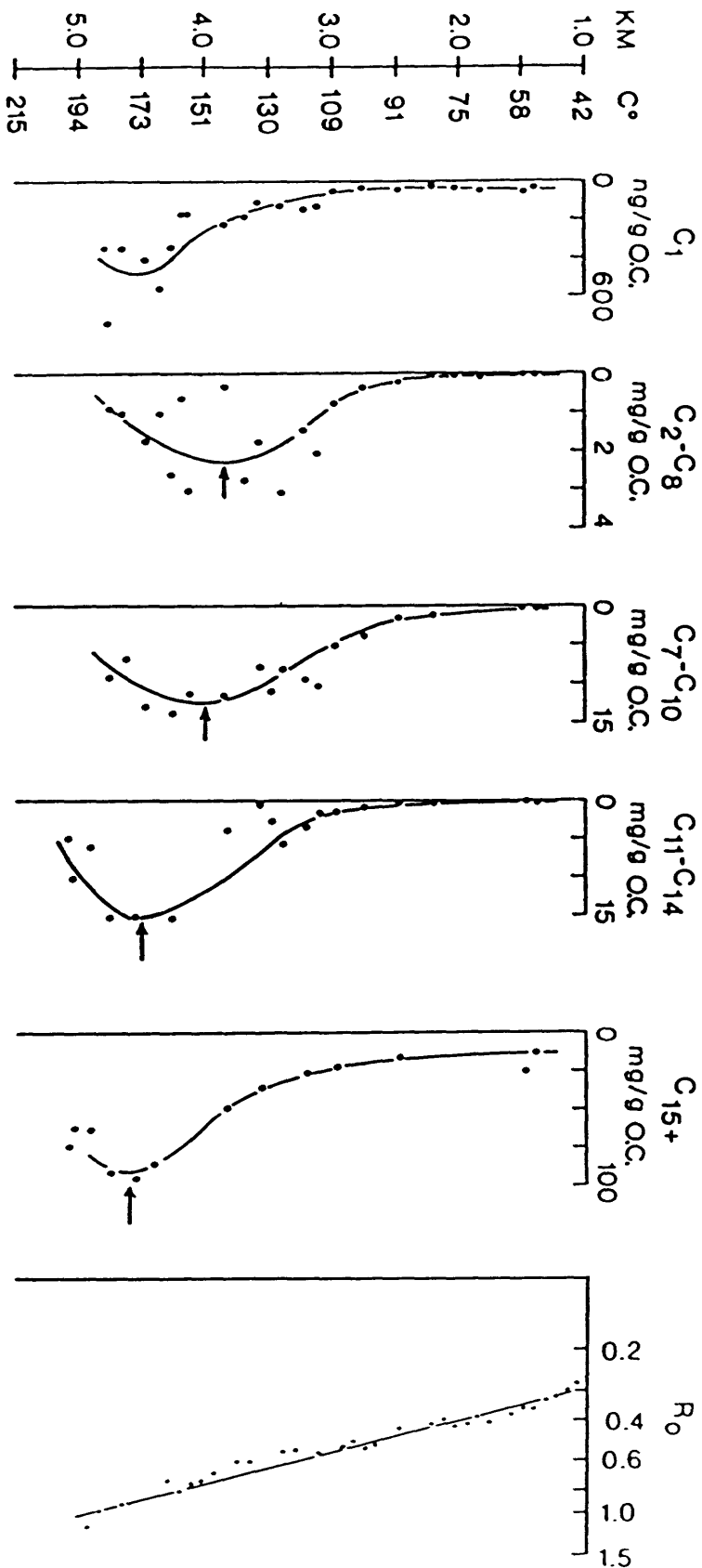


Figure 9.

Plot of C₁ (normalized to organic carbon-nanograms/g O.C.), C₂-C₈, C₇-C₁₀, C₁₁-C₁₄, and C₁₅+ HC's (all normalized to organic carbon-mg/g O.C.), and R₀, all versus burial depth and burial temperature for the offshore Texas Gulf Coast COST #1 well. Arrows signify concentration maxima for the various HC species. Data from Huc and Hunt (1980) and Vaples (1981).

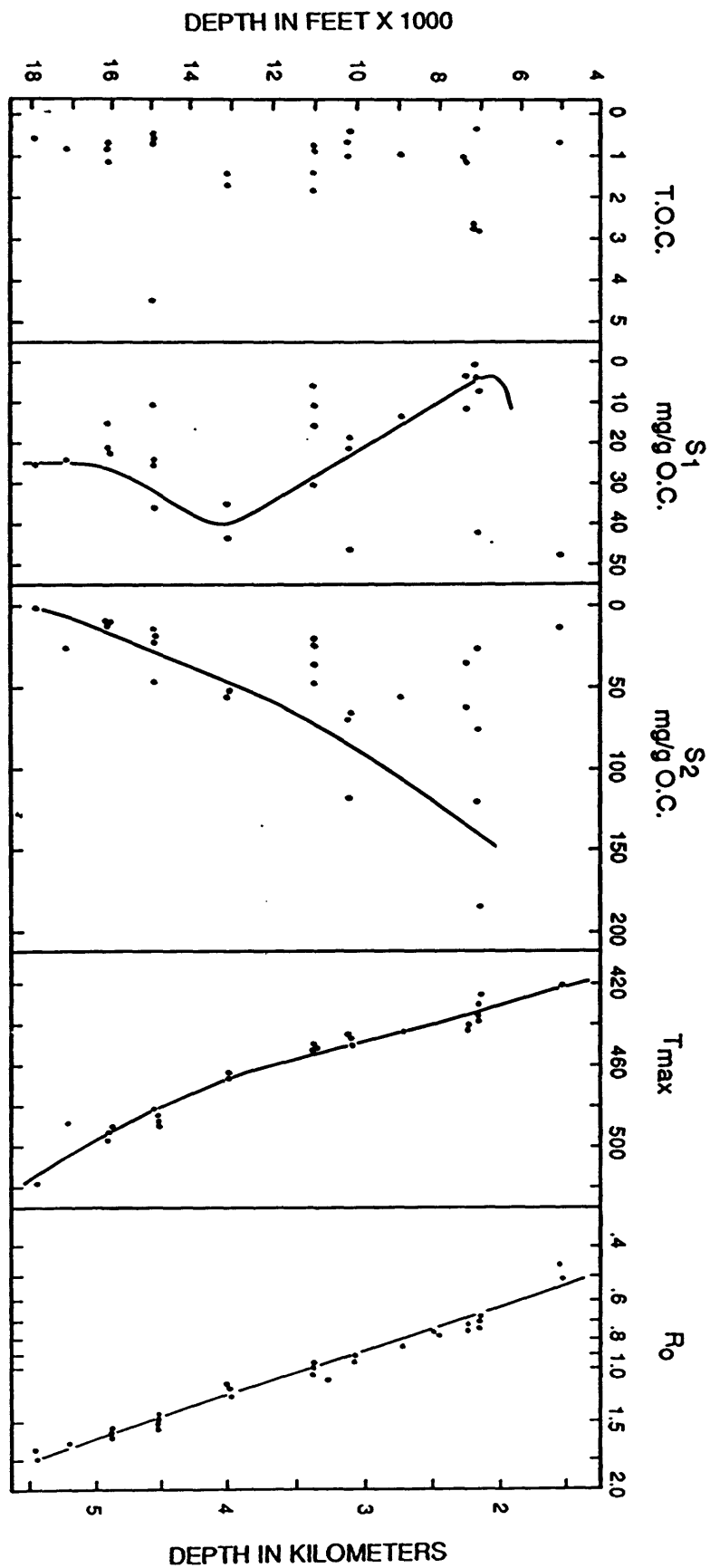


Figure 10.

Plot of T.O.C., the S_1 and S_2 ROCK EVAL pyrolysis peaks (normalized to organic carbon - mg/g O.C.^2), T_{max} and R_o , all versus burial depth, for rocks with T.O.C. contents of 0.3 percent and greater from the El Paso Natural Gas Vagon Wheel-1 well, Sublette Co., Wyoming. The solid line of the R_o plot represents the line generated by linear regression analysis of the R_o data and has a correlation coefficient of $r = 0.990$ to the data. Data from Lav (1984).

a maximum near $R_o = 0.8$ to 0.9 , nor a decrease with increase in maturation rank to the expected value of zero at $R_o = 1.35$. Instead, with the exception of three samples, the S_1 peak, with some scatter, increases with increase in maturation rank to a maximum of 40-50 mg/g O.C. at $R_o = 1.35$, and thereafter decreases with further increase in maturation rank to values of around 20 mg/g O.C. at total depth. These S_1 data contradict the hypothesis of a $C_{15} + HC$ thermal deadline at $R_o = 1.35$. If the low concentrations of $C_{15} + HC$'s at $R_o \geq 1.00$ (figures 1-3, 6, 7 and 9) are due to the thermal destruction of HC's, then explaining the maximum in the S_1 pyrolysis peak values of figure 10 at $R_o = 1.35$ becomes very difficult. Further, the high S_1 values at maturation ranks of $R_o = 1.0$ to $1.35+$ in figure 10 are not an isolated case, other examples exist (Figs. 11-13). I believe that the high S_1 values of figures 10-13 at elevated maturation ranks are due to less efficient primary migration than was the case in the data of figures 1-3, 6, 7 and 9.

Law (1984) noted that the fluvial, Upper Cretaceous to Lower Tertiary rocks in his study contained abundant interbeds of coals (some as thick as 12 m) and high T.O.C. carbonaceous shales. Gas-bearing sandstones in Law's (1984) study area were irregular, discontinuous lenses, with poor, or no, fluid communication, and low (irreducible) water contents. Abnormal fluid pressuring of the gas phase was present throughout the basin, and at maturation ranks of $R_o > 0.8$, steep increases in fluid pressures were often correlated with significant increases in T.O.C. contents. Given these characteristics, the hypothesis is advanced that the high S_1 values at elevated maturation ranks in figure 10, are due to a basin-wide retardation of primary migration by gaseous solution due to different causes. The ubiquitousness of an overpressured gas phase at $R_o > 0.8$ in the rocks of this basin, including the fine-grained rocks, suggests that primary migration by gaseous solution did not go to completion in the basin, or this gas phase would not be present in the first place. Thus, all the $C_5 +$ (and $C_{15} +$) HC's generated in these rocks at R_o values > 0.8 were not stripped from the rocks, as was the case in the samples of figures 1-3, 6, 7 and 9.

Figure 11 gives organic-geochemical data (Price, 1988b) from the fine-grained rocks of the Ralph Lowe-1 well, drilled 15 km (9.32 mi) southeast of Fort Stockton, Pecos Co., Texas, over the depocenter of the Delaware basin. Maceral analysis shows that the OM in these fine-grained rocks is oxygen-rich OM. The S_1 data from this well do not support the hypothesis of a $C_{15} + HC$ thermal deadline by $R_o = 1.35$, as between $R_o = 1.0$ and 2.6 , the S_1 values are moderate to high (25 to 68 mg/g O.C.). Plots of the ROCK EVAL transformation ratio (T.R.), T_{max} , and R_o all show strong increases, and minimal scatter, with increase in depth. An exception to this is the T_{max} data for unextracted samples. In ROCK EVAL pyrolysis, the resins and asphaltenes (NSO's) are largely or totally contained in the S_2 pyrolysis peak (Clemetz, 1979; Price and others, 1984). Thus, T_{max} can be affected by the NSO's in a rock sample. In figure 11, it is evident that Soxhlet extraction of the rock samples leads to an increase, sometimes substantial, in the T_{max} values. Also, the extracted samples yield a much more regular plot of T_{max} versus depth than do the unextracted samples, as shown by the solid line in the T_{max} plot of figure 11. This line is a visual best fit to the T_{max} data for the Soxhlet-extracted samples. If the hydrogen index is equated to the amount of HC generation potential on kerogen, then the best measure of a T_{max} value, and the true measure of the HC generation potential of kerogen, would be for solvent-extracted samples, where the NSO's are not contributing to the S_2 pyrolysis peak.

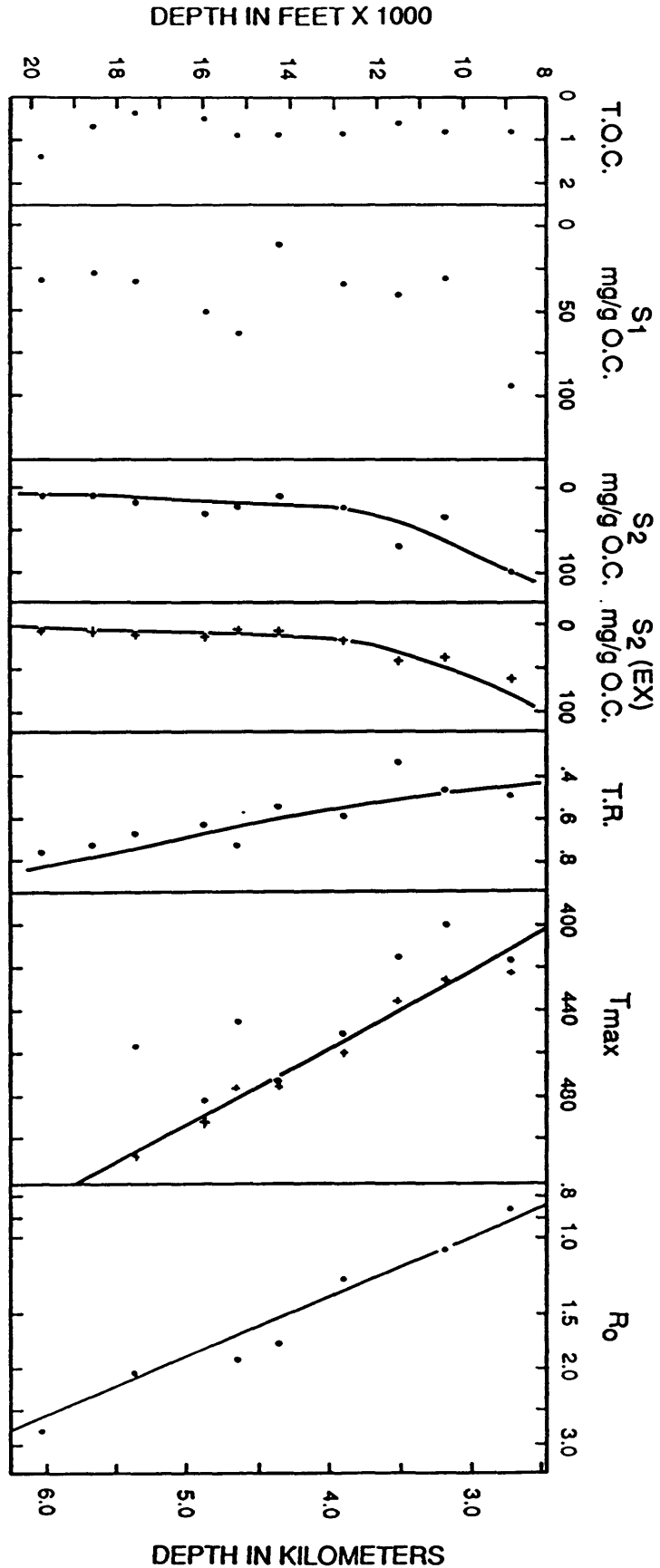


Figure 11.

Plot of T.O.C., the S_1 and S_2 RÖCK EVAL pyrolysis peaks (normalized to organic carbon-mg/g O.C.), the transformation ratio (T.R., also called the production index, or P.I. and equal to S_1/S_1+S_2), T_{max} and R_o , all versus depth for the Ralph Love-1 well, Pecos Co., Texas. Values of the S_2 pyrolysis peak and T_{max} for rock sample splits which were Soxhlet extracted (EX) are designated by crosses. The solid line on the R_o plot results from linear regression analysis of the R_o data (including four deeper samples not shown in this figure), and has a correlation coefficient of $r = 0.992$ to the data.

BURNOUT OF OXYGEN-RICH OM

The coals in figure 3 lose most of their generation potential between $R_o = 0.81$ to 1.57 and are approaching zero generation potential by $R_o = 2.0$. Data from other investigators (Fig. 10), and data from deep wells which I have studied (including Figs. 11 and 12), also demonstrate a loss of HC generation potential in oxygen-rich OM by $R_o = 1.8$ to 2.0 .

The organic geochemistry of the rocks of the 6.9 km (22,700 ft) Shell McNair #1 well, Hinds County, Mississippi, was reported by Price and others (1979). Composite samples of the dominantly reddish-hued rocks from 2.44-6.46 km (8,000-21,200 ft) in this well contained only oxygen-rich OM, had low T.O.C. contents (generally 0.15-0.50 percent), and had low to moderate amounts of solvent-extractable bitumen normalized to organic carbon (generally 15-40 mg/g O.C.). Between 6.46 - 6.61 km (21,200-21,700 ft), a lithologic change took place in the rocks, with an increase in gray to dark-gray shales, accompanied by significant organic-geochemical changes. Both the bitumen and C_{15+} HC coefficients, which had generally been constant and low over the 2.44-6.46 km (8,000-21,200 ft) interval, exhibited dramatic increases. Also, the hydrogen to carbon ratio of the kerogen in these rocks, which had continuously decreased over this same depth interval, reversed itself and strongly increased. These organic-geochemical changes were all due to a change to more hydrogen-rich kerogen in the deeper rocks from oxygen-rich kerogen in the shallower (2.44-6.46 km, 8,000-21,200 ft) rocks. ROCK EVAL pyrolysis and R_o analysis were not carried out in the original study (Price and others, 1979) and have since been performed. The S_1 pyrolysis peak has uniformly low values (3-10 mg/g O.C.) from 2.44 to 6.46 km (8,000 to 21,200 ft), and these values increase dramatically (to 40-130 mg/g O.C.) at depth in the rocks with hydrogen-rich kerogen. The hydrogen index shows a continuous decrease from values of 30-40 mg/g O.C. at 2.44 km (8,000 ft) to zero between 5.49 to 5.64 km (18,000 to 18,500 ft), which corresponds to $R_o = 1.85$ to 1.95 , again confirming the burnout of HC generation potential in oxygen-rich kerogen by $R_o = 1.8$ to 2.0 , as observed in figures 3, 10 and 11.

It would be a convenient conclusion that the loss of HC generation potential (kerogen burnout) in oxygen-rich OM at $R_o = 1.8$ to 2.0 also represents the thermal deadline for C_{15+} HC's (the oil deadline). However, data from different deep well bores (including the McNair-1), with high maturation rank rocks, indicate that the C_{15+} HC deadline occurs at maturation ranks greater than $R_o = 2.0$. In the McNair-1 well, rocks with hydrogen-rich kerogen are present at depths in excess of 6.61 km (21,700 ft). The kerogen in these rocks still retains measurable HC generation potential (20-75 mg/g O.C.) at $R_o \geq 2.5$, besides high concentrations of C_{15+} bitumen and high S_1 pyrolysis peak values (fig. 12). This deep remnant HC generation potential is attributed to stronger chemical bonds in hydrogen-rich OM than in oxygen-rich OM. Thus, due to the weaker bonds, in oxygen-rich OM, kerogen burnout occurs at lower maturation ranks ($R_o = 1.8-2.0$) than it does in hydrogen-rich OM.

Deep rocks in the Ralph Lowe-1 well bore (not shown in figure 11, see Price, 1988b) demonstrate features similar to those of the deep rocks in the McNair-1 well bore. In the deep rocks of the Ralph Lowe-1, OM type also changes from oxygen rich to hydrogen rich, a change accompanied by increases in the T.O.C. content, in the S_1 pyrolysis peak, and in the kerogen atomic H/C ratio. The S_2 pyrolysis peak also increases for Soxhlet-extracted samples to values of 25-125

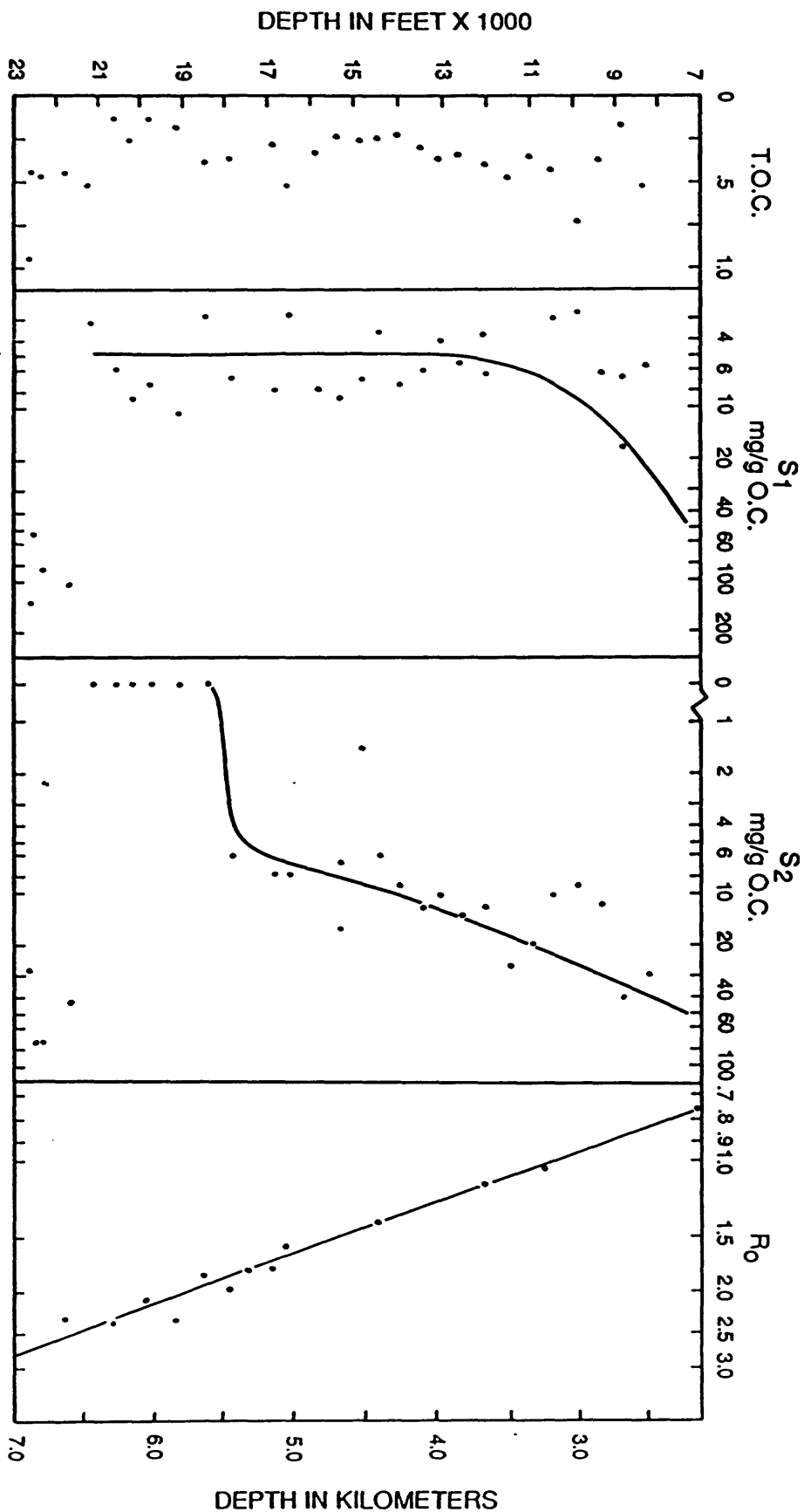


Figure 12.

Plot of T.O.C., the S₁ and S₂ ROCK EVAL pyrolysis peaks (normalized to organic carbon-mg/g O.C.), and R₀ all versus depth for the Shell McNair-1 well, Hinds Co., Mississippi. The values for the S₁ and S₂ pyrolysis peaks are plotted on a logarithmic scale (because of the wide range in values of both measurements). The range of values for the S₂ peak has been broken to zero, on the logarithmic scale, so that zero values for this measurement for the deeper samples could be plotted. The solid line for the R₀ values results from linear regression analysis of the R₀ data, and has a correlation coefficient of $r = 0.927$ to the data.

mg/g O.C. from values of zero or near zero for samples between 4.57 to 6.10 km (15,000-20,000 ft). A large body of data also has been published (Price and others, 1979, 1981; Price 1982, 1983- Table 1) which demonstrates that significant concentrations of C_{15}^{+} HC's and significant amounts of remnant HC generation potential (S_2 pyrolysis peaks) remain in fine-grained rocks with hydrogen-rich OM at R_o values far in excess of 2.0. Discussion of the maturation rank necessary for the TIHG in hydrogen-rich OM and the maturation rank at which C_{15}^{+} HC's are finally thermally destroyed is outside the scope of this paper. However, the bonds which must be broken in the destruction of C_{15}^{+} HC's are clearly stronger than those which were broken in either oxygen-rich, or hydrogen-rich OM to generate those C_{15}^{+} HC's in the first place. The thermal deadline for C_{15}^{+} HC's (and, therefore, crude oil) by $R_o = 1.35$ is improbable when at these ranks: 1) significant HC generation potential remains on oxygen-rich OM, and 2) significant concentrations of C_{15}^{+} HC's or moderate to high values for the S_1 pyrolysis peak can remain in some rocks. Similarly, it is unlikely that the thermal deadline of C_{15}^{+} HC's occurs at $R_o = 2.00$ (based on the burnout of HC-generation potential in oxygen-rich OM) when significant HC-generation potential remains in rocks with hydrogen-rich OM at these and higher maturation ranks, and when significant concentrations of C_{15}^{+} HC's remain in rocks with hydrogen-rich OM at ranks of $R_o \geq 2.0$.

$R_o = 0.6$ AND HC ACCUMULATION

The association of $R_o = 0.5$ to 0.6 (more so $R_o = 0.6$) with the TIHG can also probably be first attributed to the geochemical studies in Douala (Albrecht and others, 1976; and Durand and Espitalié, 1976). In figure 1, the first noticeable increase in the C_{15}^{+} HC coefficient at 1200 m (3,940 ft), as shown by the arrow, occurs at $R_o = 0.6$. Similar results have been reported from many areas by investigators who have studied different sequences of fine-grained rocks with oxygen-rich OM. The association of $R_o = 0.5$ to 0.6 with the first detectable increase in the concentration of C_{15}^{+} HC's in fine-grained rocks is also evident in figures 2, 3, 6, 7, and 9. In all these cases, there is a significant buildup in the concentration of C_{15}^{+} HC's over $R_o = 0.6$ to 0.8 to a maximum by $R_o = 0.80$ to 0.85 . The marked increase in C_{15}^{+} HC's at $R_o = 0.6$ is due to the initial generation of these HC's from oxygen-rich kerogen. These concentration buildups from $R_o = 0.6$ to 0.8 take place because most, if not all, of the newly-generated HC's remain in the rocks at the generation site. However, the oil industry has, in general, accepted $R_o = 0.6$ as the lowest level of thermal maturity at which oil deposits can accumulate. In other words, it has been assumed that primary migration and accumulation of oil coincide with the TIHG at $R_o = 0.6$. It is a hypothesis of this paper that this assumption has led to an acceptance of a maturation rank too low to possibly result in the accumulation of oil deposits from oxygen-rich OM.

In the pyrolysis data for coals of figure 3, at $R_o = 0.6$, there is no detectable decrease in the maximum (or minimum) values of the hydrogen indices of the coals. The first detectable decrease occurs at $R_o = 0.81$ as shown by the arrow at that rank. Over the maturation-rank range $R_o = 0.81$ to 1.57 , the hydrogen index decreases from mean maximal values of about 280 mg/g O.C. to mean maximal values of about 75 mg/g O.C. However, this decrease in the hydrogen index is not accompanied by an increase in values of the S_1 pyrolysis peak. This relationship indicates that the newly generated HC's migrated from the coals immediately after generation. Only with the advent of intense primary migration, can the generated HC's possibly accumulate into a HC deposit. In the

above case, the R_o value of 0.8, and not 0.6, is a better representation of the first possibility of the formation of an oil deposit from HC's generated from these coals. Another indication of the commencement of intense primary migration in fine-grained rocks with oxygen-rich OM is the maturation rank where the values of either the S_1 pyrolysis peak or the $C_{15}+$ HC coefficient exhibit drastic decreases from their maximal values. These decreases commonly, but apparently not always, occur at $R_o = 0.8$ to 0.9 (Table 2). The one exception to this, in table 2, is at the Paloma field, Calif.

Table 2

R_o values at the hypothesized commencement of intense primary migration for the areas discussed in this paper.

Figure	Area	R_o value at threshold of intense primary petroleum migration
1	Douala, Africa	0.81
2	U.S. Bureau of Mines Coals	0.81
3	Institut Francais du Pétrole Coals	0.85
6	Mahakam Delta, Indonesia	C_6-C_9 HC's 0.79
		$C_{10}-C_{14}$ HC's 0.84
		$C_{25}-C_{35}$ HC's 0.85
7	Mahakam Delta, Indonesia	0.81
9	Offshore Texas Gulf Coast	$C_{15}+$ HC's 0.85
13	Paloma field, Calif.	1.16

Figure 13 gives a plot of T.O.C. and various ROCK EVAL measurements (see figure caption) versus present day (maximal) equilibrium burial temperatures from Hood and Castaño (1974) for core samples from wells at the Paloma field, Southern San Joaquin Valley basin, California. Values for the S_1 pyrolysis peak (mg/g O.C.) increase slightly at 122°C which may correspond to the TIHG for these samples. This temperature concurs with the burial temperature of 120°C which Phillipi (1965) found for the TIHG in the neighboring Los Angeles basin. One could also interpret that the TIHG at Paloma is at the first significant increase of either the S_1 pyrolysis peak or the T.R., which would be 165°C and 158°C respectively. The bulge in the T.R. values for samples between 78° to 93°C, is unrelated to HC generation; instead, it is probably due to organic-geochemical characteristics of these samples which were inherited during deposition. These samples have low T.O.C. contents (0.15 to 0.35 percent), low S_1 values, and low to average hydrogen indices, which are a mirror reversal of the T.R. values. In the calculations of the T.R. values, the low S_2 values of the 78° to 93°C samples give rise to relatively high T.R. values, compared to adjoining samples. The T.R. values increase slightly between 100° and 155°C, and significantly from 155°C to a maximum value of 0.737 at 206°C. At burial temperatures greater than 206°C, with the exception of one sample, T.R. values decrease. This decrease is believed to reflect the onset of intense primary migration with resultant decreases in the S_1 pyrolysis peak, and, therefore, in the T.R. The S_1 pyrolysis peak (Fig. 13) increases gradually between 122° and 165°C, and significantly from 165°C to a maximum at a burial temperature of 203°C (assumed R_o value of 1.16 from the equation in figure 19 of Price, 1983), and then decreases with further increase in burial temperature.

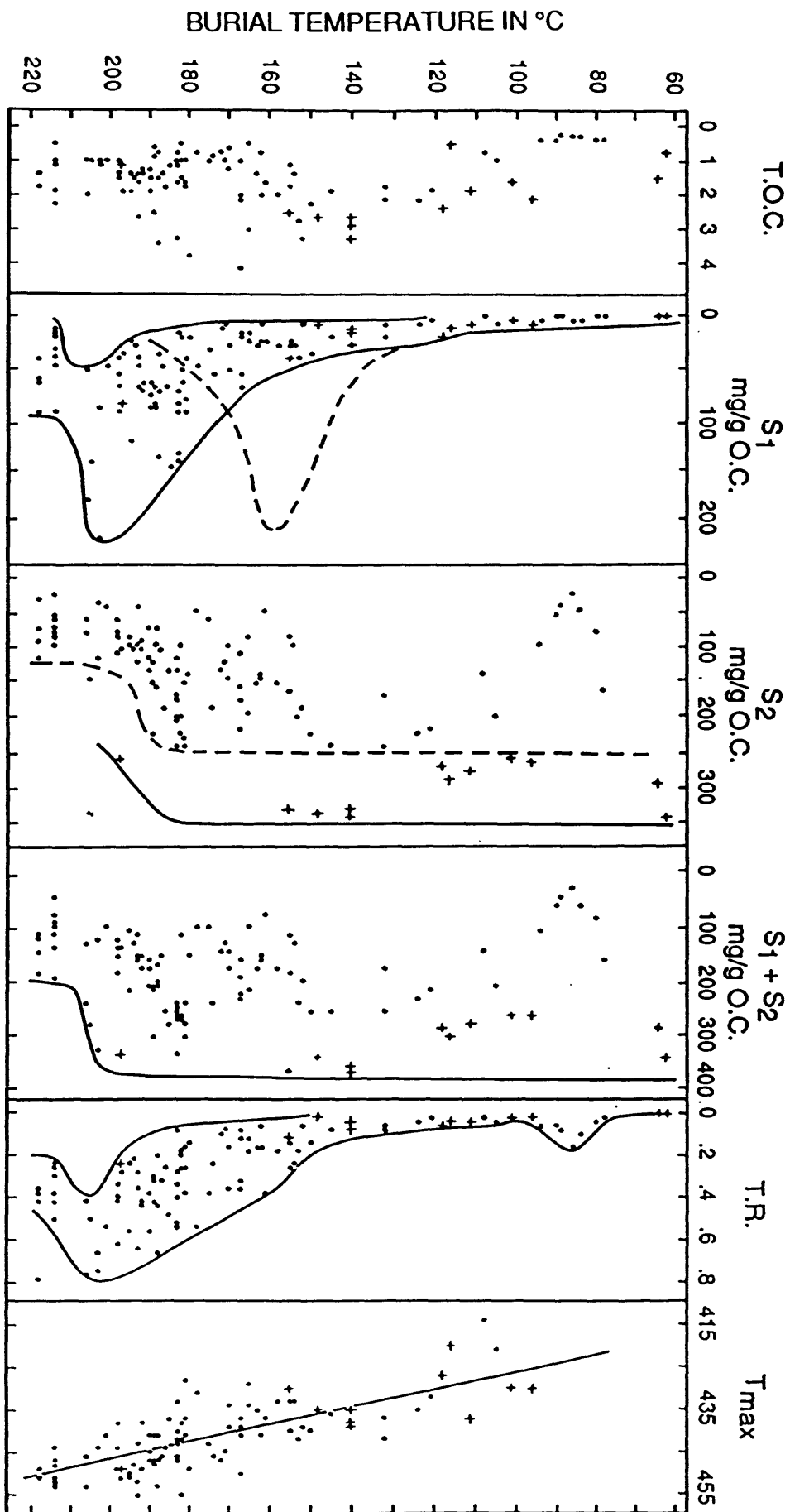


Figure 13.

Plot of T.O.C., the S₁, S₂, and sum of the S₁ and S₂ ROCK EVAL pyrolysis peaks (all normalized to organic carbon—mg/g O.C.), T.R., and T_{max} all versus present-day (probably maximal) equilibrium burial temperature in °C for core samples from well bores in the Paloma field, California. Dots signify samples with S₂ values of less than 250 mg/g O.C., and crosses signify samples with S₂ values of 250–350 mg/g O.C. Various lines are explained in text.

In figure 13, for samples with hydrogen indices at or below 250 mg/g O.C., as delineated by the dashed line, the first detectable decrease in the values of the S_2 pyrolysis peak (also shown by the dashed line) occurs at a burial temperature of 184°C (assumed $R_o = .97$). This decrease is interpreted to represent the commencement of intense HC generation, and it occurs at a somewhat higher maturation rank than the rank ($R_o = 0.8$) for the coals of figure 3.

In the rocks at Paloma, intense primary migration begins at a burial temperature of 203°C (assumed $R_o = 1.16$) as witnessed by the strong decrease in the S_1 pyrolysis peak in figure 13 with increase in burial temperature above 203°C. Thus, intense primary migration commences at Paloma at a higher maturation rank than that in figures 1-3, 6, 7 and 9 ($R_o = 0.81$ to 0.85 - Table 2). The plot of the sum of the S_1 and S_2 pyrolysis peaks in figure 13 is another indication of the relatively late commencement of intense primary migration at Paloma. Maximum values for the sum of the two pyrolysis peaks remain constant, as shown by the solid line, up to 203°C. This suggests that only a portion, if any, of the newly generated HC's, over the burial temperature range 120° to 203°C, moved out of the shales from their generation sites.

In figure 13, T_{max} increases from 414°-421°C at a burial temperature of 105°C, to 450°C by a burial temperature of 218°C. This is shown by the solid line in the T_{max} plot which is a visual best fit to the data. T_{max} in the Paloma samples with burial temperatures higher than 150°C probably has been suppressed due to the high contents of solvent-extractable bitumen (and therefore NSO compounds) in these samples. As in the case with the Ralph Lowe well, solvent extraction of the deep Paloma samples with high S_1 values would likely cause a substantial increase in T_{max} . Also, as discussed below, the OM in the rocks at Paloma appears to be more hydrogen-rich than "normal" Type III OM. This higher hydrogen content would also suppress T_{max} values slightly versus burial temperature, due to the suppression of all organic maturation indices, versus burial temperature, in hydrogen-rich OM (Price and others, 1984; Price and Barker, 1985; Price, 1988b). T_{max} for the rocks at Paloma thus is not expected to exhibit the same correlation versus burial temperature and R_o (Table 1) which typical Type III OM does.

The S_1 data of figure 13 contradict the hypothesis of thermal destruction of C_{15}^{+} HC's over the maturation rank of $R_o = 0.9$ to 1.35 (burial temperatures 174°-227°C, from Price, 1983). Also, the S_1 data of figure 13 do not conform, in two ways, to the trends observed in the S_1 data of figures 1, 3, 6, 7 and 9. First, the S_1 data at Paloma do not increase over the burial temperature interval 120° to 160°C (assumed $R_o = 0.6$ to 0.81) to a maximum by burial temperatures of 160° to 163°C (assumed $R_o = 0.81$ to 0.83), and then decrease to low values by burial temperatures of 185°C (assumed $R_o = 1.0$). This expected trend is shown by the dashed line in the plot of the S_1 data of figure 13. Second, instead, the S_1 peak continuously increases to a maximum at a burial temperature of 203°C (assumed $R_o = 1.16$), and then decreases to lower values (but still quite high - 40 to 95 mg/g O.C.) by a burial temperature of 218°C (assumed $R_o = 1.40$).

The trends in the S_1 data at Paloma are possibly due to primary migration phenomena acting either alone or in consort with variations in OM type. At Paloma, over the burial-temperature range 112° to 146°C, ten samples were analyzed with hydrogen indices in excess of 350 mg/g O.C., one sample having a

value of 590 mg/g O.C. As the OM in these ten samples clearly was not oxygen-rich Type III OM, these samples were excluded from figure 13. However, the excluded samples may indicate that the rocks at Paloma contain a hydrogen-rich end member of Type III (oxygen-rich) OM. In the plot of the hydrogen indices in figure 13, at temperatures below 184°C (the first detectable decrease in the mean maximum values of the S₂ peak), most of the S₂ values range between 100 to 250 mg/g O.C., with maximum values of up to 350 mg/g O.C. These are high hydrogen indices for oxygen-rich OM, as average hydrogen indices for fine-grained rocks with oxygen-rich OM from other areas, usually fall in the range of 50 to 120 mg/g O.C. Thus, the OM in the rocks at Paloma may have slightly stronger chemical bonds than "normal" oxygen-rich OM, and as such, HC generation at Paloma requires higher burial temperatures, than "normal". Or perhaps the generated HC's have less gases and more C₅+ HC's than the products generated from "normal" oxygen-rich OM. If so, primary migration by gaseous solution might not be as effective as in other cases (Figs. 1-3, 6, 7 and 9), and more C₅+ HC's would remain in the rocks to higher maturation ranks than usual. Whatever the reason, the S₁ data of figure 13 (and the S₁ data of figures 10 and 11) show that in rocks with oxygen-rich OM, a maximum in the HC coefficient does not always occur by R_o = 0.81 to 0.83 followed by a decline to zero or near zero values for the HC coefficient by R_o = 1.00 to 1.35. Geologic time cannot be invoked as the cause for the retardation of HC generation and primary migration at Paloma. The burial histories at Paloma, in the Texas COST #1 well (Fig. 9), and for the rocks of the Mahakam delta (Figs. 6 and 7) are all about the same. Further, the trends of the C₁₅+ HC's of the Texas COST #1 well and the S₁ data from the Mahakam delta closely replicate the trends of equivalent data from older rocks (Figs. 1-3).

At this time, it is impossible to say if: 1) Paloma is a unique situation, or 2) Paloma represents the behavior of the hydrogen-rich end member of Type III OM, or 3) an entire, as yet undefined, spectrum of generation-migration behavior exists for oxygen-rich OM. As a working hypothesis, it is assumed here that the trends of figures 1-3, 6, 7 and 9 and the trends at Paloma represent the behavior of the two end members of oxygen-rich OM. However, only with other detailed studies, such as those represented by figures 3 and 13, in which rocks with oxygen-rich OM have been exposed to a wide range of maturation ranks, will the question be resolved.

At Paloma, not only is a maturation rank of R_o = 0.6 unrealistic for the first possibility of the generation and accumulation of oil deposits from those rocks, but a rank of R_o = 0.81 to 0.85 is also too low. The first possibility of the rocks at Paloma yielding an oil deposit occurs with the commencement of intense primary migration, at an assumed R_o value of 1.16 (burial temperature 203°C).

DISCUSSION

Timing of Primary Migration

With one exception (Paloma), in figures 1-3, 6, 7, 9 and 13, intense primary petroleum migration was hypothesized to commence at R_o = 0.81 to 0.85 (Table 2). Although intense primary migration apparently commences only at R_o = 0.8, some degree of primary migration may take place at maturation ranks below R_o = 0.8 in rocks with oxygen-rich OM. Primary migration by gaseous solution depends on factors other than maturation rank, i.e. - T.O.C. content, fluid dynamics,

etc. For example, Leythausen and others (1984, p. 206) found evidence of primary migration from a thin shale adjacent to a sandstone, whereas no detectable migration had occurred from the middle of a thick shale in the same sequence and at the same maturation rank ($R_o = 0.82$, $R_o = 0.77$). They postulated that the thin shale had better fluid communication with an adjacent sandstone, which allowed primary migration to take place earlier than from the middle of the thick shale, which had poor fluid communication with a sandstone.

The Threshold of Intense HC Generation

$R_o = 0.6$ is recognized as the threshold of intense HC generation (TIHG). However, two data sets of this paper (Figs. 3 and 13) suggest that: 1) This threshold is not abrupt, but is gradual, occurring over a rather wide maturation rank. 2) The intense generation of C_{15+} HC's actually begins at the first noticeable decrease in values of the S_2 pyrolysis peak. 3) The commencement of intense HC generation, and the commencement of intense primary petroleum migration, in rocks with oxygen-rich OM are closely intertwined. In the data of figure 3, which are assumed here to represent the usual case for oxygen-rich OM, the TIHG spans $R_o = 0.60$ to 0.81 ; and intense HC generation (and intense primary petroleum migration begin) at $R_o = 0.81$. At Paloma, which is assumed to represent the hydrogen-rich end member of Type III OM, the TIHG spans (all R_o values assumed) $R_o = 0.60$ to 0.97 (present-day equilibrium and probable maximal burial temperatures of 122° to 184°C), intense HC generation commences at $R_o = 0.97$, and intense primary migration commences at $R_o = 1.16$ (burial temperature 203°C).

Rank Variations and HC Concentrations

Apparently all oxygen-rich OM loses all HC generation potential by $R_o = 1.8$ to 2.0 . However, the behavior of C_{15+} HC's and/or of the S_1 pyrolysis peak at R_o values >1.0 is variable. For example, the S_1 pyrolysis peaks of figures 10, 11, and 13 from $R_o = 1.0$ to 2.0 , have moderate to high values, instead of the low to zero values exhibited in figures 1-3, 6, 7, and 9. Furthermore, ROCK EVAL analyses carried out on other rocks with oxygen-rich OM, show that this is not uncommon. Whether or not C_{15+} HC's go to zero, or near zero, concentrations at elevated maturation ranks is assumed here to be a question of primary migration efficiency. Where primary migration is impeded, moderate to high values of C_{15+} HC's may be present in fine-grained rocks with oxygen-rich OM at maturation ranks ranging from $R_o = 1.0$ - 2.0 . For example, poor fluid hydrodynamics and/or poor "plumbing", abnormal fluid pressures, or a deep-basin gas phase with only irreducible water (all of which may have been active in the Green River basin - Fig. 10) will impede or essentially halt primary migration by gaseous solution.

In figures 3 and 13, it is not a coincidence that the commencement of intense HC generation and intense primary migration are so close to each other in maturation rank: (assumed) $R_o = 0.97$ and 1.16 respectively at Paloma, and both at $R_o = 0.81$ for the coals. It is only when intense HC generation commences that enough HC gas is generated in the fine-grained rocks to: 1) saturate shale pore waters with respect to the aqueous solubility of the HC gases, 2) allow the formation of a free-gas phase in these rocks, a gas phase which takes C_5+ HC's into solution, and 3) allow this free-gas phase to expand and microfracture the rocks so that primary migration may take place. Oxygen-rich

OM as an Oil Source

It has been assumed above, that oxygen-rich OM has the capability to yield commercial oil deposits; however, this assumption is not necessarily valid. There is no question that oxygen-rich OM has the capacity to generate HC's and that these generated HC's do migrate from fine-grained rocks. Further, the maturation ranks at which these processes occur have been delineated, at least in a preliminary fashion, in this article. However, whether or not these HC's can concentrate and accumulate into an oil deposit, after primary migration, is another matter. There are too many variables and too little definitive data to know at this point. Such variables are the T.O.C. and hydrogen index values for the fine-grained rocks under discussion; the percentage of the S_2 pyrolysis peak which is converted to methane, ethane through butane, the C_5 - C_{10} HC's and C_{10}^+ HC's; the rock porosity; the salinity, CO_2 content, temperature, and pressure of rock pore waters; the concentration of biogenic methane in rock pore waters; the critical gas saturation level which must be reached for movement of a free-gas phase; and the HC concentration in the sand pore waters. Any attempted quantification to these, and other variables, would have such great uncertainty that mass-balance calculations would be meaningless. However, certain insights, observations, and limitations to the situation can be discussed.

A huge amount of light (C_1 - C_9) HC's is required to saturate shale and sand pore waters and this amount of hydrocarbons depends on burial temperatures and pressures, pore water salinities, CO_2 contents, etc. Until all sediment pore waters are saturated with respect to the HC gases, no free-gas phase can form. If sediment pore waters are undersaturated with respect to HC gases, a free-gas phase will quickly be dissolved into these undersaturated waters. With the burial conditions under consideration ($R_o = 0.6$ to 2.0 , burial temperatures of 120° to $278^\circ C$ from Price, 1983, Fig. 19), aqueous solubility levels for C_{15}^+ HC's will be low and can be disregarded for most of this range (Price, 1976, 1981a). However, over this range of burial temperatures (and pressures), once a free-gas phase forms, it has a substantial carrying capacity for C_5^+ HC's, including C_{15}^+ HC's (Price and others, 1983). After the volume concentration of this free-gas phase, saturated with C_5^+ HC's, exceeds the critical gas saturation level of the shales in which it forms (probably in the range of 1-5 volume percent of the porosity), and after microfracturing of the shales has occurred, this free-gas phase can then move into sandstone reservoirs or carrier beds. Once in sandstone, this free-gas phase must exceed the critical gas saturation level of the sandstone before the gas phase can move towards a possible accumulation. The myriad of shows, stains, and small uneconomic HC deposits present in any petroleum basin also must be added to the mass of HC's outlined above. Clearly the total mass of HC's which precede and support the formation of economic oil deposits is huge, no matter what assumptions would be made in any mass-balance calculations.

Given this conclusion, it follows that in the case of oxygen-rich OM, high-T.O.C., fine-grained rocks with low water contents and moderate to high hydrogen indices (150-250 mg/g O.C.) are much more likely to generate commercial HC deposits than low-T.O.C. (T.O.C. <0.5 weight percent), fine-grained rocks with low hydrogen indices (10-75 mg/g O.C.) and high, water-saturated porosity. Coals and carbonaceous shales are examples of the first class, and the Miocene to Pliocene shales of the coastal and offshore Gulf Coast, the Upper Cretaceous

to lower Tertiary shales of the Rocky Mountain basins and the Upper Cretaceous to Tertiary shales of the Sacramento Valley basin, California, all are examples of the second class.

Coals as Oil Source Rocks

Coals have been dismissed as possible oil source rocks by different investigators (including Teichmüller, 1974, p. 387; Tissot and Welte, 1978, p. 223-224; and Radke and others, 1980) on the basis of the following arguments, either alone or in combination: 1) Coals generate only gas and not C_{15}^{+} HC's. 2) Any C_{15}^{+} HC's that are generated by coals are irreversibly chemically adsorbed into or onto the coal or trapped in the microporosity or molecular-seive like structure of the coal, unable to ever migrate. As such, these HC's are eventually cracked in situ to methane. The large decreases in the C_{15}^{+} HC concentrations of coals over $R_o = 0.85$ to 1.35 have been attributed to such cracking. 3) Coals are almost never spatially associated with oil deposits.

On the other hand, other investigators, including Durand (1982), Durand and Paratte (1983), Teichmüller and Durand (1983), and Tissot (1984), have put forth arguments and data supporting the position that coals can be source rocks for oil deposits.

Figure 4 of this paper, from data of Teichmüller and Durand (1983), replies to the hypothesis that coals generate only methane. Up to a rank of $T_{max} = 438^{\circ}C$ ($R_o = .66$), at least half the products pyrolyzed from the coals are C_{15}^{+} HC's, and up to ranks of $T_{max} = 500^{\circ}C$ ($R_o = 1.76$), at least 25 percent of the products are C_{15}^{+} HC's. Figure 5 supports the work of Teichmüller and Durand (1983) in this regard.

It is true that coals generate copious amounts of gas at all maturation ranks, including huge amounts of CO_2 (Fig. 14) even at low maturation ranks. However, these large gas volumes are precisely why C_{15}^{+} HC's would not be trapped in coals very long after their generation. I believe that coals are repeatedly microfractured and healed due to the continual build up and escape of these gases. Teichmüller (1974, p. 382) described the coal "maceral" exsudatinite (also called exsudatinite) as a resinous or asphaltic like material found as fillings or linings of cracks and fissures in coals at ranks as low as $R_o = 0.45$. Exsudatinite becomes more abundant in coals as maturation rank increases (see Table III of Teichmüller and Durand, 1983). The gaseous-crude oil solubility data of Price and others (1983) demonstrate the substantial carrying capacity that CO_2 -rich gas has for crude oil, even at low burial temperatures and pressures ($R_o = 0.45$). At this rank, by the data of figure 14, a huge amount of CO_2 would be generated by coals in Nature. A CO_2 -rich gas phase at low maturation rank will take the limited amount of available HC's, as well as the more abundant resins and asphaltenes, into solution. As the gas phase becomes overpressured, eventually the coal is microfractured. The drop in pressure accompanying the microfracturing will cause the highest molecular weight (asphaltic) material to exsolve from the gaseous phase and precipitate as a lining or filling of exsudatinite in the microfracture. By this scenario, exsudatinite would not be a coal maceral at all, but rather a high-molecular-weight bitumen that has been dissolved by a CO_2 -rich gas phase and precipitated during the pressure decrease from microfracturing. The very existence of exsudatinite in coals at low maturation ranks is a probable

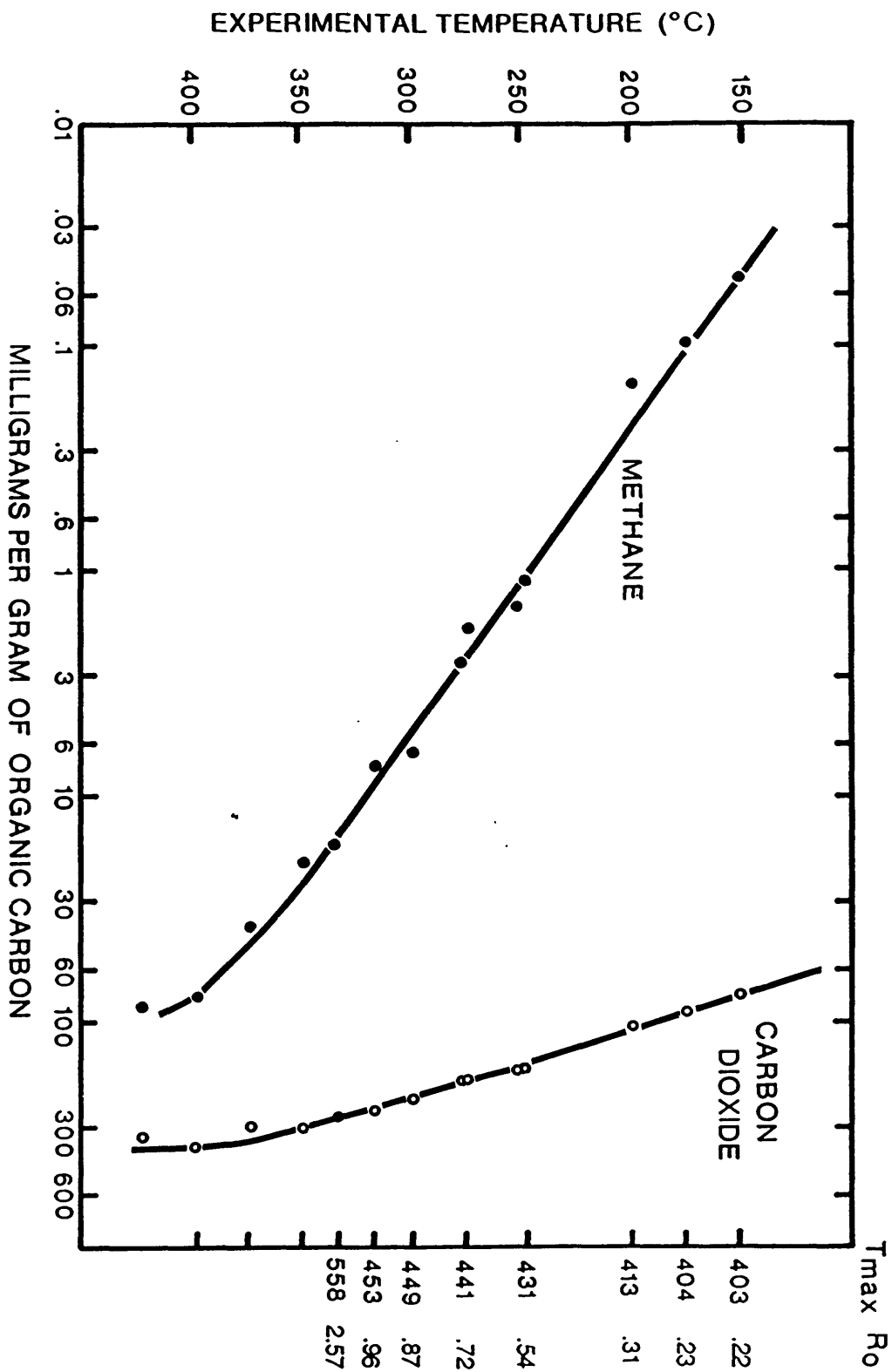


Figure 14. Plot of the amount of methane and carbon dioxide in mg/g O.C. versus experimental temperature, measured T_{max} , and inferred R_o (from table 1) from hydrous pyrolysis of the Paleocene Rattlesnake Butte lignite.

manifestation of the efficacy of primary migration in coals by gaseous solution. In such a sequence of events, C_{15}^+ HC's at ranks of $R_o \geq 0.85$, would not be trapped in coals and eventually be thermally cracked to gas. In fact, newly generated C_{15}^+ HC's at these maturation ranks probably spend very little residence time at their generation sites in coals.

In figure 3, the mean hydrogen index at the maximum (shown by feathered arrow) of the S_2 plot of the coals can be visually estimated at about 220 mg/g O.C. From table III of Teichmüller and Durand (1983), a T.O.C. content for these coals at $R_o = 0.65$ ($R_m = 0.70$) can be taken as 78 percent. These T.O.C. and S_2 values equate to 171,600 ppm of generation products for these coals. From figure 4, at $R_o = 0.65$, 75 percent of the HC product would be C_5^+ HC's and 50 percent would be C_{15}^+ HC's. A "black shale" with 10 percent T.O.C. and a hydrogen index of 800 mg/g O.C. would be considered a premier source rock. Yet this rock would have a generation capacity of "only" 80,000 ppm, less than half that of the coal example. If such numbers do not qualify coals as probable oil source rocks, then there is little justification for the hypothesis that any fine-grained rock with oxygen-rich OM could be a source rock.

The last commonly quoted argument for coals not being possible oil-source rocks is that oil deposits and coals are rarely spatially associated. From figure 3, the major loss in the S_2 pyrolysis peak of the coals occurs over $R_o = 0.81$ to 1.57 (bracketed arrows). Most oil deposits are found at burial depths corresponding to lower maturation ranks than these. Thus, oil deposits would not be expected to be spatially associated with coals, if coals were acting as their source rocks, as the coals would always be buried deeper in the section than the oil deposits which they generated. In my opinion, this is the usual relationship between oil deposits and their source rocks, no matter what the source rock. Source rocks are usually found deeper than, and not spatially associated with, the oil deposits that they generate.

If coals are ever shown to be oil source rocks, it will not necessarily follow that all fine-grained rocks with oxygen-rich OM are source rocks, or even that all coals are source rocks. It is unlikely that shales with T.O.C. contents of 0.3 to 1.0 percent and with hydrogen indices of 30 to 100 mg/g O.C. could be source rocks. Such rocks probably generate barely enough HC's to saturate shale and sand pore waters and porosities with the needed levels of background HC concentrations. The coals which Teichmüller and Durand (1983) analyzed have very high hydrogen indices compared with some other coals such as the 37 coals from the Williston basin of figure 15. ROCK EVAL T_{max} values for these coals range from 407° to 435°C and burial depths range from 25.9 to 734 m (85 to 2410 ft). From figure 15, a median hydrogen index can be visually estimated at about 46 mg/g O.C. A T.O.C. content of 60.0 percent would give a generation potential of 27,600 ppm, a value substantially less than the median value (171,600 ppm) calculated for the coals studied by Teichmüller and Durand (1983). Further, only a part of this generation potential of 27,600 ppm is for oil-like HC's.

Hydrous pyrolysis was carried out on samples of the Paleocene Rattlesnake Butte lignite, Billings Co., North Dakota, sec. 26, T.41N., R.98W (Price, 1988a). The coal had a burial depth of 26 m (86 ft), and the T.O.C. and S_2 values of the unreacted lignite were 43.68 percent and 52 mg/g O.C respectively. The amounts of the various generation products from hydrous pyrolysis of the

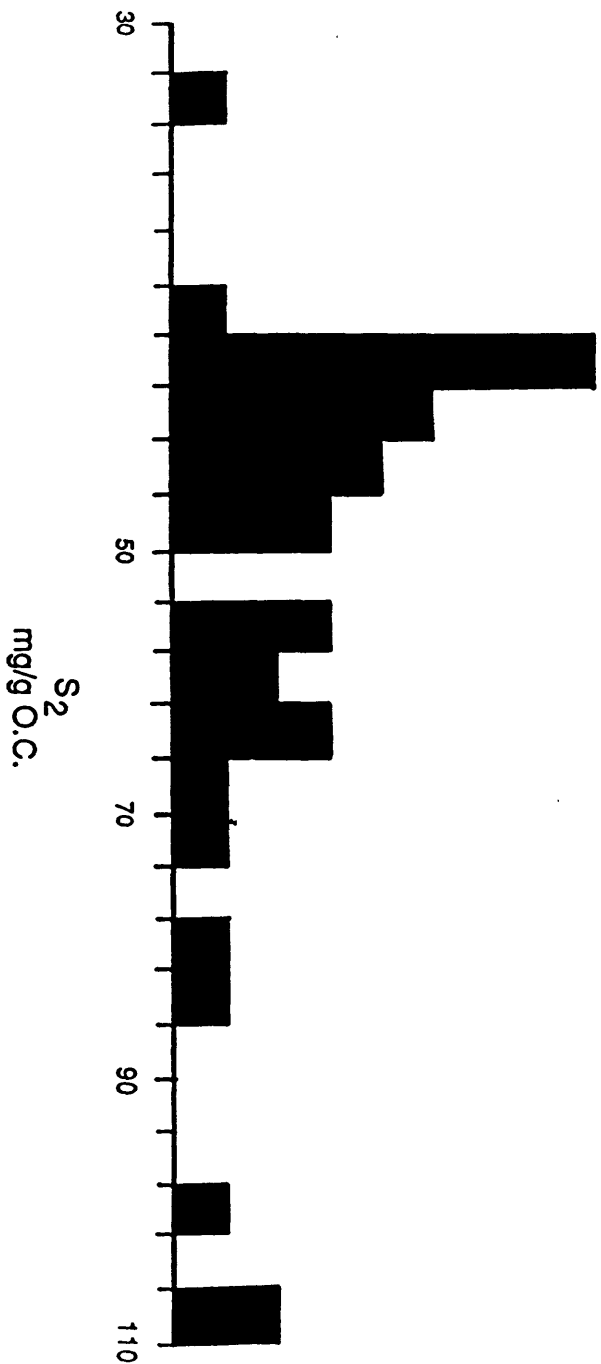
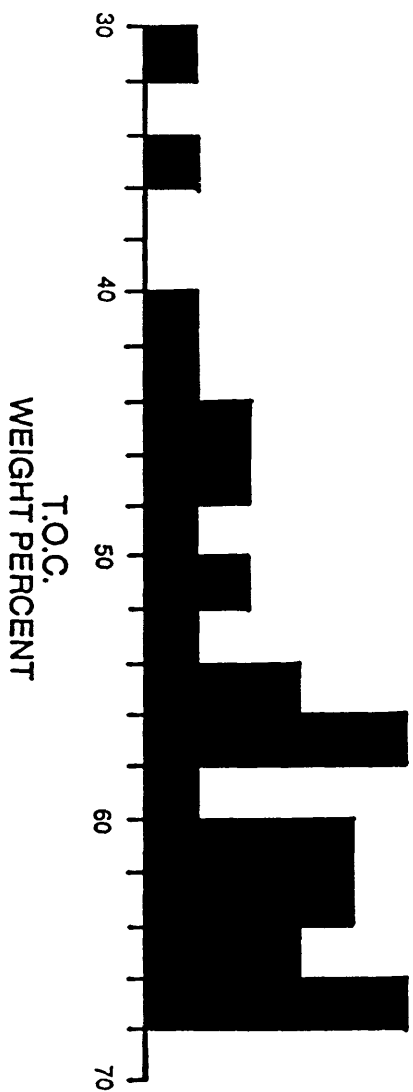


Figure 15.

Histograms showing T.O.C. and hydrogen indices for 37 coal samples from four different well bores (North Dakota Geological Survey well numbers: 25, 527, 2615 and 6616) in the North Dakota portion of the Williston basin. The coals are from the Paleocene and Eocene Golden Valley Formation, the Paleocene Fort Union Formation, and the Upper Cretaceous Hell Creek and Fox Hills Formations.

Rattlesnake Butte lignite at different reaction temperatures are given in figure 16 in mg/g O.C. Intense HC generation reaches a maximum between 316° and 320°C. The thermal destruction of saturated HC's begins at about 333°C, and becomes pronounced by 350°C where the C₉-C₁₅ and C₁₅+ saturated HC's have decreased to low values (0.171 and 0.144 mg/g O.C., respectively). The weight percentages that the various organic compounds (methane through the asphaltenes) make up of the total generated products (with and without CO₂ and N₂), at a temperature (316°C) near the maximum of HC generation, is shown in figure 17. The C₅-C₈ HC's and C₉+ saturated HC's make up only 7.48 percent of the total generated products, yet these compounds comprise a major portion of 0.850-0.825 specific gravity (35°-40°) API oils. Thus, the median value of 27,600 ppm of generated products for the coals of figure 16 would be reduced to 2,063 ppm useful products, or 3,500-4,000 ppm (12.7 to 14.5 percent) useful products allowing for the C₉+ aromatic HC's, resins, and asphaltenes found in oils. A coal with a useful generation-product capacity of only 4,000 ppm is not such an impressive source rock, and it is not clear if such a rock could be responsible for an oil deposit.

In a similar manner, the average generation potential (171,600 ppm) of the coals of Teichmüller and Durand (1983) should also be reduced to "useful products". The far more hydrogen-rich coals of these authors would yield a higher percentage of useful products, let us assume between 20 to 50 percent, or between 34,320 to 85,800 ppm. Even these reduced numbers are still very impressive for any class of source rock.

This discussion certainly does not prove if coals are oil source rocks or not. That question will only be answered by designing and carrying out research specific to the question. It is, however, an important question. If coals can source oil deposits, they would do so at lower maturation ranks than would hydrogen-rich OM, which requires higher burial temperatures to break the stronger bonds in that kerogen (Price and Barker, 1985; Price and others, 1984). Thus, the maturation-rank requirements and burial history plots for mainstage HC generation from coals, would be much different than for HC generation from hydrogen-rich OM, a point relevant to both resource appraisal and organic-geochemical modeling in oil exploration.

Primary Migration by Aqueous Solution

I have previously advocated primary petroleum migration by aqueous solution, on the basis of quantitative and crude-oil qualitative considerations, (Price, 1976, 1977, 1981a and b). Crude oil-aqueous solubility data (Price 1981a) showed that at minimum burial temperatures of 275°C ($R_o = 1.95$, Price, 1983), constraints against primary migration by aqueous solution, from quantitative and crude-oil qualitative considerations, were negated. Specifically: 1) shale pore waters at these, and higher, burial temperatures can dissolve HC's at concentrations high enough to result in oil deposits, and 2) the distributions of HC's dissolved in these waters are compositionally similar or identical to the HC distributions of oils. A consideration against such a hot, deep primary migration of petroleum by aqueous solution is that HC's cannot thermally survive to such high burial temperatures and/or maturation ranks (Barker, 1977). This consideration has been negated by the results of organic-geochemical analyses of deeply buried shales, analyses which demonstrate that significant amounts of both C₁₅+ HC's, and HC generation potential on kerogen, survive to high maturation ranks (Price, 1977; 1981b, p. 94-95; 1982; 1983, p. 6-10; 1988b; and

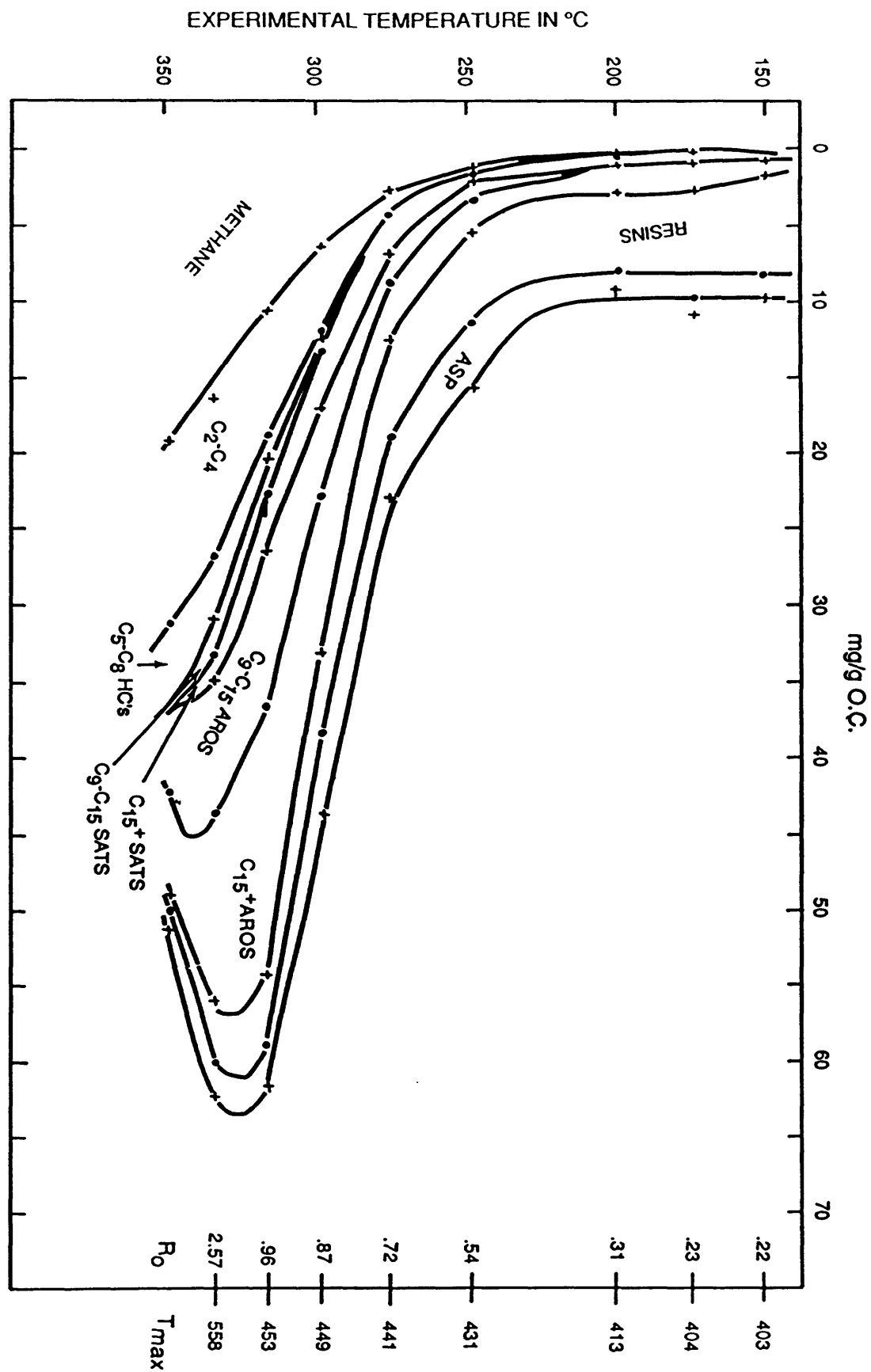
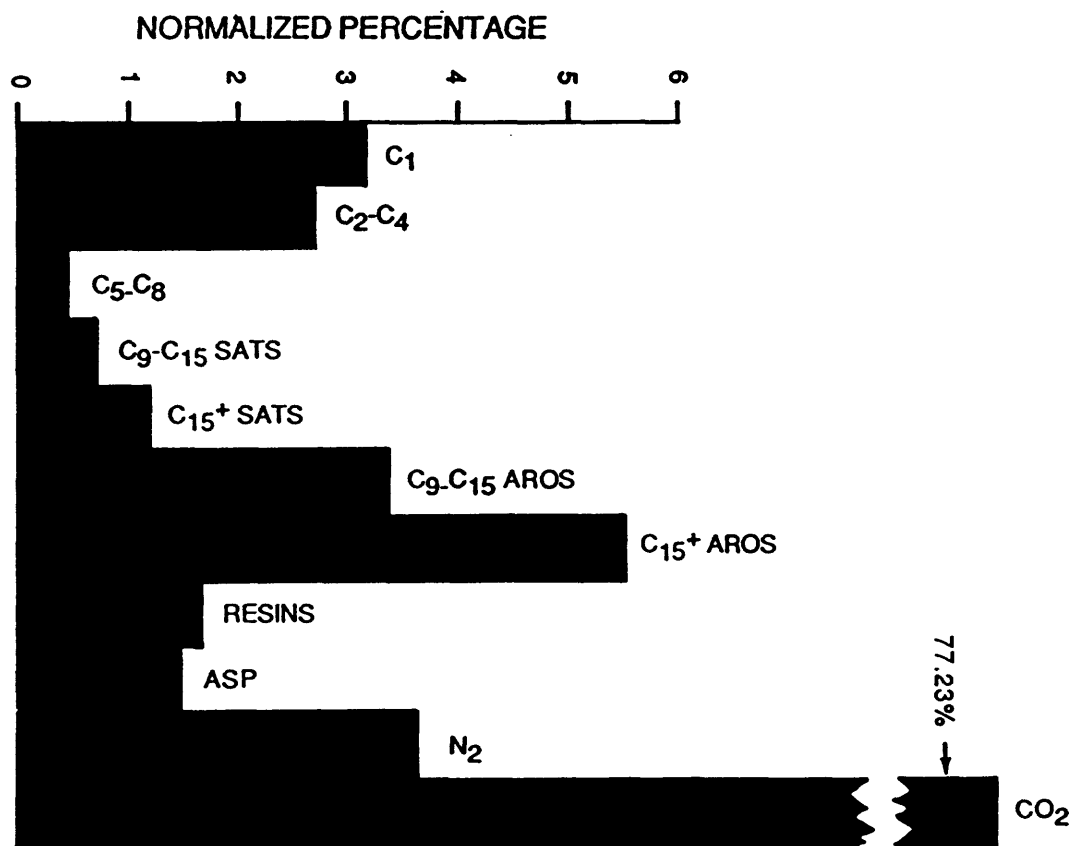
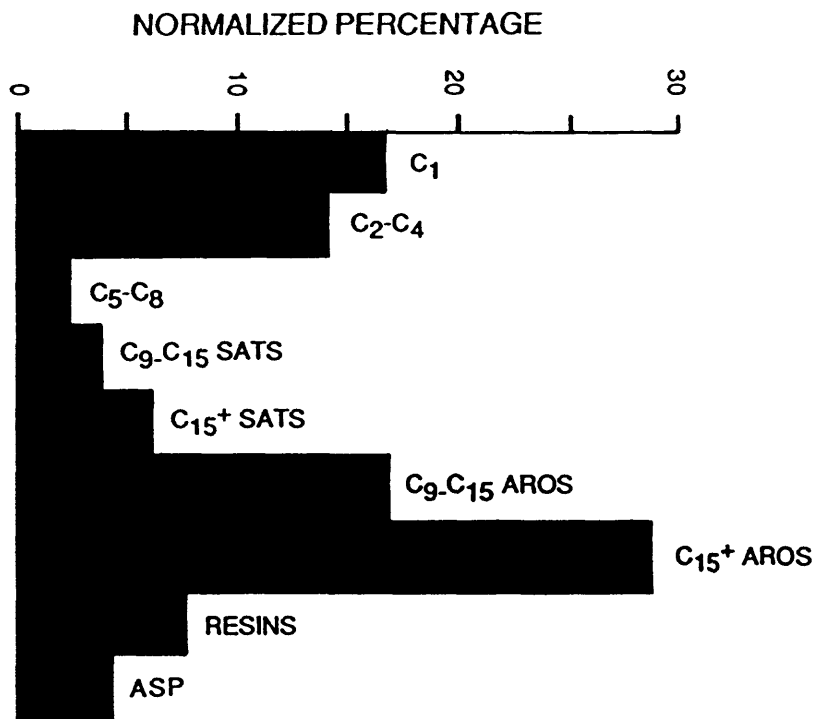


Figure 16. Plot of amounts (normalized to organic carbon-mg/g O.C.) of various generated products versus experimental temperature, measured T_{max} , and inferred R_o (from table 1) for hydrous pyrolysis of the Paleocene Rattlesnake Butte lignite. SATS = saturated HC's, AROS = aromatic HC's, RES = Resins, and ASP = asphaltenes.

Figure 17.

Plot of relative percentages (by weight) of various organic compounds generated at 316°C by hydrous pyrolysis of the Paleocene Rattlesnake Butte lignite. SATS = saturated HC's, AROS = aromatic HC's, and ASP = asphaltenes. Two plots are given, one including CO₂ and N₂ as products, and one excluding CO₂ and N₂ as products.



Price and others, 1979, 1981). The OM of the shales which yielded these results was totally or largely hydrogen-rich OM. From these data, I made the erroneous assumption (Price, 1981b) that all shales would have significant concentrations of $C_{15}+$ HC's and at least remnant HC generation potential at high burial temperatures and/or maturation ranks.

This assumption is incorrect for shales whose kerogen is composed of oxygen-rich OM. As discussed, this OM type loses all its generation potential by $R_o = 1.8$ to 2.0 , precisely the maturation rank where primary migration by aqueous solution can first become effective. In some cases (Figs. 10 and 11), moderate amounts of solvent-extractable $C_{15}+$ HC's remain in rocks with oxygen-rich OM to maturation ranks of at least $R_o = 2.0$. However, in many other cases (Figs. 1-3), low to zero concentrations of $C_{15}+$ HC's accompany the total loss of HC generation potential by $R_o = 2.0$ in such rocks. Thus, it follows that aqueous solution of HC's is not a probable primary migration mechanism in rocks with oxygen-rich OM for two reasons: 1) Primary migration by gaseous solution removes most or all of the indigenous and generated HC's from these rocks before primary migration by aqueous solution can ever become effective. 2) These rocks have no remaining HC generation potential at the maturation ranks where primary migration by aqueous solution first becomes effective. It is ironic that the rocks involved with the optimum scenario for primary petroleum migration by aqueous solution, thick deltaic shale sections with abnormal fluid contents and abnormal formation pressures, are dominated by oxygen-rich OM, which negates this migration mechanism. Primary migration by aqueous solution is simply not possible in such rocks because a highly effective primary migration by gaseous solution occurs earlier in the burial history of such rocks.

Primary migration by aqueous solution from typical "black shale" source rocks (rocks containing at least 5 to 10 percent T.O.C. and hydrogen indices of 500 mg/g O.C. or greater) is also unlikely. The shales of the Devonian-Mississippian Formation Bakken Formation of the Williston basin serves as an example. As discussed in Price and others (1984), this rock has very low porosity, with only irreducible water in the limited pore space of the rock. This shale lost all of its mobile water long before intense HC generation commenced; and when mainstage HC generation did commence in this rock, there was simply no pore water left to act as an agent of primary migration. Jones (1978) has also discussed the unlikelihood of primary petroleum migration by aqueous solution from "black shale"-type source rocks; and the rocks he discusses share the same characteristics, which prohibit primary petroleum migration by aqueous solution, as the shales of the Bakken Formation.

The only situation that I can now envision where $C_{15}+$ HC primary migration by aqueous solution might be effective is in thick shale sections which have retained abnormal contents of pore water to high maturation ranks or burial temperatures, and which also have moderate T.O.C. contents (1 to 5 percent) and significant amounts of hydrogen-rich OM. However, even hydrogen-rich OM may lose a significant percentage of its HC generation potential before the maturation rank is reached where primary migration by aqueous solution could become effective. However, because higher maturation ranks are needed for kerogen burnout in hydrogen-rich OM compared to oxygen-rich OM, remnant, and sometimes substantial, HC generation potential remains on hydrogen-rich OM to high maturation ranks. Also, hydrogen-rich OM has much higher ratios of generated C_5+ products to generated methane and carbon dioxide compared to

oxygen-rich OM (Fig. 8). Therefore, with hydrogen-rich OM, primary migration by gaseous solution does not strip the rocks of C_{5+} (and C_{15+}) HC's by $R_o = 1.8$ to 2.0 , as is sometimes the case with oxygen-rich OM. Substantial amounts of C_{15+} HC's and HC generation potential have been documented in rocks with hydrogen-rich OM at high maturation ranks, where primary migration by aqueous solution would be effective. Such a migration mechanism (Price, 1976) would depend on focusing large volumes of deep basinal pore waters, carrying dissolved HC's through lateral conduits (sandstones, etc.) to fault zones and up the fault zones where HC exsolution would occur. The exsolved HC's would then be channeled off the fault and into a suitable trap at shallower depths where accumulation would take place. However, whether or not such a scenario exists in Nature, and can make a meaningful contribution to the formation of economically significant oil deposits, is open to conjecture. Due to the high aqueous solubilities of the C_1-C_9 HC's (McAuliffe, 1966, 1969; Price, 1976, 1981A), primary migration of C_1-C_9 HC's by aqueous solution is still theoretically probable, in my opinion.

Examples of aromatic-rich condensates associated with gas deposits exist. Aqueous solution at burial temperatures of 90° to 250°C selectively takes aromatic HC's, over saturated HC's, into solution (Price, 1976; 1981A). It is, therefore, possible that primary migration by aqueous solution may have played some role in the accumulation of at least the C_{5+} HC's in these deposits.

In the past, I have overestimated the role of molecular solution as an agent of primary migration and now believe that, at best, it plays only a minor role in the accumulation of C_{15+} HC's in oil deposits. However, molecular solution plays other important roles related to oil and gas deposits. For example, molecular solution is probably responsible for the diffusion of HC's throughout the pore waters of sedimentary basins. Also, by diffusion, molecular solution acts as the gathering agent which allows a HC free-gas phase in the shale porosity to take C_{5+} HC's into gaseous solution before the gas phase migrates from the rocks (Price, 1988a). Molecular solution also plays a key role in crude-oil degradation by water washing (Price, 1980; LaFargue and Barker, 1988).

CONCLUSIONS

1) Many examples exist, in rocks with oxygen-rich OM, of a precipitous decrease in the concentration of C_{15+} HC's, or the values of the S_1 pyrolysis peak, from maximum values at $R_o = 0.8$ to zero or near zero values by $R_o = 1.35$. These decreases have been attributed to, and accepted as, due to the thermal destruction of C_{15+} HC's in all fine-grained rocks by these maturation ranks. However, data from this study suggest that this hypothesis may be incorrect:

- A) Oxygen-rich OM does not lose its capacity to generate C_{15+} HC's until $R_o = 1.8$ to 2.0 . Thus, moderate to high concentrations of C_{15+} HC's, or high S_1 pyrolysis peak values, can remain in fine-grained rocks with oxygen-rich OM over the maturation-rank range $R_o = 1.0$ to 2.0 .
- B) Moderate to high concentrations of C_{15+} HC's, moderate to high S_1 pyrolysis peak values, and moderate (remnant) C_{15+} HC generation capacity remain in fine-grained rocks with hydrogen-rich OM at maturation ranks far in excess of $R_o = 1.35$ or even $R_o = 2.0$.

- C) If the decrease in $C_{15}+$ HC's from $R_o = 0.8$ to 1.35 were due to their thermal destruction, then an increase in $C_{14}-$ (and especially C_1-C_7) HC concentrations should occur over this maturation rank. However, the concentration of $C_{14}-$ HC's also decreases over this maturation-rank range.
- 2) The decrease in $C_{15}+$ HC concentrations to zero values by $R_o = 1.35$, that has been documented in rocks with oxygen-rich OM from different areas, can also be explained by intense primary petroleum migration, by gaseous solution, from these rocks.
 - 3) In the rocks at the Paloma field, California, intense HC generation and intense primary migration have been retarded compared to other fine-grained rocks with oxygen-rich OM. It is hypothesized that this retardation is due to the OM at Paloma being at the hydrogen-rich end of Type III (oxygen-rich) OM. However, this retardation could also be due to other reasons.
 - 4) Although a limited amount of primary migration (especially in coals) may take place below $R_o = 0.8$, intense primary migration commences in coals and in rocks with oxygen-rich OM by $R_o = 0.81$ to 0.85. In rocks with more hydrogen-rich Type III OM (hydrogen indices of 150-350 mg/g O.C.) the commencement of intense primary migration apparently may be delayed to higher maturation ranks (assumed $R_o = 1.16$ at Paloma).
 - 5) The concentrations of $C_{15}+$ HC's, or values of the S_1 pyrolysis peak, in fine-grained rocks with oxygen-rich OM, at maturation ranks of $R_o = 1.0$ to 2.0, can be variable for each case under consideration, ranging from zero, or near zero values, through moderate to high values. This variation is hypothesized as due to heterogeneity in the efficacy of primary migration between the different cases.
 - 6) $R_o = 0.6$ has been documented in many studies of oxygen-rich OM as the threshold of intense HC generation for this OM type. However, this threshold spans a wide maturation-rank range ($R_o = 0.6$ to 0.8 for oxygen-rich Type III OM, or $R_o = 0.6-0.97$ for hydrogen-rich Type III OM-Paloma) before intense HC generation actually commences.
 - 7) $R_o = 0.6$ has been considered the lowest maturation rank at which fine-grained rocks with oxygen-rich OM may first generate oil deposits. Oil deposits only result after intense primary migration commences, which appears to occur at $R_o = 0.81$ to 0.85 in most cases but apparently can occur as high as $R_o = 1.16$ with hydrogen-rich Type III OM (Paloma). The minimum maturation ranks at which Type III OM can be expected to yield oil deposits is actually probably higher than $R_o = 0.8$ to 1.16, as oil deposits would be expected only after primary migration had been operative for some time. Possibly R_o values of 1.0 to 1.4 would be more realistic.
 - 8) Coals have been rejected as oil source rocks because: A) Coals allegedly generate only gases and not significant amounts of $C_{15}+$ HC's. B) Even if coals generated significant amounts of $C_{15}+$ HC's, these HC's purportedly would be irreversibly trapped in the coals and eventually cracked to methane. C) Coals are never spatially associated with oil deposits.

- 9) Thermal vaporization and hydrous pyrolysis of coals show that even high rank coals have significant percentages of C_{15}^+ HC's in their generated products.
- 10) The documented ample gas volumes generated by coals (even at low maturation ranks) are hypothesized to microfracture coals and dissolve and transport C_5^+ (and C_{15}^+) HC's and NSO compounds from coal generation sites by gaseous solution. Carbon dioxide plays a major role here. Exsudatinite serves as evidence of this microfracturing and migration. The efficacy of this primary migration is hypothesized as the reason for low contents of C_{15}^+ HC's in coals (and some other fine-grained rocks) at maturation ranks of $R_o \geq 0.9$.
- 11) The major loss of HC generation potential in coals occurs over the maturation-rank range $R_o = 0.81$ to 1.57 . Oil deposits are usually found at depths shallower than those corresponding to such maturation ranks. Therefore, coals should not be expected to be spatially associated with oil deposits, if coals were acting as an oil source. The lack of a spatial association between oils and their source rocks is believed to be the usual situation, no matter what the type of source rock.
- 12) Coals with hydrogen indices of 150–300 mg/g O.C. would be premier source rocks by conventional source rock criteria.
- 13) The results of hydrous-pyrolysis experiments suggest that hydrogen-poor coals (hydrogen of 20–50 mg/g O.C.) do not yield adequate amounts of "useful" generation products to allow the conclusion that such coals would be good oil source rocks.
- 14) Mass balance considerations suggest that shales with 0.3–1.0 percent T.O.C. and hydrogen indices of 30–100 mg/g O.C. probably would not generate oil deposits. Such rocks may not even generate enough HC's to satisfy the background HC concentrations found in petroleum-bearing sedimentary basins.
- 15) The question if some coals, and/or carbonaceous shales with oxygen-rich OM, can generate oil deposits is important. The maturation rank requirements for HC generation from coals would be significantly lower than for HC generation from hydrogen-rich OM. This point is germane to resource assessment and to organic-geochemical modeling as applied to petroleum exploration.
- 16) Primary migration by aqueous solution is not likely from rocks with oxygen-rich OM because: 1) Primary migration by gaseous solution usually removes most, or all, of the indigenous and generated HC's from these rocks before primary migration by aqueous solution can become effective (275°C , $R_o = 1.95$). 2) Oxygen-rich OM completely loses its HC generation potential by $R_o = 1.8$ to 2.0 .
- 17) Primary migration by aqueous solution from "black shale"-type source rocks is not likely, as only irreducible water remains in the low porosity of these rocks by the time intense HC generation commences.

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