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Considerations of Oil Origin, Migration, and Accumulation at Caillou Island and Elsewhere in the Gulf Coast

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ABSTRACT

In the oil fields of the bay Marchand-Caillou Island salt-ridge complex, offshore Louisiana, geometric considerations of oil location, extensive faulting associated with this salt ridge, and the compartmentalized nature of each oil reservoir, all argue against an updip, lateral oil migration from a source to the south of the salt ridge, and suggest a local origin for the oils. ROCK EVAL analysis demonstrates that the Upper Tertiary clastics at Caillou Island have ultra-poor, source-rock characteristics, a fact universal for Pleistocene-Oligiocene shales throughout the Gulf Coast. An origin of the Caillou Island oils from the shales interbedded with the oil sands is improbable because of: 1) this ultra-poor organic nature of the shales, 2) their limited volume from geometric considerations, 3) their low maturation rank, 4) primary migration considerations, and 5) compositional differences between shale bitumen and oil. Proponents of the argument that the large volumes of Tertiary clastics make up for their organic-poor nature (the "something from nothing" proposal), have disregarded four vast hydrocarbon (HC) sinks, which cancel out favorable calculated ratios of generated HC's to in-place HC's. By process of elimination, an origin and migration of the Caillou Island (and other Gulf Coast oils) from depth appears to be the only viable alternative.

With increase in both depth of burial and age of rock in the Gulf Coast, organic richness increases in fine-grained rocks, although these increases are not constant with respect to either geographic location or geologic age. Three possible sources are proposed at depth for the Neogene (including the Caillou Island) oils: 1) thick sections of moderately organic-rich (total organic carbon (T.O.C.) = 2-5+%), hydrogen indices (HI's) = 300-450+) Eocene to Upper Cretaceous (or older) shales with hydrogen-rich (Types I and II organic matter (OM); 2) Lower Cretaceous to Jurassic black shales with high T.O.C. contents, high HI's and Types I and II OM; and 3) Eocene-Paleocene hydrogen-rich coals and carbonaceous shales. A call upon any one of these as a source of the Neogene oils will involve HC generation and migration at maturation ranks moderately to considerably above R_o = 1.35, which is the hypothesized thermal deadline for C_{15}+ HC's. However, the three principal lines of evidence which support the hypothesis of a thermal deadline for C_{15}+ HC's at R_o = 1.35 can be explained by other causes and a large body of data contradicts it. Although this hypothesis is considered by many to be organic-geochemical law, I believe it to be in error.

A substantial data base from both the laboratory and the natural system suggests that the different OM Types have far different reaction kinetics due to greatly different kerogen bond strengths. Type III OM undergoes: 1) the first detectable HC generation at R_o = 0.6, 2) both intense HC generation and primary migration with the first possibility of commercial oil accumulation) at R_o = 0.8, 3) maximum HC generation over R_o = 0.8 to 1.6 or 2.0, and 4) loss of all HC generation potential (kerogen burnout) by R_o = 2.0. Types I and II (hydrogen-rich) OM apparently undergo intense HC generation and migration at more elevated (but yet undefined) maturation ranks, and suffer loss of all HC generation potential at $R_o \geq 7.0$. The three principal arguments against coals being possible oil-source rocks can be adequately replied to. Persuasive lines of logic and evidence exist which suggest that hydrogen-rich coals can be oil source rocks, and in other parts of the world, it is taken for granted that they are.

In light of these points, the preferred explanation here for the origin of the oils at Caillou Island, and for most other Neogene Gulf Coast oils, is deeper HC generation from older, organic-rich rocks, and vertical migration of these oils up major fault zones, with emplacement of the oils in shallower

sandstones. By this scenario, the fault zone becomes the most important element in Gulf Coast HC exploration, and specific exploration targets can be predicted from this model.

INTRODUCTION

A study of the Caillou Island oils was undertaken with the hypotheses that: 1) oils in vertically-stacked reservoirs there had originated from the same source rock(s) deeper than the deepest reservoired oil; 2) the oils had migrated vertically up fault zones to be emplaced in shallower reservoirs (Price, 1976, 1980a); and 3) that the oils there would thus be genetically related. The oils at Caillou Island (and most likely the other adjacent oil fields) are of one genetically-related oil family (Price, 1989a and 1990), and Requejo and Halpern (1990) report the same conclusions for the South Pass 61 oil field, offshore Louisiana.

The origin of the Neogene (and other) Gulf Coast oils, in spite of a massive published and unpublished research effort, is still an unsolved enigma. Different investigators have different opinions concerning oil origin, migration, and accumulation in the Gulf Coast; however, enough geologic and organic-geochemical data are available, such that reasonable limitations can be assumed concerning the origin of oil at Caillou Island and at other areas of the Gulf Coast. Such is the purpose of this paper.

SHALE ORGANIC GEOCHEMISTRY AT CAILLOU ISLAND

ROCK EVAL and limited R_o analyses, (Fig. 1) were performed on cuttings chips from a deep (6,678 m, 21,918 ft) well in the Caillou Island oil field, the Texaco Inc. State Lease 4666-1, Sec. Bay 23S 20E, Terrebonne Parish, Louisiana. The geothermal gradient, from Moses (1961), for this area of Louisiana is given in figure 2 with circulated temperatures supplied by Texaco Inc. for five deep wells of the area. Some uncertainty exists for the deep burial temperatures at Caillou Island. Moses (1961, Fig. 1), whose data usually are quite dependable, gives a geothermal gradient of 1.25°F/100 ft (22.3°C/km) for this area, based on best estimates of equilibrium burial temperatures. However, the circulated temperature data for this area plot on a line nonparallel to the line generated by the geothermal gradient data given by Moses (1961). Assuming that Moses' (1961) data are correct and that the circulated temperatures are reasonable, a "dog leg" must exist in the geothermal gradient, at depth, at Caillou Island. Such dog legs in geothermal gradients: 1) are common throughout the Texas-Louisiana Gulf Coast; 2) are many times associated with the onset of the abnormal fluid pressure zone (Price, 1976); and 3) have been documented by many different investigators, including Jones (1969), Wallace (1970), Schmidt (1971), and Fertl and Timko (1971).

Times since cessation of circulation were not supplied with the Texaco temperature data for the Caillou Island wells, so applying correction factors to these data to estimate equilibrium burial temperatures is untrustworthy. Two of the wells (Lake Barre State Lease 4070 LL&E "B" A-5 and Caillou Island State Lease 4666-1, side track) had slightly higher temperatures than the other three wells of figure 2. This suggests that the times since circulation was halted, before temperatures were measured, were longer in these two wells, than in the other three wells. Linear regression analysis of the temperature data from all five wells results in the short-dashed line (Fig. 2), which has a correlation coefficient of $r = 0.933$ to the data; and linear regression analysis of the three wells with lower temperature measurements results in the long-dashed line (Fig. 2), which has a correlation coefficient of $r = 0.970$ to the data. The correction factors of Price (1982) were applied only to the lower temperature data (long-dashed line, Fig. 2), which resulted in the dog-leg

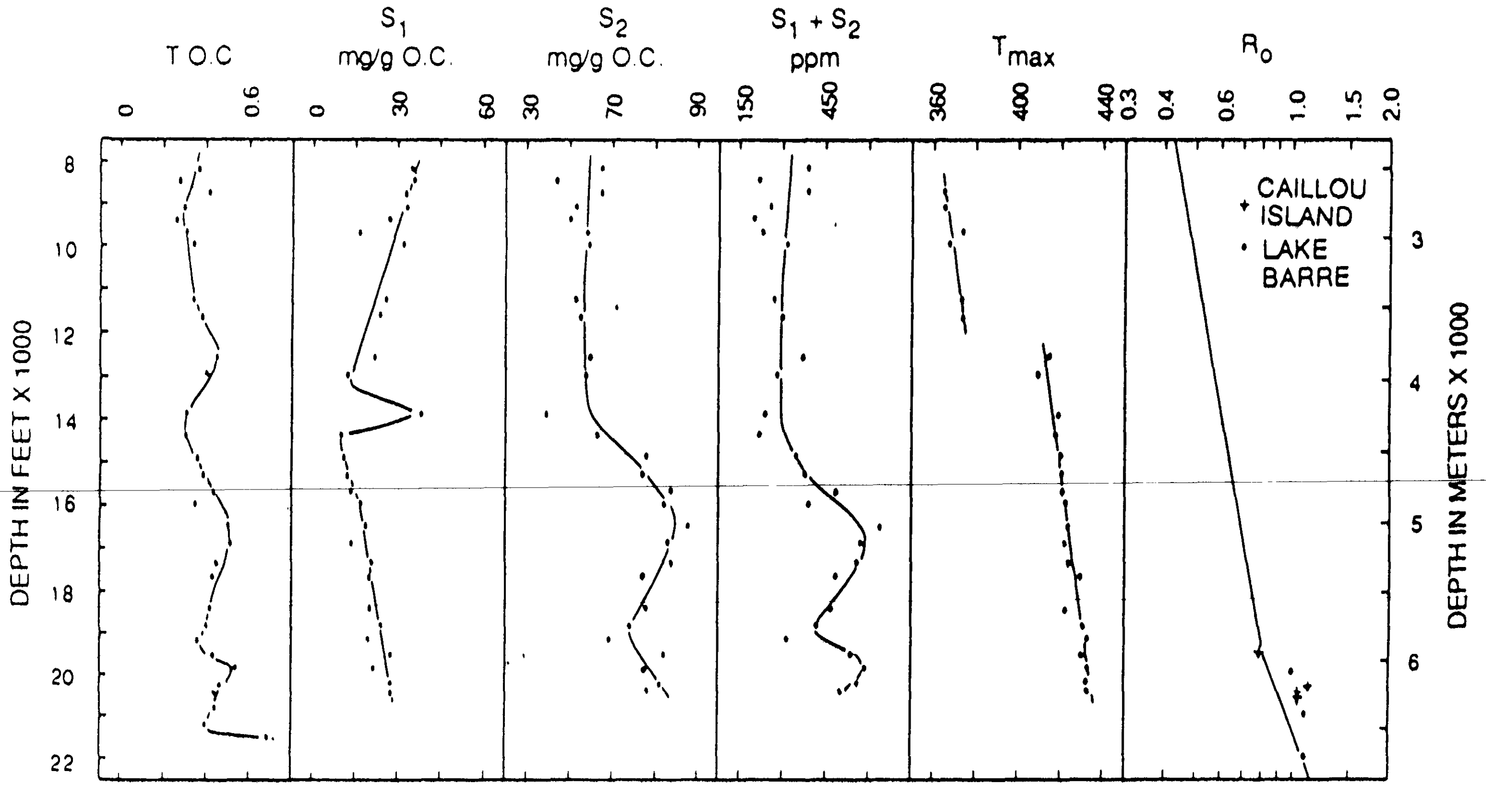

Figure 1. Total organic carbon contents (T.O.C.); the ROCK EVAL S_1 and S_2 (HI) pyrolysis peaks in milligrams per gram of organic carbon (S_1 and S_2 respectively, mg/g O.C.); the sum of the S_1 and S_2 pyrolysis peaks in parts per million by rock weight (S_1+S_2 ppm); and the temperature in °C at the maximum of the S_2 pyrolysis peak (T_{max}) for rock samples from the Texaco Inc. Caillou Island State Lease 4666-1 well bore. Vitrinite reflectance (R_o) data are for rocks from wells in the Caillou Island oil field ("+'s) and from the Lake Barre oil field (dots). Curved and straight lines are explained in text. Data from Table 12, Price (1989a).

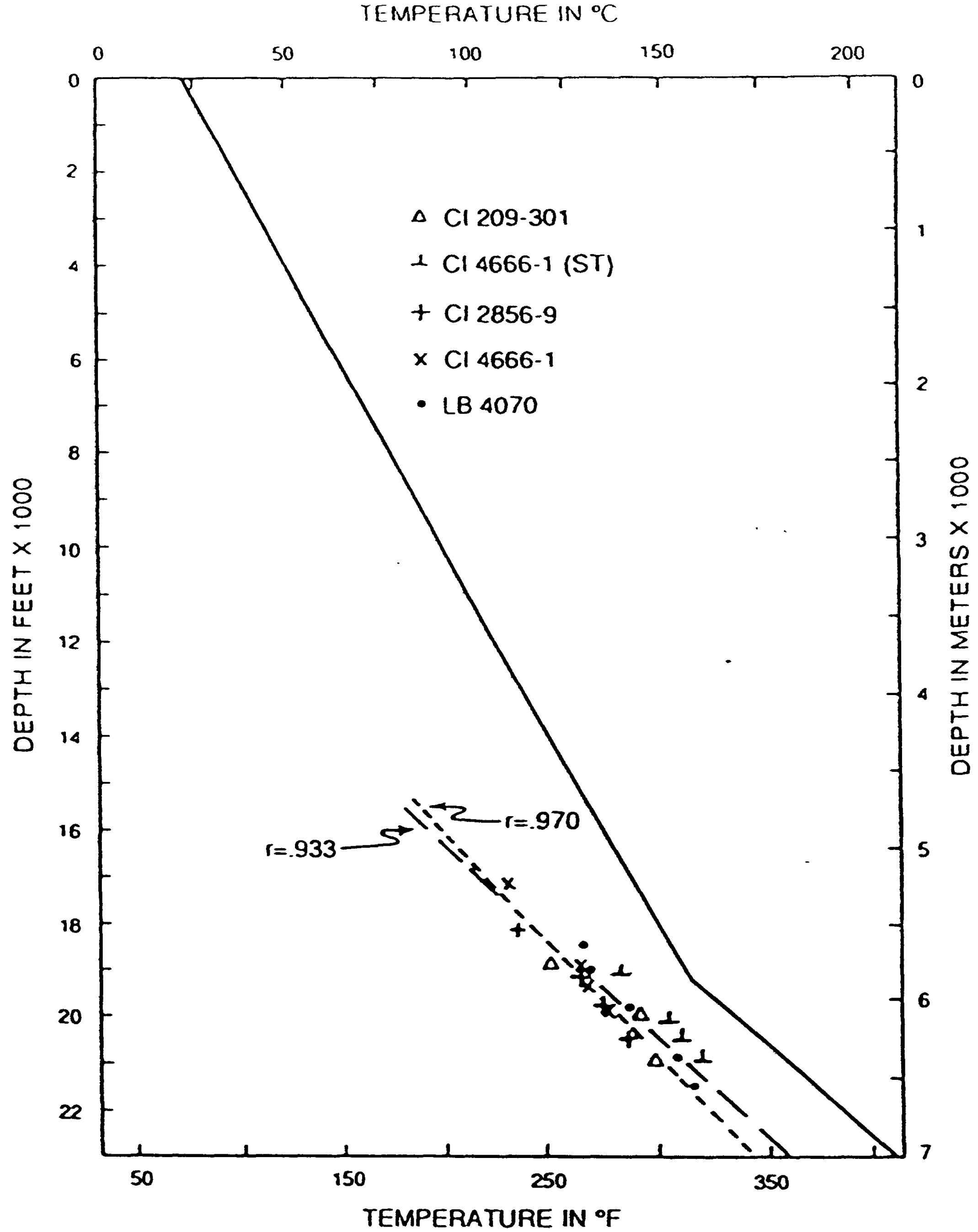

Figure 2. Circulated temperatures and geothermal gradient estimates for the Csillou Island oil field. Dashed and solid lines are explained in text. CI 4666-1 is the Texaco-1 State Lease 4666, Caillou Island field; CI 2856-9 is the Texaco-9 State Lease 2856, Caillou Island field; CI 209-301 is the Texaco-209 State Lease 301, Caillou Island field; CI 4666-1 (ST) is the Texaco-1 State Lease 4666 side track, Caillou Island field; and LB 4070 is the Texaco-5 LL&E (Louisiana Land and Exploration?) "B", Unit "A", State Lease 4070, Lake Barre field. All vells are in Terrebonne Parish, Louisiana. All data supplied by Texaco Inc.

portion of the solid line (Fig. 2). Thus, the dog-legged, solid line is taken as the best estimate of equilibrium burial temperatures at Caillou Island.

Some degree of corroboration of these burial temperatures (Fig. 2) exists in the R_o plot of figure 1. The solid dog-leg line of that plot represents the expected R_o profile based on the estimated temperatures of figure 2, and the equation from figure 19 of Price (1983) for calculating R_o values from equilibrium (or maximum paleo) temperature data. The dots and x's represent actual R_o data determined from rocks of the Caillou Island-Lake Barre areas, and these data agree reasonably with the calculated R_o profile.

In figure 1, total organic carbon (T.O.C.) data are low and, with the exception of the deepest sample, range between 0.26 to 0.55% throughout the well, with a general trend of slightly increasing T.O.C. contents with depth. Superimposed on this overall trend is a pseudo sine-like curve below 3,048 m (10,000 ft) which may be the result of variations in depositional conditions. The ROCK EVAL S_1 pyrolysis peak values exhibit a continuous decrease from the 2,492 m (8,176 ft) sample from around 35 mg/g O.C. to a minimum of 12.5 mg/g O.C. for the 3,955 m (12,976 ft) sample. A spike in the S_1 pyrolysis peak values to 38.7 mg/g O.C. occurs in the 4,2356 m (13,8967 ft) sample. This corresponds to an estimated R_o value of 0.60 (Fig. 1) and a burial temperature of 120°C, precisely the maturation rank and/or burial temperature which many other studies have recorded at the threshold of intense HC generation (TIHG) for Type III organic matter (OM). It is, of course, ill-advised to call for the TIHG on the basis of one data point. On the other hand, it is too coincidental that this high value for the S_1 pyrolysis peak would occur precisely at $R_o = 0.6$ and 120°C. If this data point does indeed represent the TIHG, then further corroboration would exist for the geothermal and R_o gradients of figures 1 and 2. With further increase in depth, the S_1 peak quickly declines to a minimum value of 10.0 mg/g O.C. and then exhibits a continual and gradual increase to values of around 27 mg/g O.C. in the deepest samples.

The ROCK EVAL hydrogen index (HI) ranges between 40-65 from 2,492-4,388 m (8,176-14,393 ft). Deeper, HI's increase significantly with depth to between 70 to 106. Thus on the basis of T.O.C. contents and HI's, the organic richness of the rocks at Caillou Island increase slightly with depth. However, the sum of the S_1 and S_2 pyrolysis peaks, show that this increase in organic richness is insignificant. Between 2,492-4,662 m (8,176-15,296 ft), this sum ranges between 200-390 ppm, with an average of around 300 ppm. From 4,784 m (15,696 ft) to total depth, this sum ranges between 320-640 ppm, with an average of around 500 ppm. Although an increase in the total HC generating capacity of a rock from 300 to 500 ppm (on average) is a significant percentage increase, even at 500 ppm, the rocks still have poor overall HC generation potential.

T_{max} continuously increases with depth; however, from 2,675 to 3,559 m (8,776 to 11,676 ft), T_{max} has unrealistically low values (366-374°C) and several lower values, 307-331°C are not plotted (Table 12, Price, 1989a). By 3,833 m (12,576 ft), T_{max} exhibits a jump (with a distinct break) to values of 410-415°C, and then continuously increases with depth to maximum values of 433°C. The shallower, and unrealistically low, T_{max} values are believed to be caused by the high S_1 values (relative to the S_2 values) of the samples over this depth range. As discussed in Price et al., (1984) and Price (1988), high-molecular-weight bitumen co-elutes with the ROCK EVAL S_2 pyrolysis peak (as noted by Clementz, 1979). This causes a decrease (sometimes significant) in T_{max} values. Almost invariably, if a sample with an unreasonably low T_{max} value is Soxhlet extracted, T_{max} increases, and sometimes radically so, because in the Soxhlet-extracted sample, only HC's cracked from the kerogen in the rock contribute to the calculation of T_{max}. The break (Fig. 1) in the T_{max} curve at about 3,718 m (12,200 ft) is believed due to the steady decrease in the values of the S_1 pyrolysis peak, with depth, over the shallower depth interval. As such, the values of the S_2 pyrolysis peak eventually become large enough to overcome the contribution of the S_1 pyrolysis peak which interferes with the calculation of T_{max}.

The transformation ratios for this well (not shown Fig. 1, see Table 12, Price 1989a) are high (ranging from 0.18 to 0.50 and averaging about 0.33) for samples from 2,492 to 4,235 m (8,176-13,896 ft). From 4,388 m (14,396 ft) to total depth, transformation ratios gradually increase from a minimum of 0.12 in the 4,388 m sample to 0.20-0.24, presumably due to HC generation. High, to unreasonably high, S_3 values (130-442 mg/g O.C.) are present in all rocks of the section, and are no doubt due to contributions of inorganic carbon dioxide from the thermal decomposition of calcite during ROCK EVAL pyrolysis. Katz (1983) has noted that this problem can be pronounced in calcite-bearing, fine-grained, organic-poor rocks, certainly characteristics of the rocks of figure 1.

The principal organic-geochemical characteristic of the rocks of figure 1, regarding the origin of the Caillou Island oils, is that the rocks are ultra-poor source rocks, and clearly would not usually be considered as possible source rocks.

OIL ORIGIN AND MIGRATION AT CAILLOU ISLAND - OPTIONS

As noted by Frey and Grimes (1979), as of 1970 most of the oil in the Caillou Island-Timbalier Bay portion of this complex was found on, and produced from, the north side of the salt ridge which has caused this structural feature (Fig. 3). As is evident from figure 4, the Caillou Island-Bay Marchand complex is heavily compartmentalized by many faults with significant throws. Such faulting presents absolute barriers for oils entering the complex from the south and migration laterally around the complex to the north side, and in fact prevents any lateral migration around the structure at all. It could be argued that the oils migrated into a young structural high which was later compartmentalized by faulting during more mature structural evolution. However, two facts argue against this: First, faulting appears to accompany all phases of structural evolution, including immature phases, in the Gulf Coast. The second fact has to do with genetic relationships among the Caillou Island oils themselves. By the methods Price (1989a, 1990) used, these oils belonged to the same genetic family. However, at the same time, the oils demonstrated enough variance such that by the method of Kaufman, et al. (1990), the oils would have to be in hydraulically-separate reservoirs. As such, the oils would have to have been emplaced in the different reservoirs by discrete and separate migrational events. On the other hand, if the oils had been in a young structural high that was later compartmentalized, then they would show genetic agreement for "reservoir matching oils" by the method Kaufman, et al. (1990). This line of reasoning also applies to many other Gulf Coast oil fields.

These considerations thus argue against an updip, lateral migration of oil from undefined source rocks to the south and downdip from this structural complex, and at the same time argue for a local origin and migration for these oils. However, the options for a local origin and migration for these oils are limited:

1) The oils originated from the interbedded shales.

2) The oils originated from a limited volume of fine-grained rocks of the southern limb of the syncline in the interdomal salt basin, to the north of the Caillou Island-Bay Marchand salt ridge. Further, due to unusual depositional conditions, these hypothesized source rocks were much more organic rich than their more southern stratigraphic equivalents analyzed in this study. This is analogous to the model represented by Dow (1984).

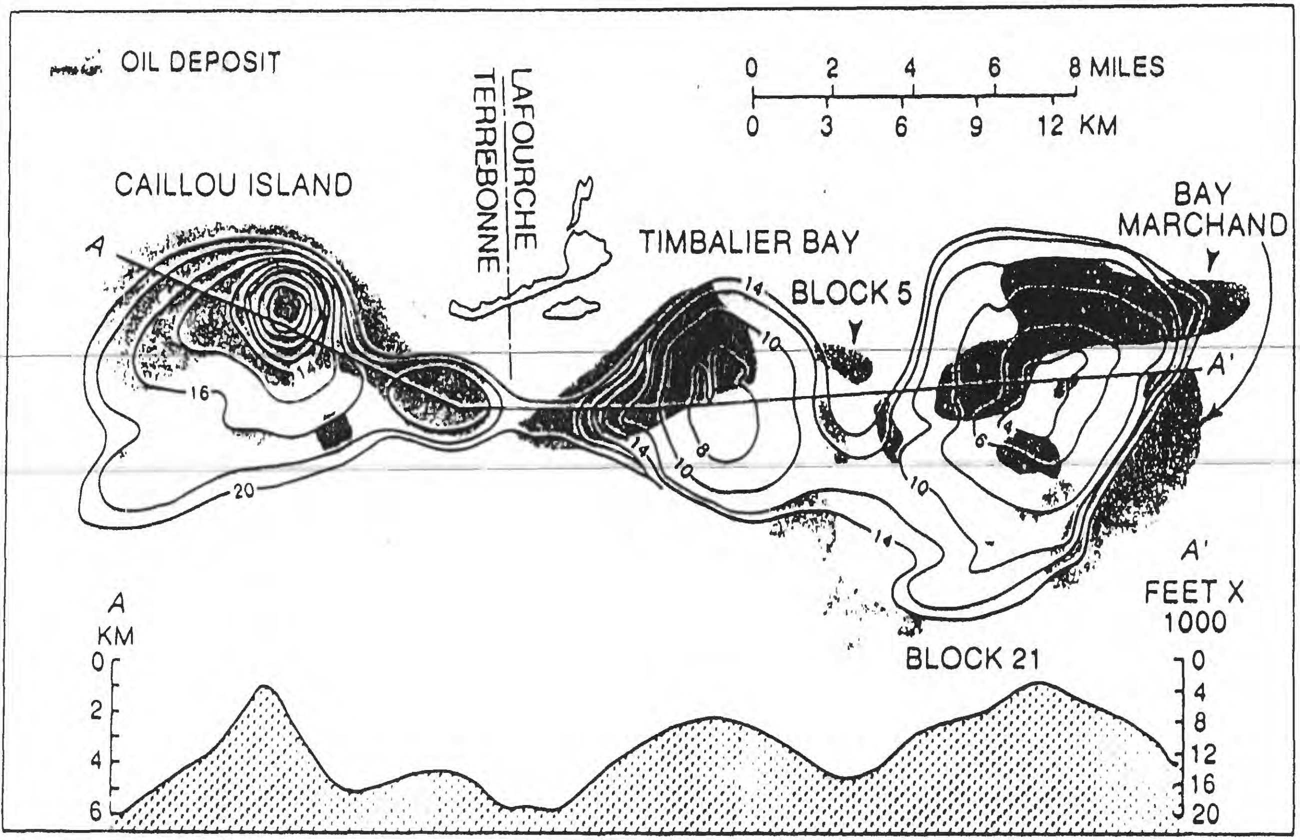

Figure 3. Structure map on top of and cross section through the Caillou Island-Bay Marchand salt ridge, Terrebonne and Lafourche Parishes, Louisiana, with oil deposits. Contours on top of salt with 2,000 ft (610 m) intervals. After Frey and Grimes (1970).

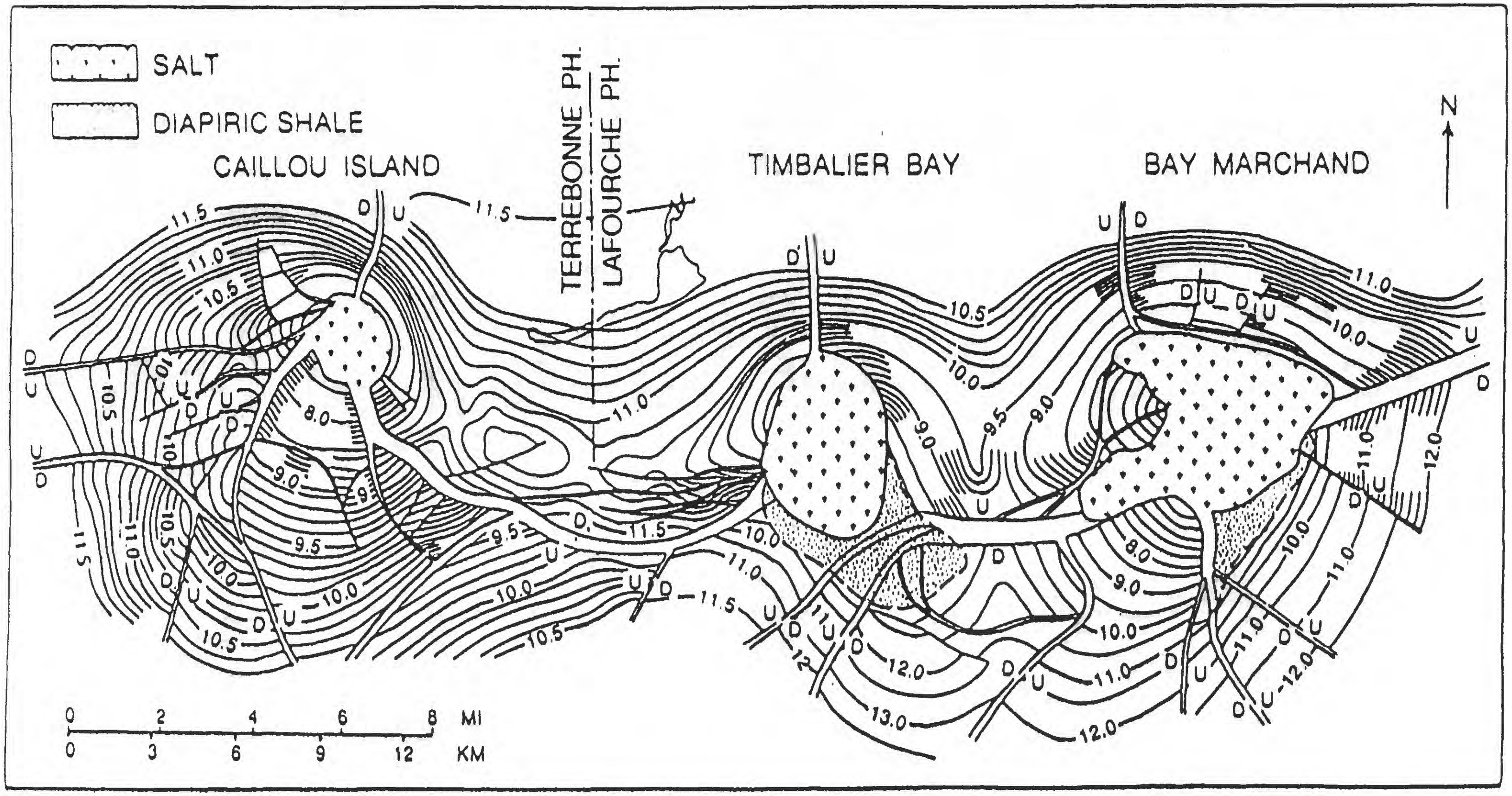

Figure 4. Structure map on top of upper Miocene sandstone for the Caillou Island-Bay Marchand salt ridge. Downside of faults are shown by the letter D or hatch marks on the downside. Contour interval is 500 ft for heavier lines and 100 ft for lighter lines. Numbers are depth in ft times 1000. After Frey and Grimes (1970).

3) The oils originated and vertically migrated from deeper, older, organic-rich, fine-grained rocks.

Oil Origin from the Interbedded Shales

Four major problems exist with this hypothesis: 1) source-rock quality, 2) source-rock volume, 3) maturation rank, and 4) primary migration.

Source Rock Quality--The data of figure 1 eloquently speak to the ultra-poor source-rock quality of the shales at Caillou Island. However, this is expected, as it is well known that post Eocene Gulf Coast shales are some of the worst and most organic-poor "source rocks" in the world.

Source Rock Volume--As discussed, the orientation of much of the oil on the northern flank of this salt-ridge complex precludes the possibility of an updip migration from a large volume of undefined source rocks to the south, downdip of the structure. This constraint leaves a relatively small volume of ultra-poor source quality shales on the southern limb of the syncline to the north of the salt complex to serve as source rocks.

Maturation Rank--The TIHG by conventional wisdom is held to occur at R_o = 0.60±.05, a rank also equated to the first possibility of source rocks yielding commercial oil deposits. This rank occurs at 4,206 m (13,800 ft) at Caillou Island (Fig. 1), and thus oil in reservoirs there, shallower than 4,206 m (13,000 ft), would have had to migrate vertically up faults, or laterally updip in carrier beds from deeper, more mature source rocks, as this oil could not have been generated by the immature shales surrounding the reservoirs. Further, Price (1989b) has hypothesized that a rank of R_o = 0.60 may be too optimistic for the accumulation of commercial oil deposits from Type III OM. Although the TIHG is clearly reached by R_o = 0.6, most of the newly-generated HC's remain at the generation site which accounts for the build-up in the HC or bitumen coefficients, or the S_1 pyrolysis peak values, from R_o = 0.60 to 0.80 (Fig. 5). This allows us to recognize the TIHG in the first place. It is only when the newly generated HC's leave the generation site, due to primary migration, that the possibility for the creation of an oil deposit arises. By the data of figure 5, this occurs at R_o = 0.8-0.9, as is evidenced by the sharp decrease in HC concentration from maximal values at this maturation rank, which is the usual case for Type III OM (Price, 1989b). Also, intense HC generation and migration from Type III OM must be accompanied by detectable decreases in the HI's of the rocks. This occurs only at maturation ranks of $R_o \geq 0.8$ (Fig. 5). Thus, a maturation rank of R_o = 0.8, rather than R_o = 0.6, may be a more realistic appraisal of the first possibility of rocks with Type III OM yielding commercial oil deposits. This rank occurs at 5,867 m (19,250 ft) in the rocks at Caillou Island (Fig. 1), which would necessitate an even greater degree of vertical oil migration. This hypothesis receives support from data on Bissada et al. (1990) who demonstrated that the n-paraffin distribution in the oil from the "70-Sand" in the Caillou Island field (reservoir depth 4,725 m; 15,500 ft; R_o estimated at 0.66, Fig. 1) was different from, and more mature than, that of the bitumen extracted from the interbedded shales.

Primary Migration--The principal problem with an origin of the Caillou Island oils from the interbedded shales is that there is no proposed realistic primary migration mechanism which can gather the widely dispersed HC's from the organic-poor, fine-grained rocks into commercial oil accumulations. Jones (1980) gave insightful comments on possible origins of oil in the Gulf Coast Tertiary. As he (and others) have noted, a bulk (separate-phase) primary-migration mechanism from Gulf Coast organic-poor shales is most improbable, as the porosities of these rocks are too high, and the organic richness too low, to allow the formation and movement of an oil phase.

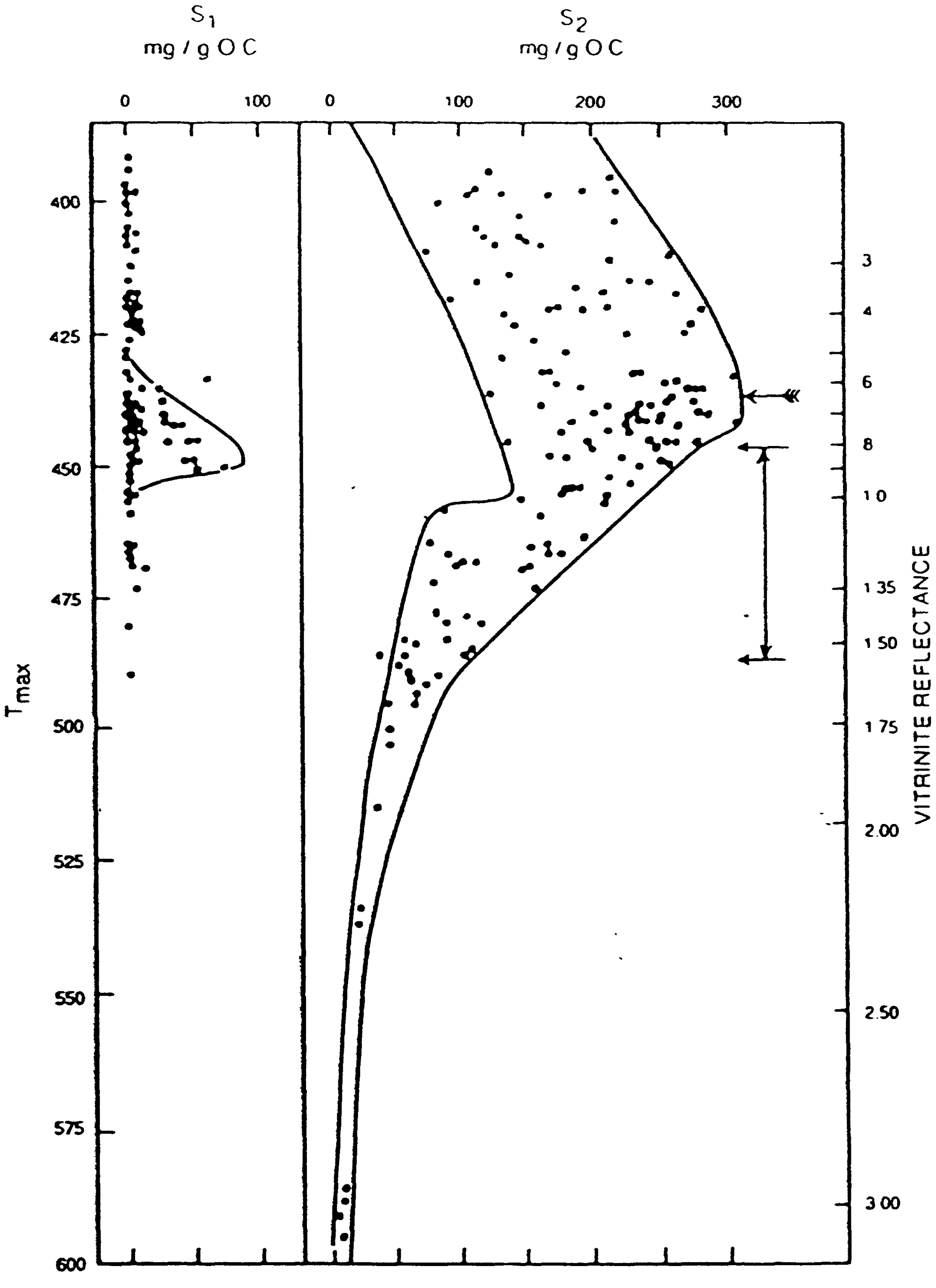

Figure 5. Plot of T_{max} and R_o versus the S_1 and S_2 pyrolysis peaks (normalized to organic carbon-mg/g O.C.) for world wide Paleozoic to Tertiary coals. The feathered arrow indicates the maximum in the HI data. The vertical arrow indicates the maximum loss in HI's. Data from Teichmüller and Durand (1983). The original vitrinite reflectance data of those authors was given in R_m values; R_m was converted to R_o by $R_m = 1.066 (R_o)$.

Migration along continuous kerogen networks is also highly unlikely because of the improbability of the existence of such networks in these organic-poor rocks.

A substantial body of laboratory data negates the possibility of primary migration by aqueous solution from Gulf Coast Tertiary shales. Price (1981a and 1981b) has shown that burial temperatures of 275°C (R_o = 1.95; Price, 1983) are required for primary migration by aqueous solution based on compositional and quantitative considerations. However, Type III OM loses all HC generation capacity by R_o = 2.00 (Fig. 5). Thus, with the Gulf Coast shales, by the burial depths when primary migration by aqueous solution would first become effective, no HC's would remain in the rocks to migrate.

Primary migration by gaseous solution from the Gulf Coast Tertiary shales has been favored by some investigators including Jones (1980, 1990). This migration mechanism has been discussed by Price (1989b and 1989c) and Price et al. (1983) in detail. As discussed below, migration by gaseous solution requires the presence of a dispersed, free-gas phase at critical gas saturation levels (probably 1-5% of the rock porosity) in the shales and sandstones from and through which the free-gas phase moves. Such a free-gas phase has substantial carrying capacities for C_5+ (including C_{15}+) HC's at elevated temperatures and pressures (Price et al. 1983). However, mass-balance considerations strongly suggest that organic-poor shales, such as Gulf Coast Tertiary shales, do not have the capability to saturate the dispersed free-gas phase with C_5+ HC's (as well as form the usual distribution of shows, stains, and small uneconomic HC deposits), and form economic oil deposits (Price, 1989c). Thus, the amount of C_5+ HC's which would be tied up in the dispersed, free-gas phase in the sands and shales through which gaseous solution is taking place is substantial and can account for most or all of the HC's generated by organic-poor shales, depending on the assumptions made. This fact has not been considered by proponents of a gas-phase primary migration mechanism for organic-poor Gulf Coast shales.

Lateral Stratigraphic Organic Variation

Another hypothesis for the origin of the Caillou Island oils is a lateral stratigraphic change of the Tertiary shales to more organic-rich rocks downdip in the interdomal salt basin to the north of the salt ridge at Caillou Island, caused by anaerobic conditions during shale deposition in the interdomal salt basin. Dow (1984) has championed variants of this hypothesis, which have been critized on the basis that such a short-range, lateral stratigraphic change to organic-rich shales has never been reported anywhere in the Tertiary Gulf Coast, despite the huge number of wells drilled there (Bissada et al., 1990; and Jones, 1990). If this proposed scenario had ever been observed in the deeper Gulf Coast rocks, it would have been reported by oral or written communication. The hypothesis of lateral organic facies variation can be dismissed because of the well-documented, uniform, organic-poor nature of the Pleistocene through Oligocene rocks throughout the entire Gulf Coast.

Deeper Origin and Vertical Migration

The last proposed scenario is an origin and vertical migration of oil from deeper, older, organic-rich, fine-grained rocks at Caillou Island. By conventional wisdom in petroleum geochemistry, this hypothesis can be dismissed because of the hypothesized thermal destruction of C_{15}+ HC's by R_o = 1.35. By extrapolation of data in figure 1, R_o = 1.35 may be expected at 7,351 m (24,120 ft) at Caillou Island. Further, the rocks at this depth would still be organic-poor Miocene-Oligiocene shales. However, a substantial body of evidence suggests that conventional wisdom may be in error on the topic of the thermal destruction of C_{15}+ HC's by R_o = 1.35. Therefore, the preferred explanation here for the origin of the Caillou Island (and other Gulf Coast) oils is an origin and vertical migration of the oils from one of three possible sources either alone or in combination: 1) Mesozoic (or older), fine-grained rocks of marine depositional origin, with high T.O.C. contents and hydrogen-rich (Types I, II, and/or II-S) OM ("black shale" source rocks; 2) Eocene-Paleocene coals; or 3) Eocene to Upper Cretaceous (or older) shales with moderately elevated (compared to Pleistocene through Oligiocene shales) T.O.C. contents and HI's. Five points of discussion relate to this preferred explanation: 1) the hypothesis of a destruction of C_{15}+ HC's by R_o = 1.35; 2) a tendency for fine-grained Gulf Coast Tertiary and Upper Cretaceous rocks to increase in inorganic richness with depth and age, apparently at any given locality in the Gulf Coast; 3) the possible existence of ultra organic-rich source rocks of Lower Cretaceous-Jurassic age in the Gulf Coast; 4) previously-unrecognized, stark kinetic differences in oil generating capacity for the different OM types; and 5) the probability that hydrogen-rich coals are oil source rocks.

R_o = 1.35 - The Oil Window--The hypothesis of the thermal destruction of C_{15}+ HC's by R_o = 1.35 is supported by three principal lines of evidence:

1) The decrease in the concentration of C_{15}+ HC's over R_o = 0.9 to 1.35 in most sequences of fine-grained rocks with Type III OM.

2) The sparsity of oil deposits in rocks at maturation ranks of R_o >1.35.

3) The occurrence of pyrobitumens coating some reservoir rocks in high-rank gas deposits, with the inference that these pyrobitumens originated from a thermal conversion of previously indigenous oil to gas.

As to the first line of evidence, Price (1989b and 1989c) has discussed, in detail, the concentration decrease of C_{15}+ HC's over R_o = 0.9-1.35 in rocks with Type III OM (Fig. 5). Four separate bodies of data (Price, 1989b) suggest that this disappearance of C_{15}+ HC's in such rocks is better explained by very efficient primary petroleum migration by gas solution, rather than by thermal destruction: First, by figure 5, the S_1 pyrolysis peak, which is roughly equivalent to C_{15}+ solvent extractable HC's, decreases to, and remains at, low values by R_o >0.9. However, at the same time, the coals retain high HI values. Further, Teichmüller and Durand (1983) demonstrated that a substantial part of this high-rank HC generation capacity was for C_{15}+ HC's (Fig. 6). Therefore, the loss of solvent extractable HC's (the S_1 pyrolysis peak) by R_o = 0.9 cannot be due to C_{15}+ HC thermal destruction, but must be due to another cause. This is because the bonds which are broken in C_{15}+ HC thermal destruction clearly must be stronger than, and have higher activation energies than, the bonds originally broken during intense C_{15}+ HC generation. Teichmüller and Durand (1983) concluded, and I agree, that the cause of this loss of C_{15}+ HC's over R_o = .9-1.35 must be primary petroleum migration. Further, the fact that Type III OM does not lose its C_{15}+ HC generation potential until R_o = 1.8-2.0 (Figs. 5 and 7) does not support the concept of C_{15}+ HC thermal destruction by R_o = 1.35.

The second line of evidence contradicting C_{15}+ HC thermal destruction by R_o = 1.35 lies in rocks which have Type III OM, are ranks at R_o >1.35, and which still retain moderate to significant concentrations of C_{15}+ HC's or high values for the S_1 pyrolysis peak. Many examples exist of rocks with Type III OM where C_{15}+ HC's, or S_1 pyrolysis peak values, are low by R_o = 0.9 and remain low to R_o >1.35. However, other examples exist where such rocks retain high values of both the S_1 pyrolysis peak and C_{15}+ HC concentrations up to R_o = 2.0 or even greater. Law (1984) reported on such a case from the Green River basin and Price (1988) reported on another from the West Texas Permian basin. Such elevated concentrations of C_{15}+ HC's in these rocks at high maturation ranks are believed due to relatively inefficient primary migration, or impedance of primary migration, compared to those cases where all C_{15}+ HC's have been stripped from the rocks at comparable maturation ranks (Price, 1988). Moderate

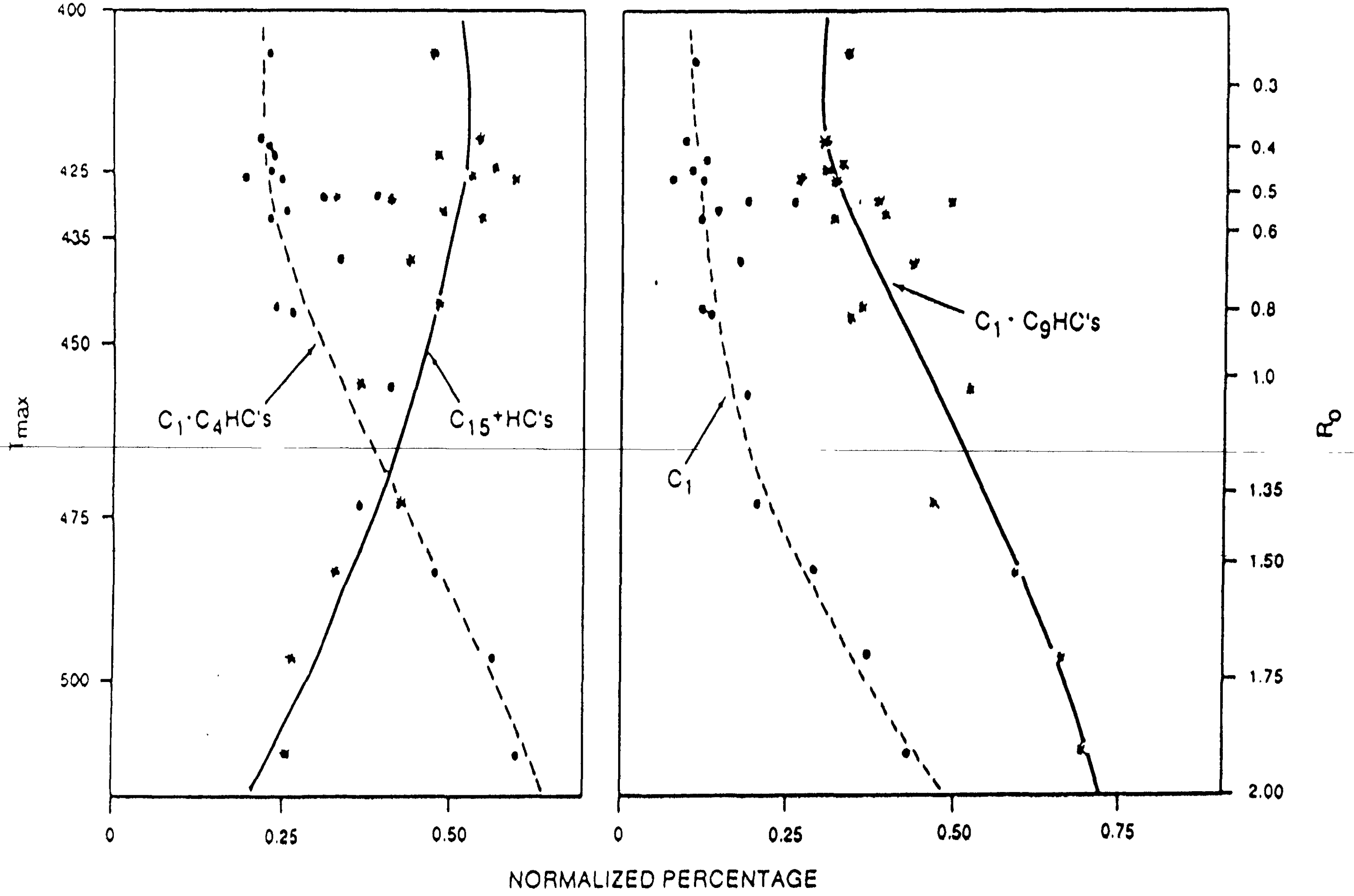

Figure 6. Composition of products from thermal vaporization of coals (ROCK EVAL pyrolysis, product trapping, and gas chromatography). R_o values derived from T_{max} values by use of Table 1 in Price (1989b). Data from Teichmüller and Durand (1983). The original vitrinite reflectance data of those authors was given in R_m values; R_m was converted to R_o by $R_m = 1.066\ (R_o)$.

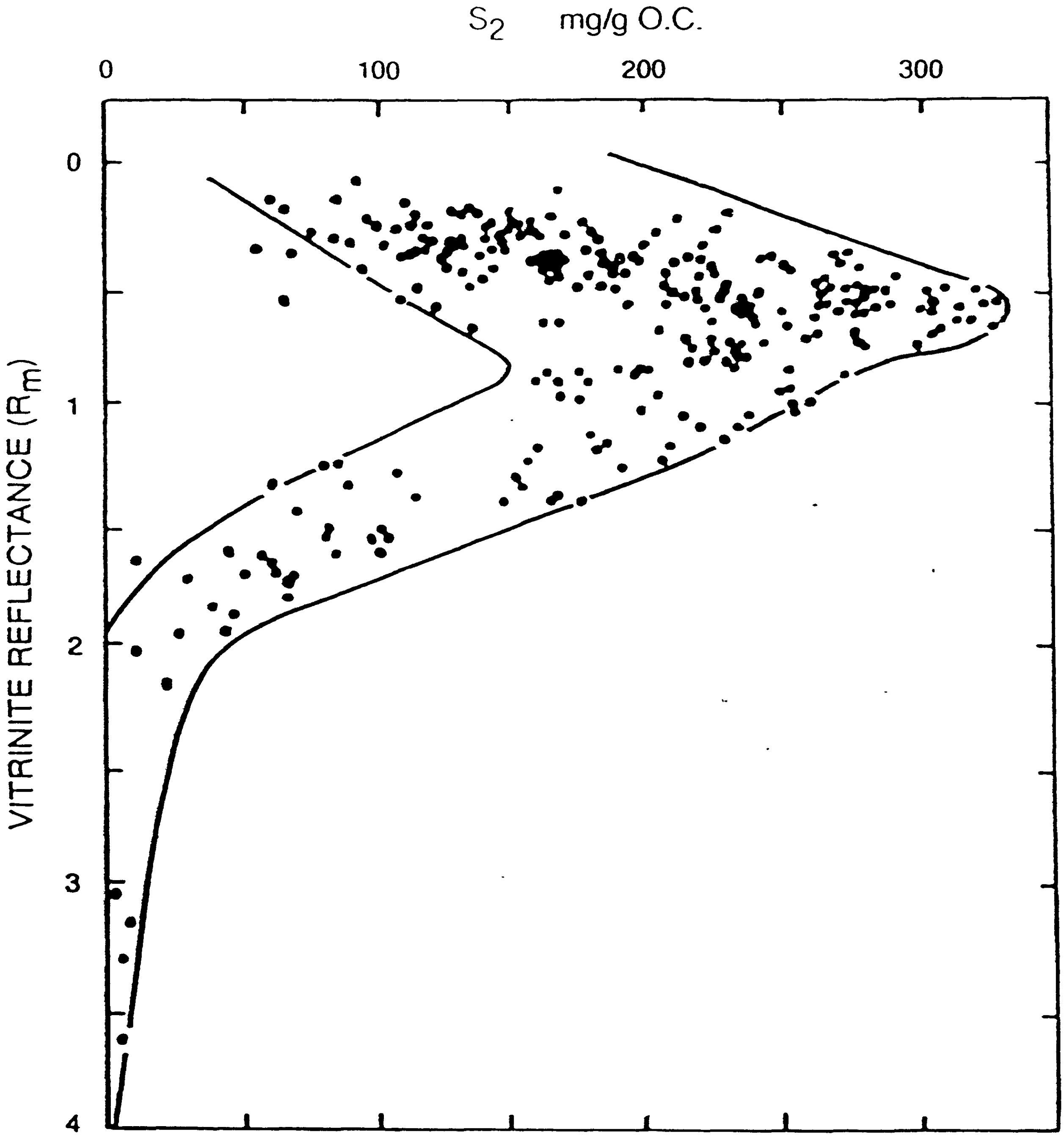

Figure 7. Plot of mean vitrinite reflectance (R_m) versus the ROCK EVAL HI in milligrams per gram of organic carbon (S_2 mg/g O.C.) for coals of worldwide distribution and all geologic ages. After Bertrand (1984).

concentrations of C_{15}+ HC's can persist in some rocks with Type III OM even past R_o = 2.0, apparently because of the loss of all HC generation potential in these rocks by R_o = 1.8-2.0. With no further capacity for gas generation, primary migration by gas solution is not possible, and any C_{15}+ HC's in the rock at this point would remain until they were finally thermally destroyed or removed by another primary migration mechanism.

A third line of evidence against C_{15}+ HC thermal destruction by R_o = 1.35 is moderate to high concentrations of C_{15}+ HC's, or high S_1 pyrolysis peak values, coupled with high to moderate HI's, to R_o values as high as 4.0-5.0 in marine-based rocks with hydrogen-rich OM. Numerous examples of this phenomenon exist (Price et al., 1979, 1981; Sajgó, 1980; Price, 1982, 1983 (Table 1), and 1988; and Price and Clayton, 1990) and Figure 8, this paper. The data from all these deep well bores also suggest that the loss of HC generation potential by R_o = 1.8-2.0 in Type III OM could not be due to the thermal destruction of C_{15}+ HC's, but instead must be due to another cause. This cause is hypothesized as the total expenditure of the relatively weak bonds (and thus all HC generation potential) in Type III OM (compared to the bonds in Type I and II OM) by R_o = 1.8-2.0.

The fourth, and last, line of evidence which contradicts the hypothesis of a thermal destruction of C_{15}+ HC's over R_o = 0.9-1.35 is that if carbon-carbon bond breakage were responsible for this decrease in C_{15}+ HC's, then this decrease should be accompanied by an increase in C_{14}-, and especially C_1-C_7 HC's. However, in all cases where this hypothesis has been examined (Durand and Oudin, 1979; Huc and Hunt, 1980; and Vandenbroucke et al., 1983), the concentrations of these lighter HC's also decrease over this maturation-rank range, presumably due to primary migration by gaseous solution (Price, 1989c).

The second fact which supports the hypothesis of a thermal destruction of C_{15}+ HC's by R_o = 1.35, is the sparsity of oil deposits in rocks at R_o >1.35. Most of the world's oil discovered to date clearly lies in a restricted range of burial temperatures and maturation ranks, for two reasons: First, this is where we have specifically looked for the oil. The second reason involves basinal fluid dynamics and oil emplacement. It is now generally recognized that much of the world's oil is reservoired in sediments too immature to have sourced that oil. Thus, some degree of vertical movement of oil up fault zones (Phillipi, 1965; Price, 1976, 1980a) is necessary. At the time of such vertical migration, abnormal fluid pressures control oil emplacement in reservoirs. Potential reservoirs, which are abnormally pressured, are closed or semi-closed fluid systems, and cannot receive fluids migrating from the deeper basin vertically up faults. At the time of oil generation, migration, and emplacement, both basinal structural activity and geothermal gradients would be expected to be maximal, and the entire deep basin would also probably be abnormally pressured. Thus, all vertically-migrating fluids would bypass the deep basin and be emplaced in the shallow basin in hydrostatic reservoirs which are able to receive these deep-basinal fluids. Therefore, even by a model of a deeper origin and vertical migration of oil, one would expect that most of the oil generated in a basin would be found at shallower depths, due to compaction, expulsion, and emplacement processes. However, in some basins, including parts of the Gulf Coast, significant deposits of ultra-deep, high-rank (R_o $\geq$1.0-1.35) oil may still be expected. Oil deposits emplaced in the shallower hydrostatic pressure zone could be later buried to much greater depths and be abnormally pressured (Price, 1980a, P. 19-20). Ultra-deep, high-rank oil may also be expected in other basins, including the Los Angeles, Ventura, and Southern San Joaquin Valley basins. In the offshore Yucatan, Mexico, the Eastern Venezuelan basin, and at Tengiz, Caspian Seg, major oil deposits have been found at burial

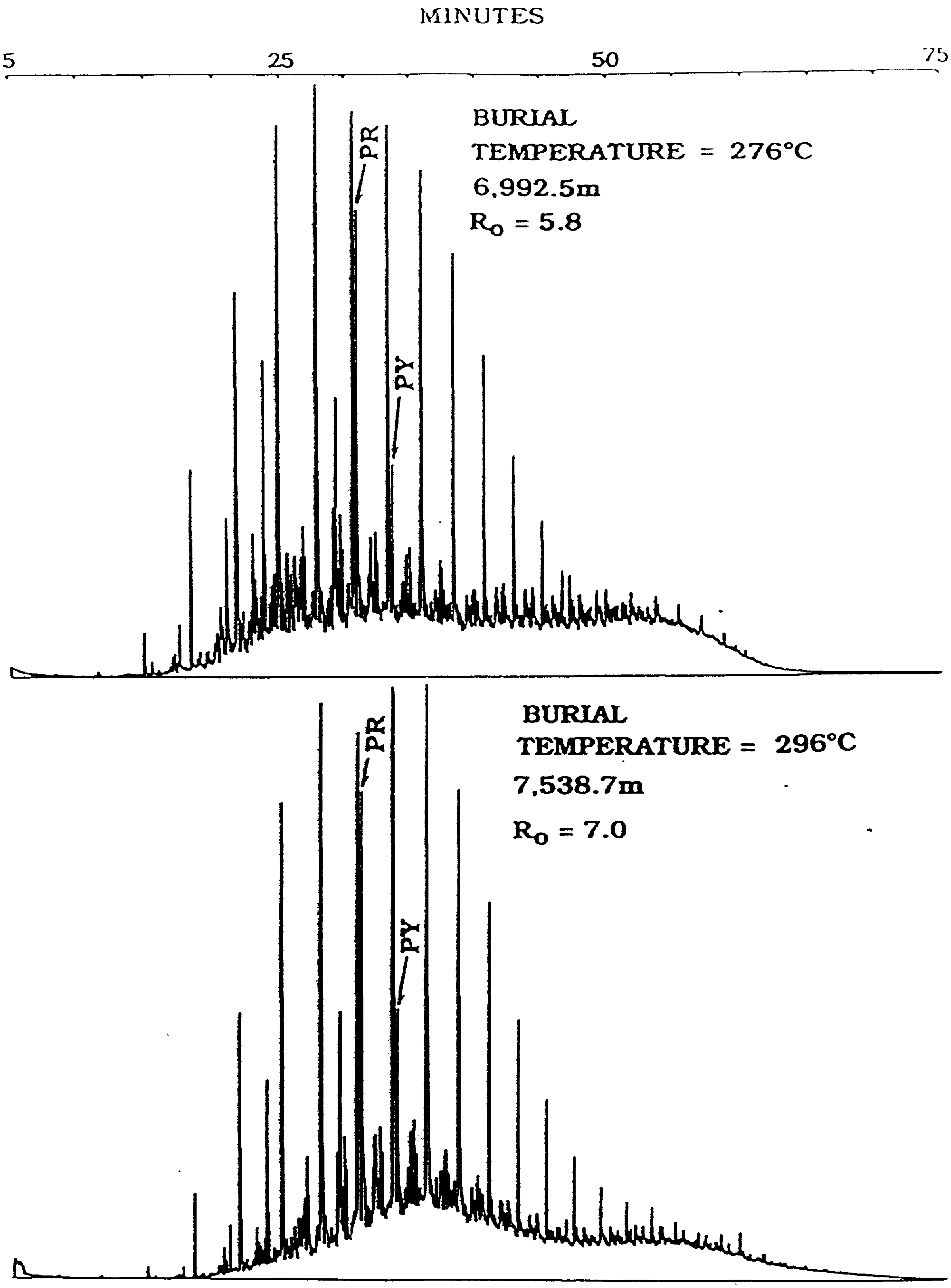

Figure 8. Gas chromatograms of C_{15}+ saturated HC's from two deep core samples (6,992.4-6,992.7 and 7,538.6-7,.538.9 m; 22,942-22,943 and 24,734-24,735 ft) from the R. G. Jacobs-1 wellbore, South Texas.

temperatures beyond the accepted upper thermal stability limit for such deposits.

On the other hand, deep, high-rank oil may not be expected in all basins. The deepest, highest-rank rocks in some petroleum basins have had all their kerogen and C_5+ HC's thermally cracked to methane at ultra-high maturation ranks. The data of Price and Clayton (1990) would suggest this occurs at ranks of $R_o \geq 7.0$. Such methane, generated in the deepest part of these basins, also moves upward and outward from the generation sites displacing any oil in deep-basinal traps, upward and outward to shallower traps, by Gussow's (1954) principle of differential entrapment (Price, 1980b, P. 92-99). When such gas generated in the deep basin moves into a trap containing oil, a substantial precipitation of asphaltenes onto the reservoir rock (deasphaltening) would occur. By this scenario, gas found in deep-basin traps would not have had a local origin. It would have been generated and migrated from still deeper (and higher-rank) rocks than those in which it is now reservoired. Thus, in some basins where thick sequences of rocks exist at ultra-high maturation ranks and at ultra-great depths, moderately deep basinal traps would be expected to contain only dry gas deposits. Examples of such basins are the Anadarko-Ardmore-Arkoma, West Texas Permian, and Wind River basins and parts of the Gulf Coast.

The third convincing piece of evidence for thermal destruction of oil by R_o = 1.35 is pyrobitumen (asphaltenes) found in a dry-gas-bearing reservoirs of different petroleum basins. Such pyrobitumen has been attributed by different investigators (including Rogers, et al., 1974; Barker, 1977; and Sassen, 1990) to be due to an in-reservoir conversion of oil to dry gas and pyrobitumen. However, as discussed above, another equally valid explanation is the movement of dry gas, generated very deep in the basin, into deep-basinal, oil-bearing traps. Here asphaltenes are precipitated onto reservoir rock, and oil is displaced out of the trap with upward and outward basinal migration, to the stable shelves of basins where the oil is now found. Once asphaltenes from crude oil are precipitated onto reservoir rock, enhanced maturation reactions could begin which would result in an asphaltene with a much high carbon content (and maturation rank) than it had when first precipitated from the oil. Hydrous-pyrolysis data of L. C. Price and L. M. Wenger show that organic maturation-thermal destruction reactions are promoted in the absence of water. Besides oil, any water originally in a deep reservoir would be displaced by dry gas streaming through the reservoir from deeper in the basin. Further, natural gas at elevated pressures and temperatures has a substantial carrying capacity for water (Price, et al., 1983, Fig. 5). A continued flow of dry gas from deeper in the basin through a previously oil-bearing reservoir would take even capillary water on the reservoir rock into solution. Any irreversibly absorbed water remaining on the reservoir rock would not be able to enter into organic-maturation reactions, and thus at the high maturation ranks of the reaction, most or all pyrolyzable organics would be lost from the precipitated asphaltenes, leaving an ultra-mature pyrobitumen.

Many examples exist from nature which appear to support the hypothesis that C_{15}+ HC's are destroyed by R_o = 1.35. However, the key observations in all these examples which support this hypothesis also have other explanations. For example, Sassen (1990) carried out a study of oil generation and thermal destruction in the Jurassic salt basins of the southeast U.S., a study in which he estimated crude oil thermal conversion to dry gas at R_o = 1.35. His maturation-rank estimates were derived by conversion of ROCK EVAL T_{max} values from the marine-based, carbonate-evaporite rocks of his study area to R_o values by the use of the R_o-T_{max} cross plot given by Tissot (1984). However, Tissot

(1984) qualified the use of his R_o-T_{max} cross plot only to coals or rocks with Type III OM. The rocks of the Sassen (1990) study are age-equivalent to the south Texas rocks studied by Price and Clayton (1990) who found a profound suppression of all maturation indices, including T_{max}, in the deep, high-rank, carbonate-evaporite rocks of the Foerster-1 wellbore. For example, by use of the Tissot (1984) plot, over 3,383-5,000 m in the Foerster well (suppressed) T_{max} values of 429°-438°C would lead to R_o estimates of 0.52-0.72, which would strongly contrast with the true determined R_o values of 1.2 at 3,300 m and 3.1 at 5,000 m. No doubt the scheme which Sassen (1990) has worked out for oil generation and thermal destruction in the Jurassic of the southeast U.S. is largely correct. However, the maturation ranks which he assigned to these events are far too low, due to the suppression of all maturation indices in marine-based, hydrogen-rich OM matter (discussed below).

The hypothesis of a thermal destruction of C_{15}+ HC's at R_o = 1.35 is accepted as an organic geochemical law by many investigators in the field. However, alternate explanations exist for the evidence which supports this hypothesis, and concurrently there is a large body of published data which contradicts this hypothesis. In my opinion, this hypothesis is in error, and other investigators have reached the same conclusion. Unquestioned acceptance of this paradigm may be one of the strongest reasons why we have not solved the Gulf Coast "source rock problem."

Increase of Organic Richness with Depth--A second point of discussion concerning a deeper origin and migration of oil at Caillou Island is an increase in organic richness with depth for the fine-grained (Tertiary-upper Cretaceous) rocks in the Gulf Coast, albeit sometimes only slightly. This trend is evident in figure 1, where T.O.C. increases from around 0.3% over 2,438-3,353 m (8,000-11,000 ft) to 0.4-0.5% at depth, and HI's increase from around 60 at shallow depths to around 90 at depth. Figure 9 gives T.O.C., ROCK EVAL, and R_o data for the Marathon Oil Co. J. Burton LeBlanc et al-1. Miocene shales have low T.O.C. contents (0.25-0.75%) which begin increasing with depth at 2,743 m (9,000 ft) to between 1.00 to 1.75% in the shales of the middle Oligiocene Frio and Eocene Wilcox Formations. ROCK EVAL HI's determined from Soxhlet-extracted shales, also increase from around 40 in the Miocene shales to around 100 in the older shales. Two shales of the Upper Cretaceous Austin Chalk Formation have T.O.C. contents of 1.75 and 2.15% and HI's of 166 and 246 mg/g O.C. These moderately high values of organic richness, for the Louisiana Gulf Coast, are probably due to an increase in marine over terrestrial OM in the carbonate-rich, Upper Cretaceous Austin Chalk. With further increase in depth to well bottom at a maturation-rank of R_o = 2.2, T.O.C. values range between 0.75-1.25% in the Upper Cretaceous shales, and HI's vary between 40-110. As discussed, Type III OM loses its HC generation capacity by R_o = 1.8-2.0 (Figs. 5 and 7; and Price, 1989b). This expected trend is shown by the dashed line in the HI plot of figure 9. That the HI's in the deepest samples at a rank of R_o >2.0 range up to 110 allows the conclusion to be drawn that the reactive OM in these deeper rocks appears to have shifted to a more hydrogen-rich OM than the Type III OM found in the shallower rocks. However, the relatively low HI's in the deepest rocks also suggest that the reactive OM in those rocks is most likely heavily diluted by inertinite. As such, the bulk characteristics of these rocks are still those of Type III OM. The dog leg in the R_o plot of figure 9 strongly correlates with dog legs in the geothermal gradient (Fig. 10) and pressure gradient (Fig. 11) for this area.

An increase in organic richness with depth for Gulf Coast Tertiary-Cretaceous rocks is also demonstrated by organic geochemical data of the Chevron R. G. Jacobs-1 (Fig. 12), drilled to 7,547 m (24,761 ft) in Goliad County,

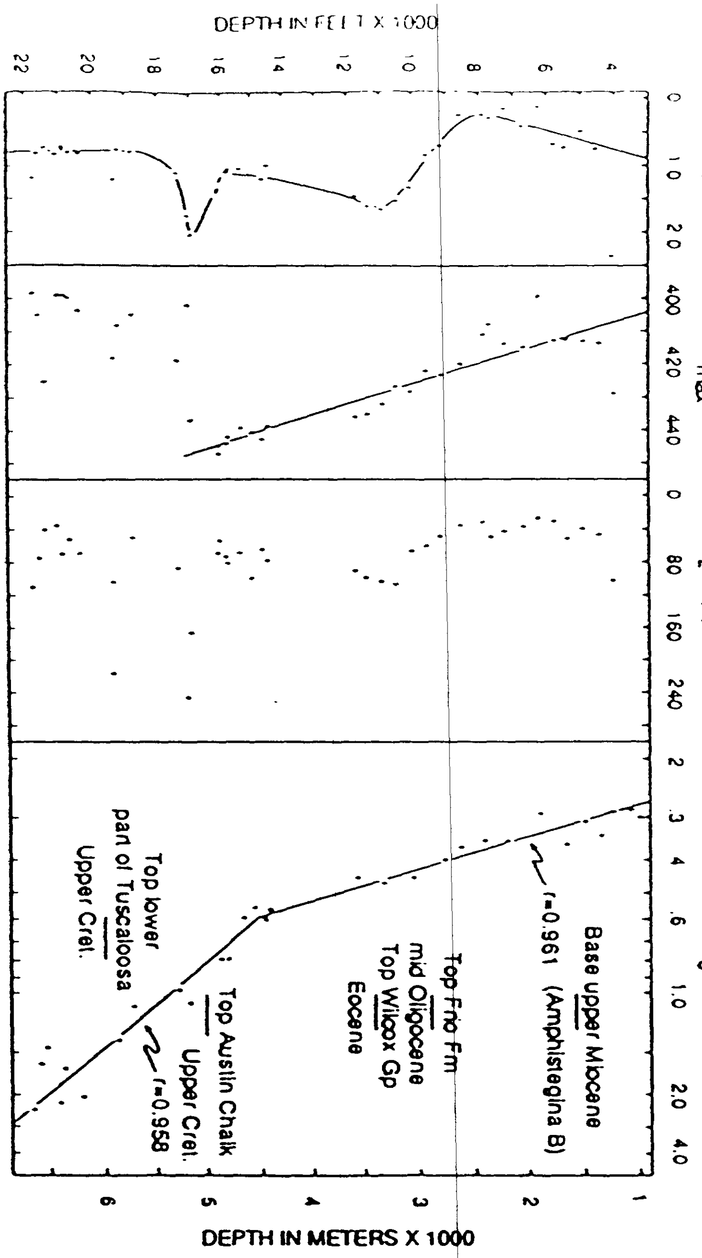

Figure 9. Plot of total organic carbon (T.O.C.), the temperature at the maximum of the ROCK EVAL S_2 pyrolysis peak in °C (T_{max}), the ROCK EVAL S_2 pyrolysis peak (HI) normalized to organic carbon (S_2 mg/g O.C.), and R_o versus depth for the Marathon Oil Co. J. Burton LeBlanc et al-1, T.6S, R.1W, Section 36, East Baton Rouge Parish, Louisiana (API 17 033 20046 00). Data from Table 13, Price (1989b). All cuttings chips samples were heavily contaminated with organic-based drilling mud, therefore, 1-2 gram splits were powdered and Soxhlet extracted for 48 hours, to remove contamination, before ROCK EVAL analysis. Curves and straight lines in the T.O.C. and T_{max} plots trace trends in the data. Dashed line in the HI plot is explained in the text. The two straight lines in the R_o plot were generated by linear regression analysis of the data above and below 4,500 m. Correlation coefficients of these regression analyses are shown.

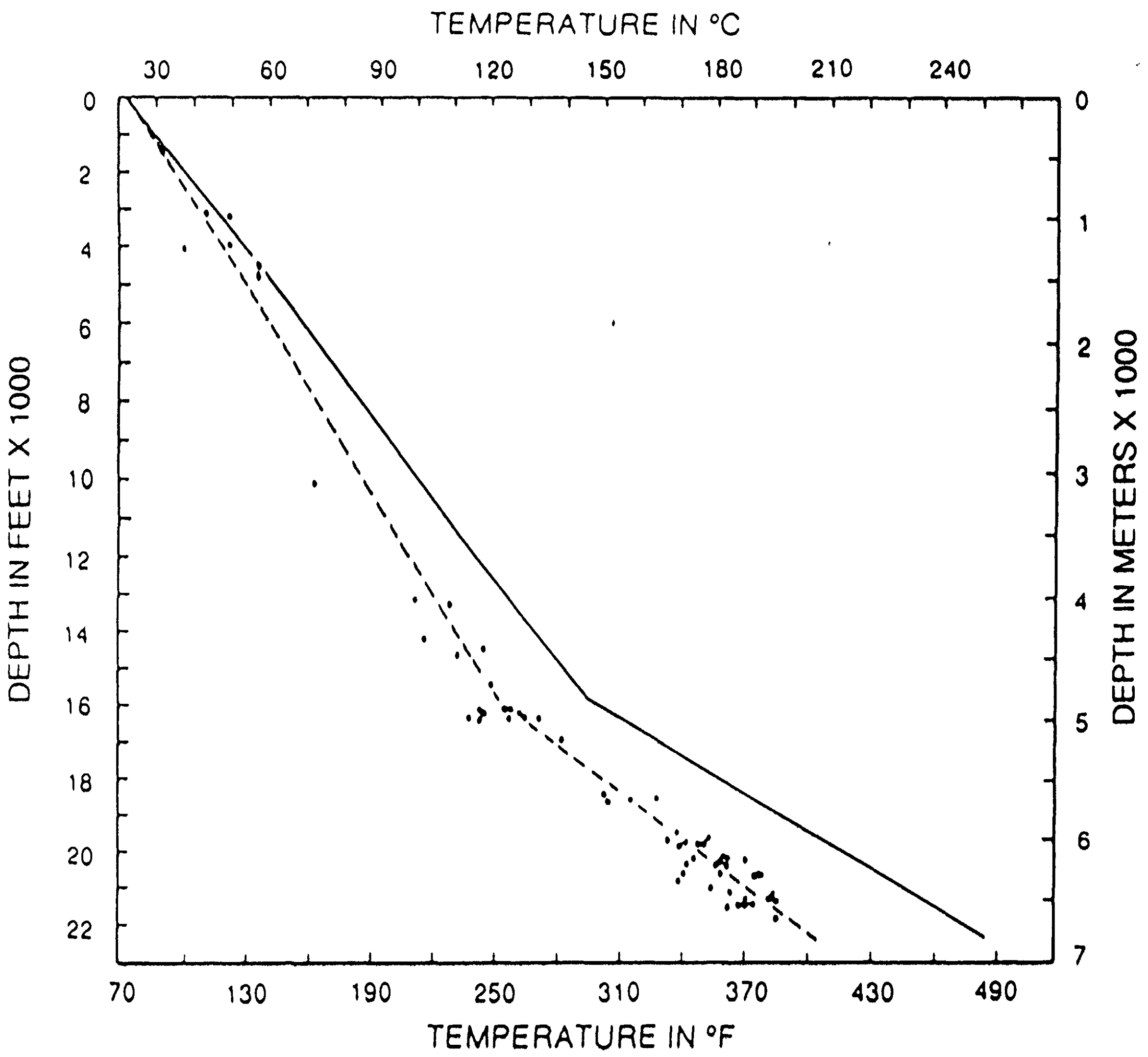

Figure 10. Burial temperatures versus depth for various wells of the Upper Cretaceous Tuscaloosa gas trend, southern Louisiana. Data compiled and supplied by Paul Jones. Dashed lines are an eyeball fit to the data; solid lines result from application of corrections to circulated temperatures. All original circulated temperature data taken less than 24 hours since circulation had stopped.

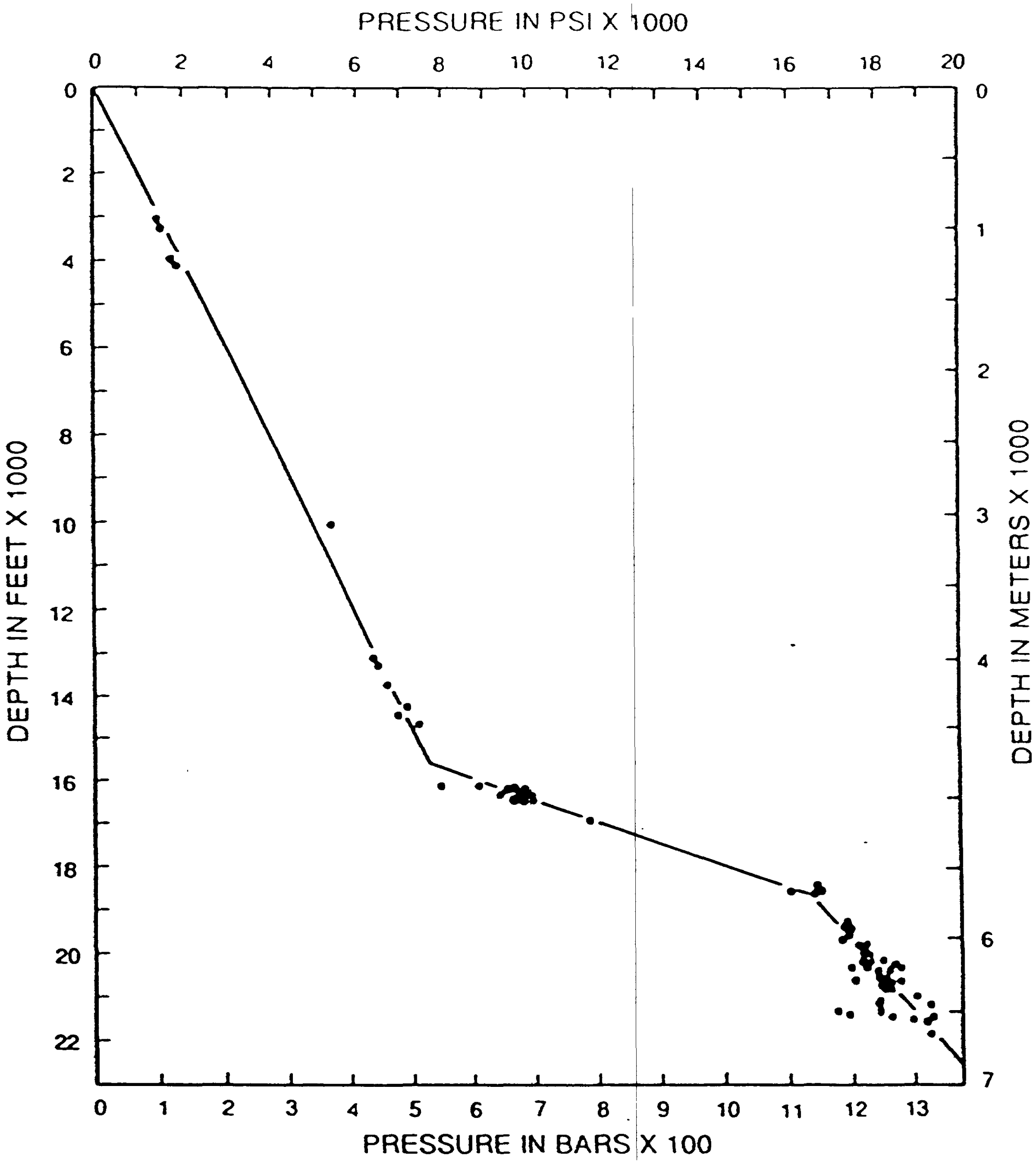

Figure 11. Fluid pressures versus depth for various vells of the Upper Cretaceous Tuscaloosa gas trend, southern Louisiana. Data compiled and supplied by Paul Jones. Solid lines are an eyeball fit to the data.

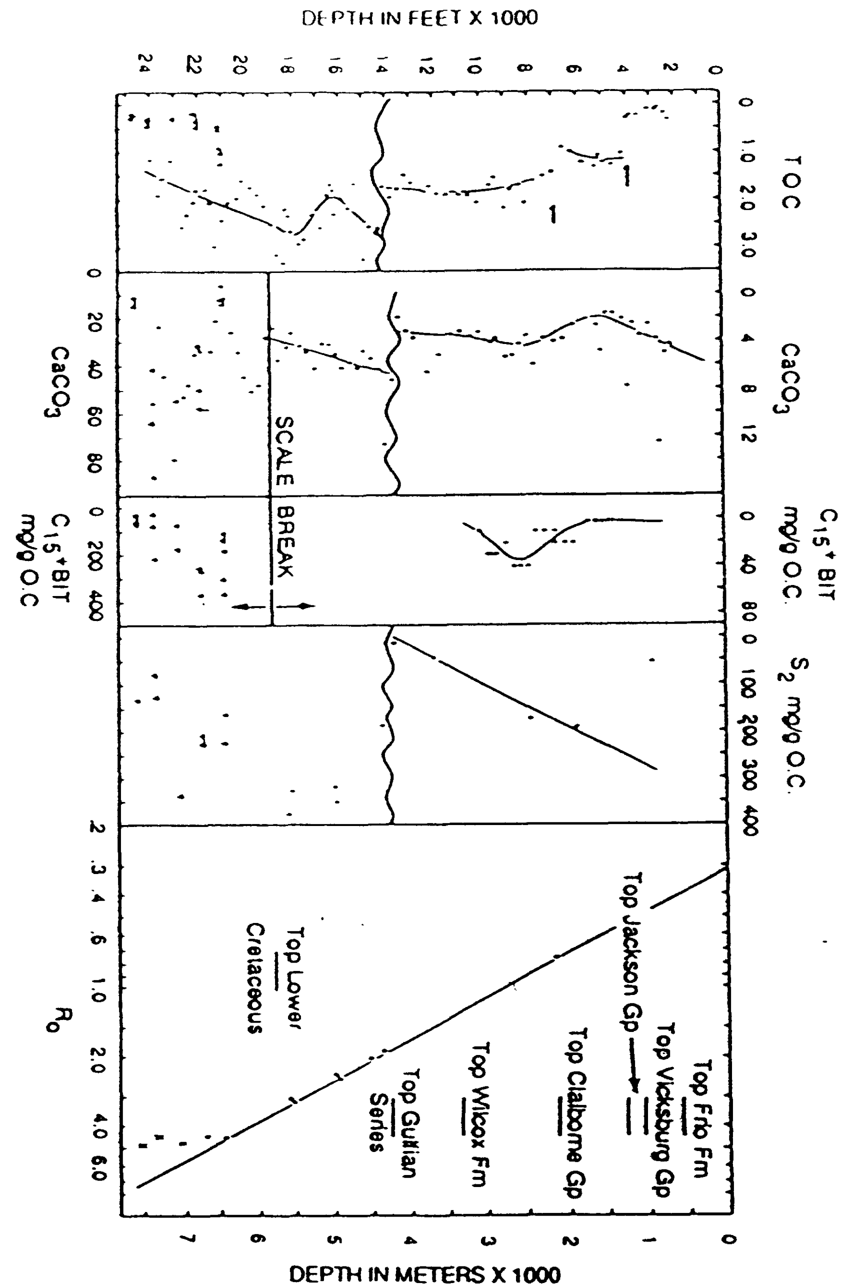

Figure 12. Total organic carbon (T.O.C.) and calcium carbonate ($CaCO_3$) contents in weight percent; C_{15+} bitumen (as determined by Soxhlet extraction) in milligrams per gram of organic carbon (C_{15+} BIT mg/g O.C.); HI's by ROCK EVAL pyrolysis (S_2 mg/g O.C.), and R_o all versus depth for the Chevron R. C. Jacobs-1, Goliad County, Texas. Estimated stratigraphic tops are from Powell and Woodbury (1971), Shinn (1971), Tipsword et al (1971), Lofton and Adams (1971), Holcomb (1971), Rainwater (1971), Newkirk (1971), Vernon (1971), and from data supplied by COFRC. Arrows, straight lines, curves, and wavy lines are explained in the text. Crosses are analyses of core samples from Price (1982). The solid line in the $CaCO_3$ and C_{15+} bitumen plots at 5,709 m (19,000 ft) signifies a break in scale for these two plots with the $CaCO_3$ and bitumen scales on the top horizontal boundary of the figure serving for samples above the solid line, and the respective scales on the bottom horizontal boundary of the figure serving for samples below the solid line. The "X's" in the R_o plot represent values which probably have some degree of R_o suppression.

Texas. The well penetrated a thick section of Tertiary-Upper Cretaceous shales to 5,822 m (19,101 ft), and from thereon, a sequence of Lower Cretaceous dark-grey to black calcareous shales, marls and argillaceous limestones. T.O.C. contents increase in a rather continuous manner with depth from shallow minimal values of around 0.10% to a maximal value of 3.31% just above the top of the Lower Cretaceous. Specific jumps in T.O.C. contents (shown by arrows, Fig. 12) occur at the top of the Upper Eocene Jackson Group, at the top of the mid Eocene Claiborne Group, and at the top of the Upper Cretaceous Gulf series (shown by wavy line). This increase in organic richness with depth is also apparent from the HI's of the rock eval analyses of these rocks (FIG. 12). Rock Eval analyses from more samples would be desirable, but unfortunately at this time only a limited number of samples are available for analysis. However, the available data allow some conclusions to be drawn. The rocks from 0-4,267 m (0-14,000 ft) appear to contain Type III OM, as the HI'S exhibit behavior typical for that OM type. The shallowest sample has very low T.O.C. and HI values, no doubt inherited from original depositional conditions. Excluding this sample from consideration, the remaining four samples from 0-4,267 m (0-14,000 ft) exhibit decreasing HI's versus depth with an HI of near zero at R_o = 1.8-2.0 (solid line, HI plot, Fig. 12) which is characteristic of Type III OM (Figs. 5 and 7, this paper; Price, 1988, 1989b; and Price and Clayton, 1990). $C_{15}+$ bitumen data from 1,372-3,048 m (4,500-10,000 ft) also exhibit behavior characteristic of Type III OM (Price, 1989b): 1) the TIHG at R_o = 0.6, 2) a maximum in the bitumen concentration at R_o = 0.8-0.9, and 3) a decrease from this maximum to low values at $R_o \geq 0.9$. At about 4,267 m (14,000 ft), an apparent lithologic break occurs as portrayed by wavy lines in the T.O.C., $CaCO_3$, and HI plots. At this break, T.O.C. and $CaCO_3$ contents exhibit significant increases, and HI's exhibit a radical jump from values around zero to values ranging from 78 to 380. Identical behavior has been noted in the rocks of other deep, high-rank well bores (Price, et al., 1979, 1981; Price, 1988; and Price and Clayton, 1990), and in all these cases (including the present case) these increases have been attributed to a shift in OM from Type III to hydrogen-rich Types I or II, or in other words, an increase in organic richness.

An increase in organic richness with age and depth of rock in the Gulf Coast is also documented by Sassen and Chinn (1990) who report upper Paleocene to lower Eocene Wilcox Group shales and middle Eocene Sparta Formation shales with impressive oil source rock characteristics: T.O.C. contents ranging from 1.5 to 7.5%, and averaging about 2.5-3.0%; and HI's ranging from 200-840, and averaging about 350. However, other data suggest that either: 1) the organic geochemical characteristics of the particular age shales which Sassen and Chinn (1990) examined are not constant throughout the Gulf Coast, or 2) the shales on which Sassen and Chinn (1990) reported are not characteristic of the entire sequence. Sassen and Chinn's (1990) samples were from wells in Point Coupee and St. Landry Parishes which are adjacent to East Baton Rouge Parish, in which the J. Burton LeBlanc et al-1 (Fig. 9) was drilled. The Eocene-Paleocene shales of the J. Burton LeBlanc et al-1 wellbore clearly do not have the levels of organic richness as the shales which Sassen and Chinn (1990) studied. The LeBlanc et al-1 shales have much lower T.O.C. contents and much lower HI's yet the wellbores from which all these samples were derived are not separated by more than 80.5 km (50 mi). Because Sassen and Chinn (1990) speak of "...evidence for thick thermally mature lower Tertiary source rocks for crude oil onshore along the axis of the Mississippi Embayment in south Louisiana.", it appears that the (above) first option is the correct one, and that the organic geochemical (source-rock) characteristics of the lower Tertiary (and possibly older) shales can vary radically, laterally in the Gulf Coast. Data of figures 9 and 12 and Sassen and Chinn's (1990) data for the Upper Cretaceous Tuscaloosa shales also support this hypothesis. The oil-source characteristics of the Upper Cretaceous Tuscaloosa shales from the J. Burton LeBlanc et al-1 well (Fig. 9) and from Sassen and Chinn's (1990) samples are remarkably similar and poor, and contrast strongly with the source rock characteristics, which are good, of the Upper Cretaceous Gulf Series shales of the Jacobs-1 well bore (Fig. 12). Thus, in different areas of the Gulf Coast, lower Tertiary to at least Upper Cretaceous shales appear to have strikingly varied source-rock characteristics, in contrast to the very monotonous and poor source quality of Gulf Coast Pleistocene through Oligocene clastics.

Sassen and Chinn (1990) state that the OM Type of the lower Tertiary shales they examined was clearly Type II and in some cases Type I. The OM of the Upper Cretaceous Gulf Series shales of the Jacobs-1 wellbore has TYPE II characteristics, although rock eval data are available on only 5 samples. thus, the possibility arises that some areas of the Gulf Coast may be underlain by fairly thick sequences of lower Tertiary to Upper Cretaceous shales with good to very good source rock characteristics (T.O.C. contents = 2.0-5.0 + %, HI's = 300-450 +, and Type II OM). However, as discussed below, a large body of data strongly suggests that Type II (hydrogen-rich) om requires substantially different and higher maturation ranks to achieve mainstage HC generation and intense primary migration, compared to Type III OM. Thus thick sequences of lower Tertiary-Upper Cretaceous shales with Type II OM and good to excellent source rock characteristics may have to achieve greater burial depths than type iii om, to yield large commercial deposits of crude oil.

Other aspects of figure 12 also warrant comment. Most of the T.O.C., $CaCO_3$, and C_{15}+ bitumen data (dots, Fig. 12) result from analyses carried at Chevron Oil Field Research Center (COFRC) La Habra, California. These data were supplied to the author in the late 1970's by Bob Jones, then Senior Research Scientist, COFRC. Some data of figure 12 (crosses, samples below 6,400 m, 21,000 ft) are taken from Price (1982), and other data (R_o analyses, ROCK EVAL analyses) result from later analyses of samples used in the Price (1982) study. Except for the deep core samples (crosses, Fig. 12) of that paper, and cuttings chips samples from 1,372-3,048 m (4,500-10,000 ft), all other samples were heavily contaminated with organic-based drilling mud. Thus, solvent extraction and C_{15}+ bitumen analysis were not possible on most of the Jacobs-1 rocks. However, exhaustive Soxhlet extraction was performed on 10 cuttings chips samples (dots HI plot, Fig. 12) supplied to the author, which removed their organic contamination, as after extraction these samples had zero or very low S_1 pyrolysis peak values (not shown Fig. 12). Thus the HI's of these samples are unaffected by the organic-based drilling mud.

The high contents of extractable bitumen in the deep core samples of the Jacobs-1 (crosses, Fig. 12) and the measurable to moderate HI's were previously ascribed to HC generation from indigenous OM in the core samples (Price, 1982); however, this was an erroneous interpretation of the data. The Chevron cores from the deep portion of the Jacobs-1 were taken because they were thought to be potential reservoir rocks. With two exceptions, the T.O.C. contents of these rocks were low (0.20-0.55%), and ROCK EVAL analysis of these deep cores demonstrated that 25-95% of these T.O.C. contents were in the form of extractable and pyrolyzable HC's. These are unrealistically high percentages of bitumen and/or potential bitumen for the total T.O.C. contents in these deep, low T.O.C. rocks. A more realistic interpretation of the Price (1982) data is that the bitumen found in these low T.O.C. "reservoir rocks" (crosses, T.O.C. plot, Fig. 12) moved in from the fine-grained, moderate-T.O.C. (1.25-3.00%)

rocks (dots, T.O.C. plot, Fig. 12, 6,400 m (21,000 ft) and deeper) interbedded with the reservoir rocks. The moderate to high HI's (89-330) of the "reservoir rocks" (crosses, Fig. 12) can be explained by the higher molecular weight fractions of the migrated bitumen being taken by the ROCK EVAL instrument for HC generation potential remaining on the kerogen (Clementz, 1979; Price et al., 1984; and Price, 1988). Subsequent ROCK EVAL analyses of Soxhlet-extracted powder from the deep Jacobs-1 cores resulted in substantially reduced T.O.C. contents (compared to sample splits of the unextracted samples) and near zero HI's. This supports the interpretation that the bitumen in these deep "reservoir rocks" of the Jacobs-1 is non-indigenous, and possibly has migrated into the rocks from the interbedded, fine-grained rocks. This interpretation is further supported by analysis of 79 core samples from this well cut between 6,203.9-6,715.6 m (20,355-22,034 ft). Porosity in these shalely limestones varied between 1.2-7.5% and averaged 4.5-5.5%, with residual oil saturations in this porosity ranging between 3.89-47.8% and averaging 18-20%. These data, and figure 8, which are from oil-stained core strongly support the contention that the hypothesis of a thermal destruction of C_{15}+ HC's by $R_o = 1.35$ is in error, as the maturation rank range of this core is between $R_o = 4.1-5.1$ with present-day temperatures of 255°-278°C. That these oil-stained core were taken and analyzed by an independent party (a major oil company), corroborate data gathered by this author from this and other deep, high-rank wells.

Jones (1980, P. 61) attributed the endurance of these ultra high-rank oil concentrations in the Jacobs-1 well bore, and the high concentrations of C_{15}+ HC's which have been found in ultra high-rank rocks from other deep wellbores, to the fact that these HC's were in closed or semi-closed, high-pressure systems, an assessment which is agreed with here. Hydrous-pyrolysis experiments (Price and Wenger, 1990) have demonstrated that increasing fluid pressure dramatically retards HC generation, maturation and thermal destruction, and as such is a major unrecognized controlling parameter of organic metamorphism. Jones (1980) believed that the situation with the deep, high-rank rocks in the Jacobs-1 wellbore was unusual; however, all throughout the offshore and inland near coastal Gulf Coast, very high fluid pressures at depth are universal (Fig. 11).

Organic-geochemical data from the Jacobs-1, LeBlanc et al-1, and Caillou Island 4666-1 well bores all demonstrate increases in organic richness with depth, both in the form of increased T.O.C. and HI values. However, this behavior does not appear to be uniform throughout the Gulf Coast regarding either the depth or the age of the rocks in which these increases take place. Bustin (1988) also noted an increase in organic richness in the clastics of the Niger Delta with burial depth and/or rock age. Thus a characteristic of deltaic deposition in general, may be increases in organic richness with both rock age and burial depth.

Cretaceous-Jurassic Organic-rich Source Rocks--Unpublished analyses exist of Lower Cretaceous-Jurassic fine-grained rocks from interior portions of the Gulf Coast basin that demonstrate some shales or marls have high T.O.C. contents, with hydrogen-rich OM and high HI's. Palacas (1984) has provided analyses of the Lower Cretaceous Sunniland limestone of the South Florida basin, and four of his rocks (Table 1) had excellent source rock qualities.

Table 1. Organic geochemical characteristics of Lower Cretaceous Sunniland Limestone samples, from Palacas (1984). Depth is given in meters (m); T.O.C. wt. % is total organic carbon in weight percent, S_1 mg/g O.C. is the S_1 ROCK EVAL pyrolysis peak normalized to organic carbon (mg/g O.C.); HI is hydrogen index. T.R. is the ROCK EVAL transformation ratio (also called P.I., or the production index, and equal to S_1/S_1+S_2); and T_{max} is the temperature in °C at the maximum of the ROCK EVAL S_2 pyrolysis peak.

Depth in m	T.O.C. wt. %	S_1 mg/g O.C.	HI	T.R.	T_{max}
3,497.4	7.04	31.7	649	.047	424°
3,586.4	12.3	40.9	845	.046	431°
3,587.9	11.5	36.5	630	.055	431°
3,588.2	7.41	30.0	608	.047	434°

Bissada et al. (1990) report analyses of Gulf Coast Mesozoic rocks outside the Cenozoic oil-production trend which show these rocks to have excellent source rock characteristics. Those authors proposed that such deeply buried source rocks under the Cenozoic oil trends could have generated Cenozoic oils, with extensive vertical migration being responsible for the emplacement of the oils.

Although published data on them are scarce, ultra-rich, Mesozoic, "black-shale" type source rocks clearly exist in the Gulf Coast. It is also clear that their potential role as source rocks can only be assessed after more data on these rocks are available. The organic geochemical characteristics of such rocks related to dependable maturation-rank (R_o) profiles versus depth, as determined from Type III OM, are needed to help answer the Gulf Coast source-rock question.

Conclusions can be drawn concerning the organic richness of rocks in the Gulf Coast: 1) Organic richness appears to increase with depth and age of rock throughout the Gulf Coast. 2) In some cases, even significant increases in organic richness may not result in adequate source rocks. 3) In other cases, such as in the Jacobs-1, thick sections of moderately organic-rich rocks may well serve as source rocks. 4) As discussed below, two very organic-rich sections apparently exist throughout the Gulf Coast: A) Eocene-Paloeocene coals and carbonaceous shales, and B) Lower Cretaceous-Jurassic fine-grained, high-T.O.C. rocks with hydrogen-rich OM and high HI's. 5) A call upon <u>any</u> deep rocks as a source section in <u>most</u> areas of the Gulf Coast, apriori will involve extensive vertical migration <u>and</u> an origin of the oil at depths and maturation ranks outside of the oil window (R_o >1.35).

Other authors (Bissada, et al., 1990; and Jones, 1990 have called for extensive vertical migration of Cenozoic trend oils from deeper, older, organic-rich rocks of different ages. However, such rocks are currently at maturation levels considerably above $R_o = 1.35$. It is a simple geometric fact that the rocks underlying many or most Gulf Coast Cenozoic oil trends at maturation ranks less than $R_o = 1.35$ are still organic-poor, Miocene-Oligiocene shales. In my opinion, this conflict allows only two possible organic-geochemical choices: 1) Prevailing organic-geochemical opinion is incorrect about the organic-poor, Pleistocene through Oligiocene shales, and these rocks are the source for the Cenozoic oils. 2) Prevailing organic-geochemical opinion is incorrect about the thermal destruction of $C_{15}+$ HC's at $R_o = 1.35$, and deeper, older more organic-rich rocks are the source for the Cenozoic oils. The latter is the preferred explanation here.

Kinetic Differences Between Different OM Types--The reaction kinetics of Type III OM are well known. Type III OM enters the TIHG by $R_o = 0.6$ (present-day burial temperature of 120°C), and commences mainstage (intense) HC generation (with measurable loss of HI's Figs. 5 and 7) by $R_o = 0.80$ (present-day burial temperature of 160°C). This generation stage is also accompanied by the onset of intense HC gas generation and thus intense primary migration by gaseous solution, which results in a sharp decrease in the concentration of $C_{15}+$ HC's as measured either by ROCK EVAL pyrolysis or by solvent extraction (Fig. 5, this paper; Price, 1989b, Figs. 1, 2, 6, 7, and 9). Type III OM loses most of its HC generation potential (as measured by the ROCK EVAL HI's) over $R_o = 0.8$ to 1.6 (bracketed arrows, Fig. 5, this paper) or 1.8 (Fig. 7) and loses essentially all of its HC generation potential by $R_o = 2.0$, as indicated by zero or near zero hydrogen indices at this maturation rank (Figs. 5 and 7, this paper; Price, 1989b, Figs. 10, 11 and 12). If the original HI's of Type III OM are moderately high (250-350), slightly higher burial temperatures are required for HC generation and migration, such as at the Paloma oil field, Southern San Joaquin Valley basin, California (Price, 1989b).

Investigators studying the Miocene Monterey Formation of onshore and offshore California have determined that the hydrogen-rich, sulfur-rich (Type II-S) OM of those rocks commences intense HC generation at low (but yet undefined) maturation ranks. No doubt other investigators, who have researched Type II-S OM at other geographic localities, have reached the same conclusion, a conclusion which is supported by hydrous-pyrolysis data of L. C. Price and L. M. Wenger (Fig. 13). The differences between the chromatograms of the extract of the unreacted Permian Phosphoria shale (Type II-S OM) and the sample reacted at 175°C are stark compared to other rocks which exhibit significantly less reaction extent at the same or higher temperatures. Thus, whereas n-paraffins are essentially absent in the unreacted Permian Phosphoria shale, they are quite evident in the 175°C sample, and extreme differences occur between the gas chromatograms of the Phosphoria unreacted and 300°C samples. However, in the Mississippian-Devonian Bakken shale (hydrogen-rich Type II OM), the gas chromatograms of the unreacted, 175°C and 275°C samples are virtually identical, which suggests that little or no reaction has taken place up to 275°C. It is only at a reaction temperature of 300°C that moderate differences in the Bakken shale gas chromatograms become apparent.

The hypothesis that marine-based, hydrogen-rich Types I and II OM require much higher maturation ranks for HC generation, primary migration, and kerogen burnout than Types II-S and III OM, and evidence for that hypothesis, have been previously presented (Price, et al, 1979, 1981, 1984; Price, 1982, 1983, 1988, 1989b; Price and Barker, 1985; and Price and Clayton, 1990) and other investigators (Kontorovich and Trofimuk, 1976; Sajgó, 1980; and Wenger and Baker, 1987) have also provided evidence for this hypothesis. A detailed review of the evidence for this hypothesis is not possible in this paper, however, a brief review is in order.

In rocks with oxygen-rich OM in the Los Angeles, Ventura, and other California petroleum basins, based on ROCK EVAL analyses of a very large USGS sample base, the TIHG is attained at burial temperatures of 120°-125° which agrees with Phillipi's (1965) conclusions regarding HC generation in these basins. However, concurrently in these basins, in rocks with high HI's, the TIHG is not detected at highly elevated burial temperatures, for example not by 200°C in the Wilmington field, Los Angeles basin (Price, 1983, Figs. 3 and 4) and not by 210°C in the Shell Taylor 653 well bore, Ventura basin (Price, 1988, P. 31). In fact, all organic maturation indices are suppressed in rocks with

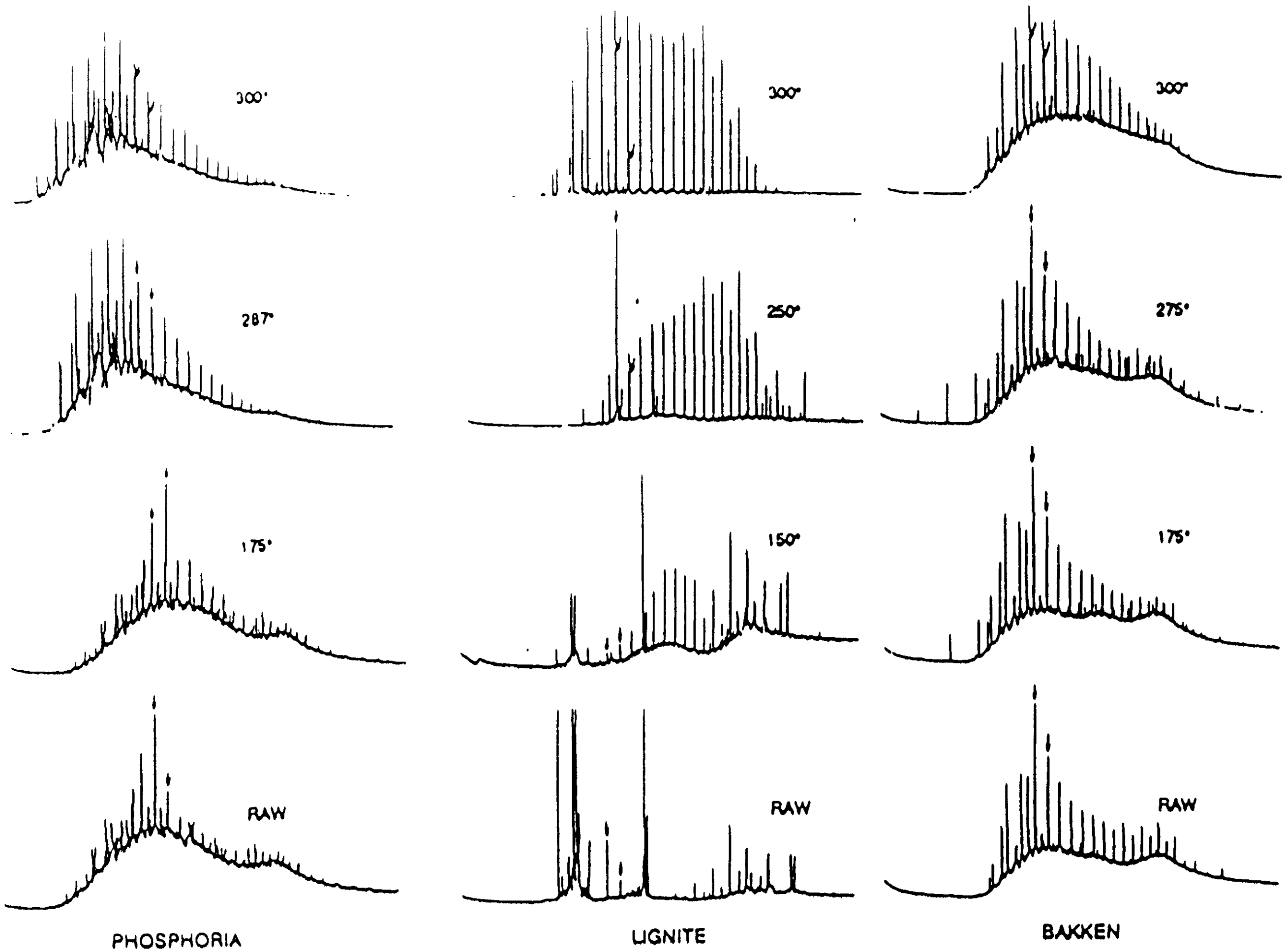

Figure 13.

Saturated HC gas chromatograms of extracts from three unreacted (RAW) rocks (Table 2) and of extracts from the same rocks subjected to hydrous pyrolysis at different reaction temperatures. The reaction temperatures in °C are given above each chromatogram. Arrows designate pristane and phytane. Vertical arrows signify that the peak heights of the two isoprenoids are greater than those of the adjacent n-paraffins. Canted arrows signify the reverse. Data of L. C. Price and L. M. Wenger.

high HI's and generally the higher the HI, the greater the degree of suppression for any given burial temperature range (Figs. 14 and 15). R_o is perhaps the most widely used organic maturation index, and increases in the values of the ROCK EVAL S_1 pyrolysis peak and the transformation ratio are easily measurable, direct consequences of $C_{15}+$ HC generation. In figures 14 and 15 as the HI of the sample increases, the values of these three parameters strongly decrease. In the California petroleum basins, rocks with high HI's retain very immature characteristics to highly elevated burial temperatures, and give no indication that they are even approaching the TIHG at these burial temperatures.

Price, et al (1984) determined that in the Williston basin, the TIHG first occurred in the Mississippian-Devonian Bakken shale, a rock characterized by hydrogen-rich Type II OM, at R_o values above 0.6, probably in the range of R_o = 1.2 to 1.9, based on R_o profiles through shallower Tertiary-Mesozoic rocks with Type III OM. Subsequent work has shown that in passing from the Cretaceous Pierre shale and younger formations (all rocks with Type III OM) into the Cretaceous Niobrara through Fall Creek formations (rocks with Type II OM, T.O.C. = 2-8% HI's = of 350-600), all organic maturation indices strongly reverse themselves and become suppressed, sometimes from moderately elevated maturation ranks (R_o = 0.6-1.0) in the younger rocks. Another example of the suppression of the TIHG, and other maturation indices in hydrogen-rich OM, exists in Pennsylvanian black shales with hydrogen-rich OM in the midcontinent region, U.S.A. (Wenger, 1987).

Differences in the reaction kinetics between the different OM Types have also been exhibited by data from organic-geochemical studies of deep well bores (Price, et al, 1979, 1981; Sagjó, 1980; Price, 1982, 1988; and Price and Clayton, 1990). In these wells, an orderly progression of organic maturation proceeds with depth in thick sequences of rocks with Type III OM, often with kerogen burnout being reached in the Type III OM by R_o = 2.0, as shown by zero or near zero HI's or by kerogen elemental hydrogen to carbon (H/C) ratios of 0.29-0.32 or lower. With further increase in depth and passage into rocks which were deposited under different conditions and which contain a marine-derived, more hydrogen-rich OM, HI's and kerogen H/C ratios increase to moderate or even high values. Further, an entirely different maturation progression takes place in these rocks, as demonstrated by the data of the Foerster-1 well bore (Price and Clayton, 1990). Thus, various organic maturation indices (whether measured from whole rocks, extracted bitumen, or macerated kerogen) after continuously increasing with depth in rock sequences with Type III OM, strongly reverse themselves to much more immature values in passing into deeper rocks with more hydrogen-rich OM. Further, double HC generation zones have been reported in some deep wells (Kontorovich and Trofimuk, 1976; Sagjó, 1980; and Price and Clayton, 1990), the shallower zone being due to Type III OM, and the deeper zone presumably being due to hydrogen-rich OM. Lastly, the deep rocks in these well bores retain measurable to moderate HC generation capacity (HI's) to extreme maturation ranks, far past R_o = 2.0, the thermal burnout for Type III OM. Data from both the Foerster-1 (Price and Clayton, 1990) and Bertha Rogers-1 (Price, et al, 1981) well bores suggest the final loss of HC generation potential in hydrogen-rich OM occurs at $R_o \geq 7.0$.

Differences in the reaction kinetics between the different OM Types most probably originate from differences in bond strengths between the different kerogens. Bonds involving sulfur are the weakest and most easily broken, followed by bonds involving oxygen. The carbon-carbon bonds of hydrogen-rich OM are strongest and only broken at higher maturation ranks. Significant

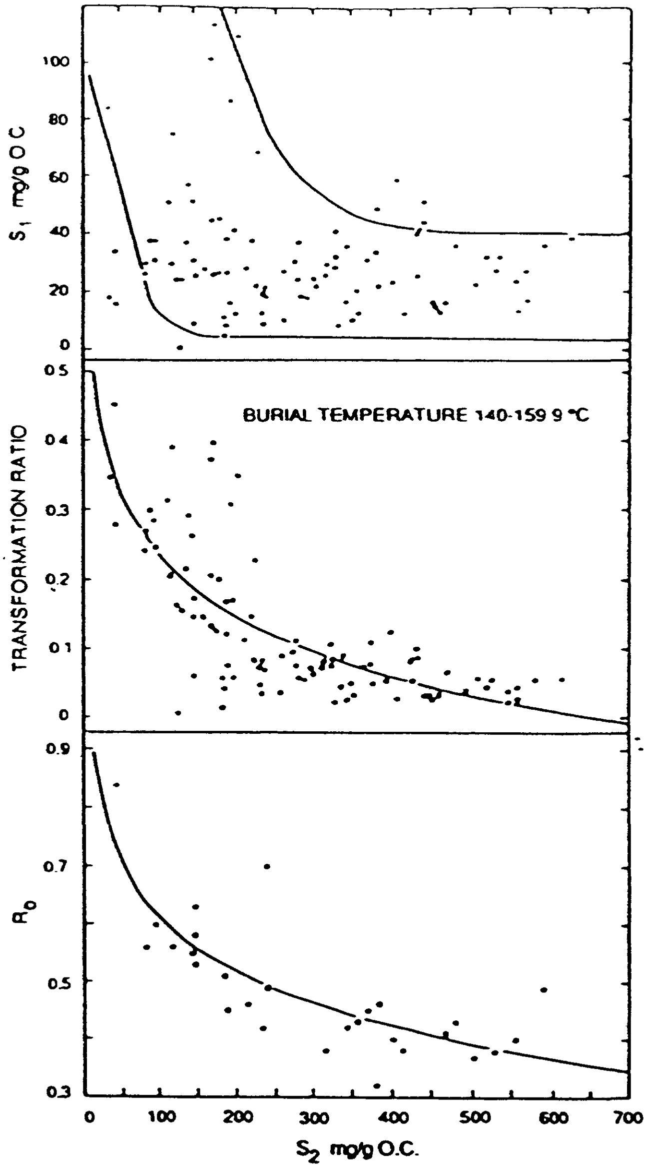

Figure 14. Plot of R_o, the ROCK EVAL Transformation Ratio (S_1/S_1+S_2, also termed the Production Index), and the ROCK EVAL S_1 pyrolysis peak normalized to organic carbon (S_1 mg/g O.C.) all versus the ROCK EVAL S_2 pyrolysis peak (HI) normalized to organic carbon (S_2 mg/g O.C.) for rocks which are from the California petroleum basins and are at equilibrium burial temperatures of 140°-159.9°C. Samples are from the Ventura central syncline, and Ventura Avenue field of the Ventura basin; from the Whittier, Long Beach, Wilmington, Santa Fe Springs, and Seal Beach fields of the Los Angeles basin; from the Baldwin Hills Community-1, Boughton Community-1 (N.W. Plunge, Santa Fe Springs field), the American Petrofina "Central C. H.-2" (central syncline, Los Angeles basin) and the Long Beach Airport-1 (NE of the Long Beach field) wellbores, all in the Los Angeles basin; from various wells in the Anahiem nose and northeast flank areas of the Los Angeles basin; from various wells in the Paloma field, Southern San Joaquin Valley basin; and from a well in the Santa Maria Valley basin. All samples except for the American Petrofina and Santa Maria Valley basin samples (cuttings chips) are core samples. The curved line in the R_o plot results from logarithmic regression analysis of the data and has a correlation coefficient of $r = 0.805$ to the data. The line in the transformation ratio plot results from logarithmic regression analysis of the data and has a correlation coefficient of $r = 0.744$ to the data. The lines in the S_1 pyrolysis peak plot define the principal sample population.

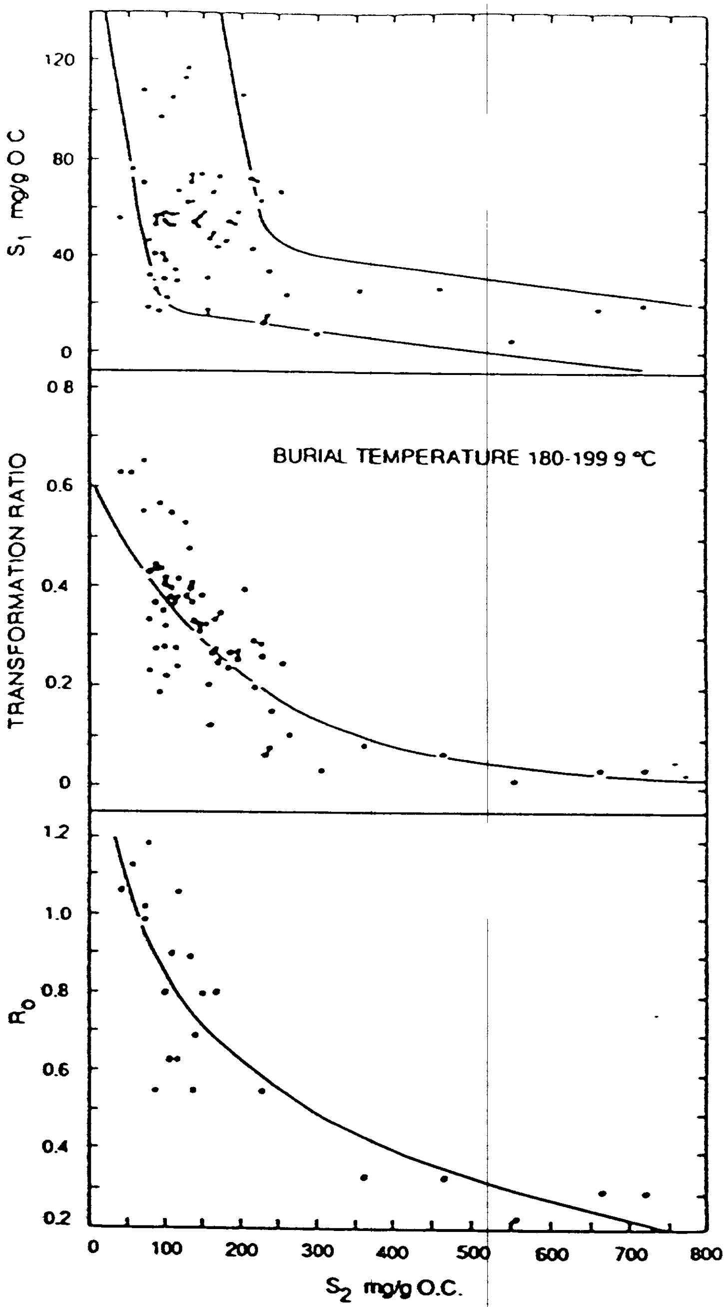

Figure 15. Plot of R_o, the ROCK EVAL Transformation Ratio (S_1/S_2+S_2, also termed the Production Index), and the ROCK EVAL S_1 pyrolysis peak normalized to organic carbon (S_1 mg/g O.C.) all versus the ROCK EVAL S_2 pyrolysis peak (HI) normalized to organic carbon (S_2 mg/g O.C), for rocks which are from the California petroleum basins and are at equilibrium burial temperatures of 180°-199.9°C. Samples are from the Wilmington field, Los Angeles basin; the Houghton Community-1 (NW plunge Santa Fe Springs field); the American Petrofina "Central C.H.-2" (central syncline Los Angeles basin; and from the Paloma field, Southern San Joaquin Valley basin. The curved line in the R_o plot results from logarithmic regression analysis of the data and has a correlation coefficient of r = 0.867 to the data. The lines in the S_1 pyrolysis peak plot define the principal sample population.

differences between reaction kinetics of different OM Types have not been previously widely observed for two reasons: 1) They have not previously been looked for. 2) They are very difficult to observe. Regarding the second point, because, as discussed, all maturation indices are suppressed in hydrogen-rich OM, I am aware of only two methods to determine correct maturation ranks in Types I and II OM: first, extrapolation or interpolation of maturation rank (preferably R_o) values from a valid depth profile determined from rocks with Type III OM, into rocks with hydrogen-rich OM; second, direct measurement of maturation ranks from rocks which have Type III OM and which are interbedded with rocks with hydrogen-rich OM. Wenger and Baker (1987) used this technique in their study of Midcontinent U.S. Pennsylvanian black shales.

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, et al, 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 = 0.80-0.90 (Fig. 5) 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. Data of Teichmüller and Durand (1983), reply to the hypothesis that coals generate only methane (Fig. 6). Up to a rank of T_{max} = 438°C (R_o = .66), at least half the products pyrolyzed from the coals they studied were C_{15}+ HC's, and up to ranks of T_{max} = 500°C (R_o = 1.76)., at least 25% of the products were C_{15}+ HC's. Hydrous pyrolysis experiments on a hydrogen-poor North Dakota lignite (Price, 1989c) demonstrate significant generation of C_{15}+ HC's (Fig. 16), and the amounts of C_{15}+ HC's which would be generated from a hydrogen-rich coal would be much larger.

It is true that coals generate copious amounts of gas at all maturation ranks, including huge amounts of CO_2 (Fig. 17) 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. Coals are most probably repeatedy microfractured and healed due to the continual build up and escape of these gases. Teichmüller (1974, p. 382) described the coal "maceral" exudatinite (also called exsudatinite) as a resinous or asphaltic like material found as fillings or linings in 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 data on oil solubility in methane of Price et al (1983) demonstrate the substantial carrying capacity that a CO_2-rich HC gas has for oil, even at low burial temperatures and pressures (R_o = 0.45). At this rank, by the data of figure 17, 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 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, exudatinite would not be a coal maceral at all, but rather a

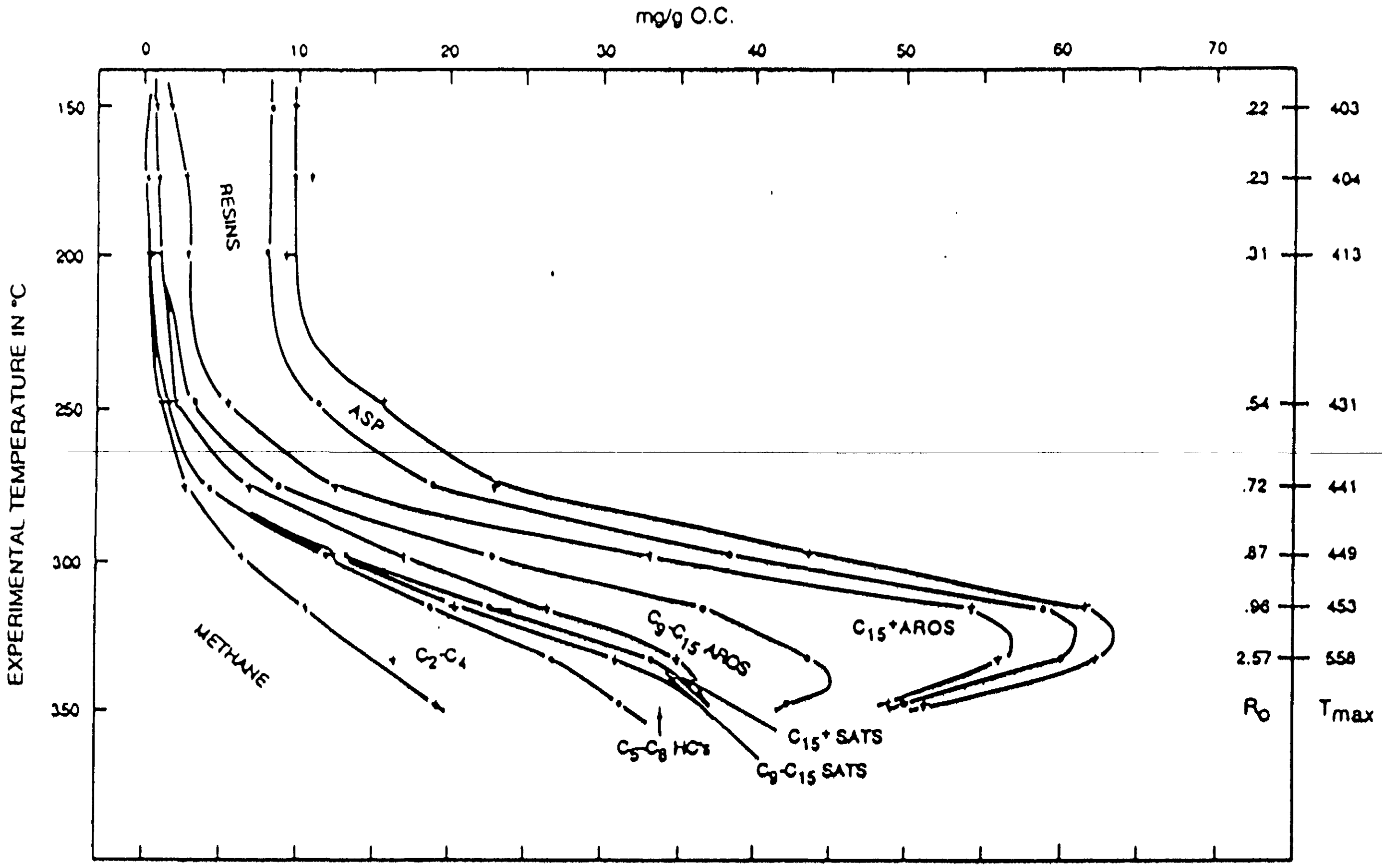

Figure 16. Relative concentrations of different HC species versus experimental temperature for hydrous pyrolysis experiments of a hydrogen-poor lignite (Table 2, and Price, 1989c). Relative concentrations were calculated for each experimental temperature for each species by dividing the amount of that species (in mg/g O.C.) at the temperature of interest by the amount of that species (in mg/g O.C.) at 150°C. T_{max} values are measured, R_o values are estimated from T_{max} values and figure 3 of Tissot (1984).

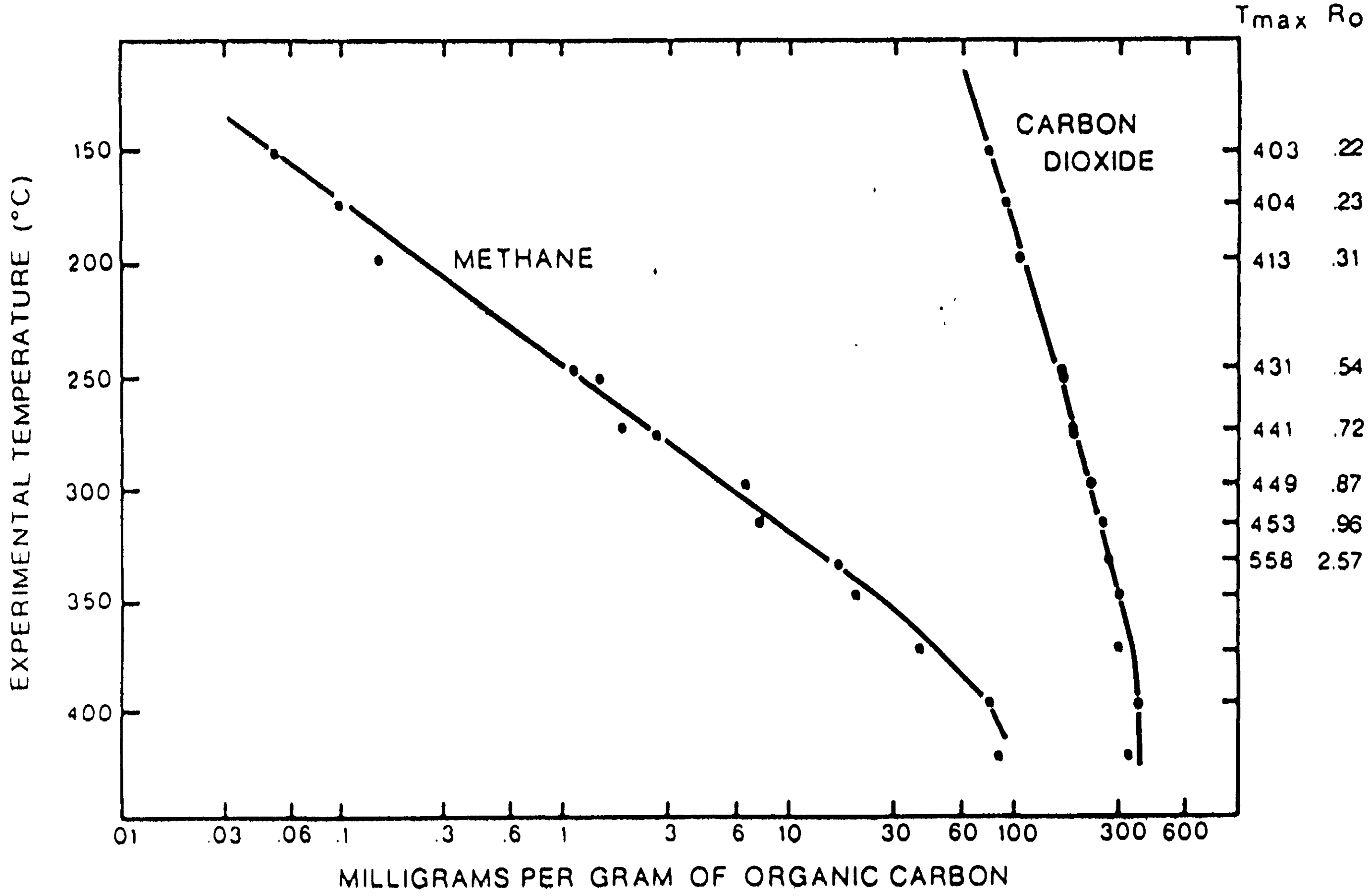

Figure 17. Amounts of methane and carbon dioxide in mg/g O.C. generated by hydrous pyrolysis of a hydrogen-poor lignite (Price, 1989c) versus experimental temperature, measured T_{max}, and estimated R_o from figure 3 of Tissot, 1984).

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 manifestation of the efficacy of primary migration in coals by gaseous solution.

In figure 5 over R_o = 0.8-1.6 (vertical arrow), a substantial loss of hydrogen indices occurs, and yet no increase in the value of the S_1 pyrolysis peak takes place. The data of figures 6 and 16 demonstrate that a substantial portion of the generated products from this loss of HI's are C_{15}+ HC's. The conclusion therefore appears inescapable that C_{15}+ HC's are being generated and migrating from coals in Nature, and not remaining in the coals to be cracked to methane.

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 5, the major loss in the S_2 pyrolysis peak of the coals occurs over R_o = 0.81 to 1.57 (vertical arrow). 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 for most source rocks, as source rocks are usually found deeper than, and not spatially associated with, the oil deposits that they generate.

In figure 5, the mean HI at the maximum of the HI plot of the coals (shown by feathered arrow) can be visually estimated at about 220. 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%, which equates to 171,600 ppm by weight of generation products for these coals. From figure 6, at R_o = 0.65, 75% of the HC product would be C_5+ HC's and 50% would be C_{15}+ HC's. A "black shale" with 10% T.O.C. and on HI of 800 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. Such numbers clearly hint at the possibility of coals acting as oil source rocks.

All coals are not necessarily oil source rocks. The coals which Teichmüller and Durand (1983) analyzed have high HI's compared with some other coals, including 37 from the Williston basin (Price, 1989b). ROCK EVAL T_{max} values for these Williston basin coals ranged from 407° to 435°C and burial depths ranged from 25.9 to 734 m (85 to 2,410 ft). Those coals had an average hydrogen index of 46 mg/g O.C. and an average T.O.C. content of 60.0%, which results in 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 experiments performed on a sample of such a hydrogen-poor lignite demonstrated that at the maximum in HC generation, the C_5-C_8 HC's and C_9+ saturated HC's made up only 7.48% of the total generated products (methane through the asphaltenes, excluding CO_2; Price, 1989b), yet these compounds comprise a major portion of 0.850-0.825 specific (35°-40° API) gravity oils. Thus, the median value of 27,600 ppm of generated products for the 37 Williston basin coals should be reduced to 2,063 ppm useful products, or perhaps 3,500-4,000 ppm (12.7 to 14.5%) useful products allowing for the C_9+ 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 as impressive source rock, and it is not clear if such a rock could be responsible for an oil deposit.

If coals can serve as effective oil source rocks for sizable oil deposits, the data of figures 5 and 7, and other considerations, suggest the maturation ranks over which this would occur. In figure 5, the maximum loss of HI's occurs over R_o = 0.8 to 1.6-2.0, which therefore appears to be the maturation ranks to which coals must be exposed to result in the generation of oil. However, the ranks at which the generated HC's would migrate from the coals by gaseous solution and accumulate into oil deposits is another matter. C_{15}+ HC concentrations in coals at ranks of $R_o \geq 0.9$ (and for the most part, in other rocks with Type III OM) are always quite low, and this was attributed above to very efficient primary petroleum migration. It is actually due both to primary petroleum migration, but more so, to loss of these HC's from core or cutting chips during the trip of these rocks up the wellbore. Research on primary migration has shown that organically mature shales ($R_o \geq 0.9$) have large amounts of indigenous generated gas within them. As such rocks ascend the wellbore, the pressures exerted on the rocks greatly decrease from the high formation pressures at depth to atmospheric pressure at wellhead. This extreme pressure decrease allows the generated gas to greatly expand in volume, leading to a violent expulsion of gas and C_{15}+ HC's from the rocks during their trip up the wellbore. Thus with mature shales, most C_{15}+ HC's are lost from the rocks long before the rocks ever get to the laboratory, and at this time it is impossible to estimate over what maturation ranks the high concentrations of generated HC's would actually migrate from the source coals or rocks.

Data (Table 2) relevant to the question of coals being possible source rocks for some Gulf Coast oils, originate from the Shell Ridgeway Management-1, drilled in Rankin County, Mississippi. From 1,518-1,689 m (4,980-5,540 ft), in the undifferentiated Eocene Wilcox and Paleocene Midway Formations, this well penetrated a continuous coal bearing sequence. (The depth at which this coal bearing sequence began is unknown, but shallower than 1,518 m (4,980 ft) which was the first available sample.) All of the cuttings-chips sample packets over this interval were composed dominantly of coal, and most were composed of all coal. It is unknown if this was due to the sequence being almost all coal or being due to the unlithified clastics having been dissolved by water, as the samples were very clean and obviously had been well washed. The possibility that the coals of this depth interval originated from caving from a more restricted coal sequence is unlikely because of the continuous increase in maturation rank with depth through this coal sequence (T_{max} and R_o values, Table 2). The HI data of Table 2 demonstrate that these coals are moderately hydrogen-rich. Even discounting for interbedded clastics, given the average organic richness (Table 2) and the thickness of this coal bearing interval, this coal sequence represents a possible source rock interval of staggering proportions. Further, it is well documented that coals are widespread throughout the entire Gulf Coast province.

Landrum et al (1988) after analyzing 150 onshore (nearshore and interior basin) Gulf Coast oils, grouped the oils into 4 main classifications. Tertiary oils of southwestern Mississippi and southern Louisiana fell into one group generated from rocks thought to be deposited in a rapidly subsiding, marginal-marine environment. This is consistent with the hypothesis that the oils at Caillou Island may have been sourced from Eocene Wilcox-Paleocene Midway Group hydrogen-rich coals below the Pleistocene through Oligiocene sediment package. Oil emplacement in shallower sandstone reservoirs would have occurred almost exclusively by primary migration by gaseous solution and vertical migration of fluids from the more deeply buried source coals up growth faults, or up faults created by salt tectonics. Further, the composition of the Neogene Gulf Coast oils is precisely what would be expected if the oils had undergone primary

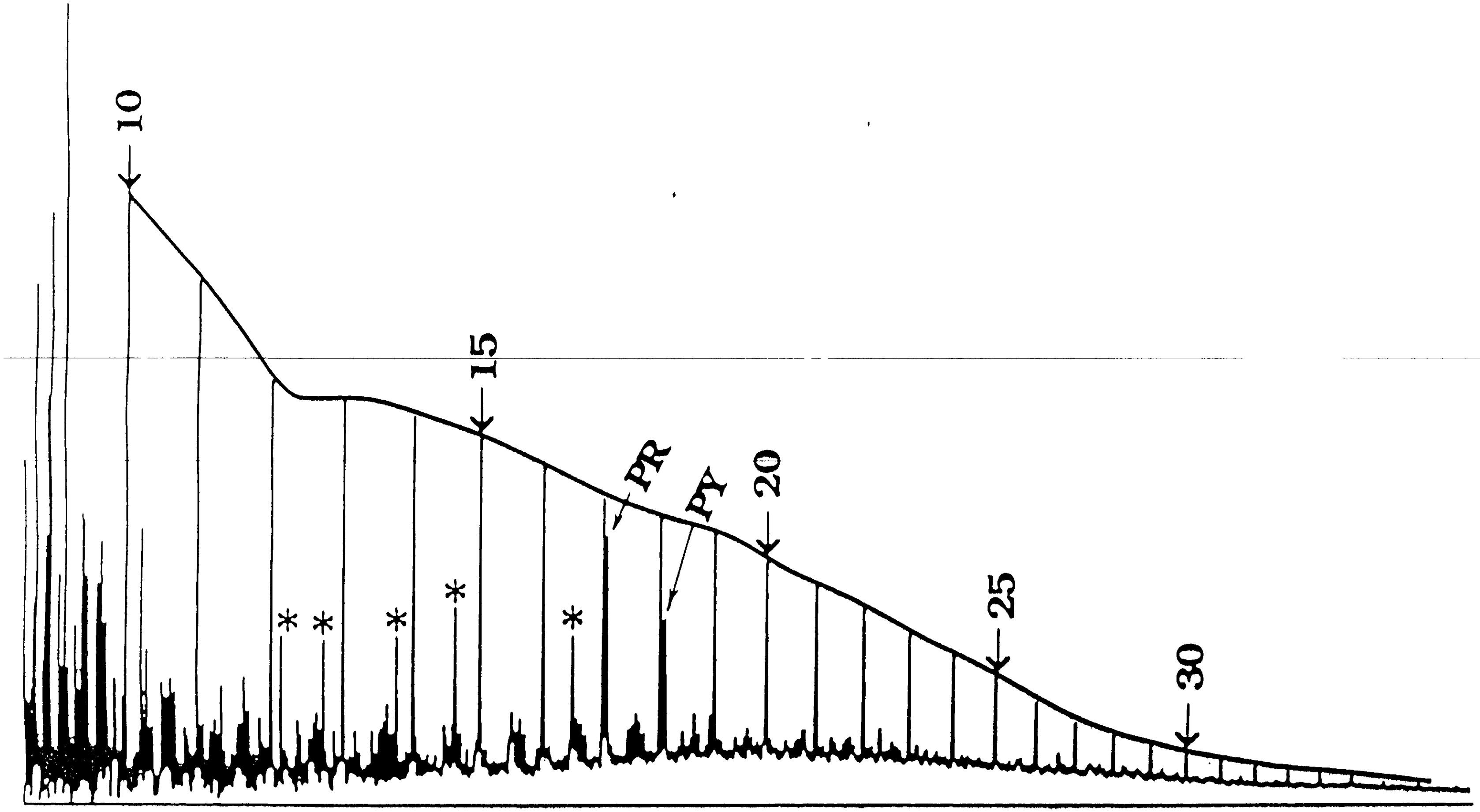

Figure 18. Gas chromatogram of the C_8+ saturated HC's of an oil from the Caillou Island oil field, offshore Louisiana. Isoprenoid HC's are marked by asterisks and PR (pristane) and PY (phytane). Every fifth n-paraffin is marked by an arrow with a number. From Price (1989a).

migration by gaseous solution. This migration mechanism heavily favors uptake of C_{15}- saturated and aromatic HC's and C_{15}+ saturated HC's, especially n-paraffins, to the exclusion of high molecular weight aromatic HC's, resins and asphaltenes (Price et al., 1983). A gas chromatogram of a Caillou Island oil is given in figure 18. This oil has a specific gravity of 0.852 (34.5° API) and is produced from Miocene sands at 6,080.5 m (19,950 ft.). The oil is composed of 82.30% C_{15}- HC's and the C_{15}+ HC's are 61.3% saturated HC's, 33.4 aromatic HC's, 3.7% resins, and 1.6% asphaltenes. The very regular n-paraffin profile of this oil also strongly suggests primary petroleum migration by gaseous solution.

It is certainly not suggested here that lower Tertiary coals have sourced all Gulf Coast oils, or even all Gulf Coast Neogene oils. As one proceeds further offshore, the thickness of Cenozoic sediments would decrease to the point that if lower Cretaceous-Jurassic black shales with hydrogen-rich OM existed far offshore, then such shales would be within the proper maturation-rank window to serve as source rocks. As one proceeds onshore, the thickness of Cenozoic sediments also decreases to the point that Lower Tertiary coals would not be buried deeply enough to have acted as source rocks. Clearly the coals of the Shell Ridgeway Management-1 wellbore are too immature to have acted as source rocks. In the interior Gulf Coast basins, it is more likely that Cretaceous-Jurassic shales with marine-derived (hydrogen-rich) om would have acted as source rocks. However, oils sourced from such rocks would have distinctly different physical, chemical, and biogeochemical characteristics than coal-sourced oils found over and adjacent to late Cenozoic depocenters. Further, the oil-source characteristics of coals may vary widely throughout the Gulf Coast: 1) In some areas, the Lower Tertiary coal section may either become too thin to volumetrically serve as a significant oil source or be absent altogether. 2) Also, HI's of coals can vary widely, from 30-60 for the hydrogen-poor Eocene-Paleocene coals of the Williston basin, to 200-300 for some of the coals of Teichmüller and Durand (1983). Other examples of hydrogen-rich coals are common: Rice, et al (1989) report a Cretaceous Fruitland formation coal with an HI of 357 in the San Juan basin, Colorado-New Mexico. Thompson, et al (1985) report analyses on nine Indonesian coals with HI's between 347-461, and Horsefield, et al (1988), give similar analyses for other Indonesian coals. Pittion and Gouadain (1985) report on Jurassic coals of the Haltenbanken area (offshore Norwegian Continental Shelf, North Sea) with HI's of 200-350. Clearly, hydrogen-rich coals with high HI's (100-450) are more likely oil sources than hydrogen-poor coals with low (30-60) HI's.

Figure 18.

The concept of coals as acting as source rocks for oil deposits for some reason is met with extreme negative prejudice among many North American investigators and petroleum explorationists, and no doubt the hypothesis of coals acting as oil source rocks in the Gulf Coast would be considered unlikely by these individuals. Yet, in some parts of the world, on the basis of many detailed studies (including Durand and Oudin, 1979; Roe and Polito, 1979; Thomas, 1982; Vandenbrouke, et al, 1983; Durand and Paratte, 1983; Schoell, et al, 1983; Bertrand, 1984; Thompson, et al, 1985; Huc, et al, 1985; Korashani, 1987; Hvoslef, et al, 1988; and Horsefield, et al, 1988), it is now taken for granted that coals have sourced sizable oil deposits: "Some of the most productive source rocks of Indonesia are Tertiary coals....", Hvoslef, et al, 1988; "Coals are oil source rocks in many of the Tertiary basins of Southeast Asia", Thompson, et al, 1985. Pleistocene through Oligiocene Gulf Coast shales with 0.3-0.5% T.O.C. contents and HI's of 40-60 would have rock generation capacities of 120-300 ppm, and "rich" Gulf Coast shales of these same ages (1%

T.O.C. and HI's of 120) would have a rock generation capacity of 1,200 ppm. It is ironic that some investigators take the position that a great volume of largely-immature, fine-grained rocks with HC generation capacities of 300 to 1,200 ppm (at the high end) have generated the substantial oil deposits of the Gulf Coast (and other basins, Bustin, 1988). At the same time, other (and in some cases, the same) investigators staunchly deny the possibility of coals ever acting as oil source rocks despite the fact that many coals are at least 150-200 times more organic rich than the organic-poor Gulf Coast shales.

The dictum that coals cannot serve as oil source rocks, in my opinion, is based on a preferred view rather than on hard data, and is a dictum which has gone unquestioned until only recently. Data from different recent studies suggest that the principal arguments against coals being oil-source rocks are invalid. The facts that coals are accepted as source rocks in different areas of the world; the organic richness of coals; the large volumes of gas that coals generate, which would greatly facilitate primary migration by gaseous solution; and that the gas-rich Neogene oils of the Gulf Coast have precisely the composition and compound distribution which would be expected to result from primary migration by gaseous solution, in my opinion, all demand a serious consideration that coals may in fact be the source rocks for some Gulf Coast oils. The question whether or not coals are oil source rocks in the Gulf Coast, will only be answered by designing and carrying out research specific to the question. It is, however, an important question. If coals have sourced Gulf Coast oils, then they would have done so at maturation ranks lower than those required by hydrogen-rich OM for HC generation. Such differences in maturation-rank requirements and burial history plots for mainstage HC generation between coals and hydrogen-rich OM would be relevant to the application of petroleum geochemistry to exploration in the Gulf Coast.

"Something from Nothing"

Some investigators (including Jones, 1980, 1983, 1989; Waples, 1981; and Bustin, 1988) have argued that the shear volume of low T.O.C. organic-poor shales in the Gulf Coast, and/or other delta systems, can overcome their ultra-poor source rock characteristics, such that they can serve as source rocks. Jones (1983, 1989) has presented calculations which suggest that the ratio of HC's generated by the organic-poor shales to in-place HC's (reservoired oils) in the Gulf Coast is on the order of 10 to 1, and, therefore, one can make "something from nothing". However, Jones' (1989) assumption that 10% of the T.O.C. contents are converted to oil like HC's is open to question. An HI of 90 would be high for the Gulf Coast organic-poor shales (Fig. 1). Also, the Neogene Gulf Coast oils generally are rich both in C_{15}-HC's and saturated HC's and poor in resins, and asphaltenes. However, shale bitumen is high in resins, asphaltenes, and aromatic HC's, and low in C_{15}-HC's. In reality, probably only 30% of both the indigenous bitumen in shales and the bitumen converted from kerogen is oil-like bitumen, which equates to a 2.7% conversion of T.O.C. contents to oil-like HC's, not a 10% conversion. This dramatically lowers the ratio of in-place to generated HC's. Bustin (1988) has argued that very favorable plumbing (good interbedding of silts, sands, and shales) in the Niger Delta has resulted in excellent drainage of HC's from the source-poor shales, which accounts for the large oil deposits there. However, there is nothing unusual about sedimentation in the Niger Delta; Gulf Coast rocks also have this extensive interbedding.

Further, proponents of the "something from nothing" proposition have not addressed four vast HC "sinks" which greatly lower the ratio of generated to in-place HC's: First, gaseous solution has become the primary migration mechanism of theoretical choice by more and more investigators in the Gulf

Coast. However, as discussed, a consequence of this mechanism is the necessity for a dispersed free-gas phase which carries high levels of dissolved C_5+ HC's, and which is at concentrations below the critical gas saturation level throughout the shales, silts and sands of the Gulf Coast, and which thus is immobile. Primary migration by gaseous solution is simply not possible without this dispersed free-gas phase (Price, 1989c), which: 1) is a vast HC sink that cancels the favorable ratio of generated to in-place HC's, and 2) establishes the possibility of a yet unrecognized geopressured resource in the Gulf Coast, and other basins (discussed below). A second HC sink is composed of the myriad of stains, shows, and small uneconomic HC deposits found throughout the rocks of the Gulf Coast. A third HC sink is the constant micro- and macroseepage that is now, and over geologic time has been, taking place in the Gulf Coast (Kennicutt and Brooks, 1990; Prikryl, 1990; and Roberts, et al, 1990). Over geologic time, such micro- and macroseepage (and the bacterial consumption of the migrating HC's) consumes staggering amounts of HC gases and C_5+ HC's (Price, 1986). A fourth HC sink is the vast amounts of HC's which are dissolved in and swept away by the meteoric water which flows off the interior craton and through the hydropressure-zone of the Gulf Coast.

Mass balance calculations (not shown here, see Wilson, et al, 1974; Price, 1980c, 1986, 1989b) with reasonable assumptions reveal that any one of these sinks, alone, much less together, consumes huge amounts of HC's. These sinks cancel out the favorable ratios of generated to in-place HC's from organic-poor shales and should be considered in any "something from nothing" scenario.

The Hard-Geopressure Resource

If gas solution is the principal primary migration mechanism in the Gulf Coast, then a previously unrecognized natural resource theoretically would exist in the deep, hard-geopressure zone of the Gulf Coast. (Hard geopressures in the Gulf Coast have been arbitrarily defined as fluid pressure gradients $\geq$0.7 psi/ft.) This resource would result from the dispersed free-gas phase at or below critical gas saturation levels in Gulf Coast sandstones and microfractured shales at moderate to high maturation ranks where HC generation and primary migration were taking place. Other sources of gas would also contribute to the resource. Theoretically, this resource could be recovered by a specialized production technique which would establish a rapid pressure drawdown in a permeable water-bearing sandstone of moderate to high porosity. Such a pressure drawdown would allow the dispersed, free-gas phase to expand (by the ideal gas law, $PV = nRT$) and occupy sandstone porosities greater than the critical gas saturation level and subsequently flow towards a production well, as the sandstone would have relative permeability with respect to gas.

This hypothetical, deep-geopressure resource differs substantially from the geopressure resource that the U.S. Department of Energy (DOE) is attempting to produce, which is: surface extraction of methane dissolved in sandstone brines (at low concentrations) with reinjection of the spent brines into shallower reservoirs, or in other words, surface extraction of a low grade resource. The DOE technique recovers little or no gas from a dispersed free-gas phase. Further, the necessary reinjection of the spent brine with the DOE technique utilizes a significant percentage of the energy obtained from the recovered methane. Lastly, the DOE production technique recovers only 1.4-3.2% of the in-place methane. On the other hand, possible production of the deep-geopressure resource would principally recover and depend upon the dispersed free-gas phase, and would also recover: 1) methane dissolved in the pore waters of sands and microfractured shales at much higher solubility levels than in the DOE resource base, because of the much higher burial temperatures and pressures than in the DOE cases; 2) attic gas (small non-commercial shows of methane) which were reached by the radius of influence of the producing well bore; and 3) methane produced from HC generation reactions in the microfractured shales due to the large formation pressure draw-down established by the producing well. Hydrous-pyrolysis data of Price and Wenger (1990) demonstrate that increasing fluid pressure greatly retards HC generation reactions. Therefore, a rapid pressure drawdown would allow such reactions, which previously were suppressed by high formation pressures, to proceed.

An extended discussion of this possible natural gas resource of the deep Gulf Coast hard-geopressure zone is outside the scope of this paper. However, the hypothesis of this resource is a natural extension of the most probable primary migration mechanism in the Gulf Coast, gas solution. Successful utilization of this possible resource would involve specialized unconventional production techniques from sandstones with unusual characteristics, and completion of necessary background research.

Correlation of Geologic Parameter(s) to Field Size

For years, attempts to correlate the size (reserves) of Gulf Coast oil and gas fields with any geologic parameter have been unsuccessful. The first most obvious and logical theoretical correlation was increasing oil reserves with increase in the size of the structure, i.e. - increase in the "gathering area" of the structure. However, unpublished studies have shown that no correlation exists between this parameter and oil and gas reserves. A number of other attempted correlations between reserve size and Gulf Coast geologic parameters have also failed to produce positive results. However, unpublished plots between reserves of Gulf Coast HC fields and the depth at which the fault associated with the producing structure soles out into bedding places, give excellent correlations. As fault sole-out depth increases, so does reserve size of the associated HC field. Further, faults with shallow sole-out depths (6,096 m, 20,000 ft or less) usually are not associated with any HC production. This correlation can be explained by the hypothesis that faults which sole out more deeply, tap more mature source rocks which are at more intense stages of HC generation and primary migration. Another unpublished study in the interdomal salt basin area of the Gulf Coast, found excellent correlations between field reserve size and depth to salt (determined by seismic) for the interdomal salt basin in which the HC's were present.

Correlations of varying degrees are also present between field reserve size and the throws of faults associated with the producing field (Figs. 19-21); however, several complicating factors are present with such plots. First, fields can be present in small structures (probably filled to spill point) which are associated with major fault zones. This leads to reserves too small for the size of the fault, where in fact the reserves under consideration may be only a small portion of all the HC's which moved along the fault, and were trapped in other structures. Second, in the Gulf Coast, the throws of many faults increase significantly with depth. However, due to fluid pressure regimes at the time of vertical migration, the HC's may have migrated to shallower depths, where fault throws were less. This would be especially expected in the case of buried fault zones which do not extend to the surface. The result could be large reserves associated with faults of only moderate throws, but where fault throw increased dramatically with depth below the producing horizons. Other complications arise from using cumulative production (CP) data instead of estimated ultimate recoverable (EUR) data, or even EUR data which can be erroneous and low and is later upgraded during field development (not an unusual case). In spite of these complications, figures 19-21 all show correlation of increasing field size with increasing fault

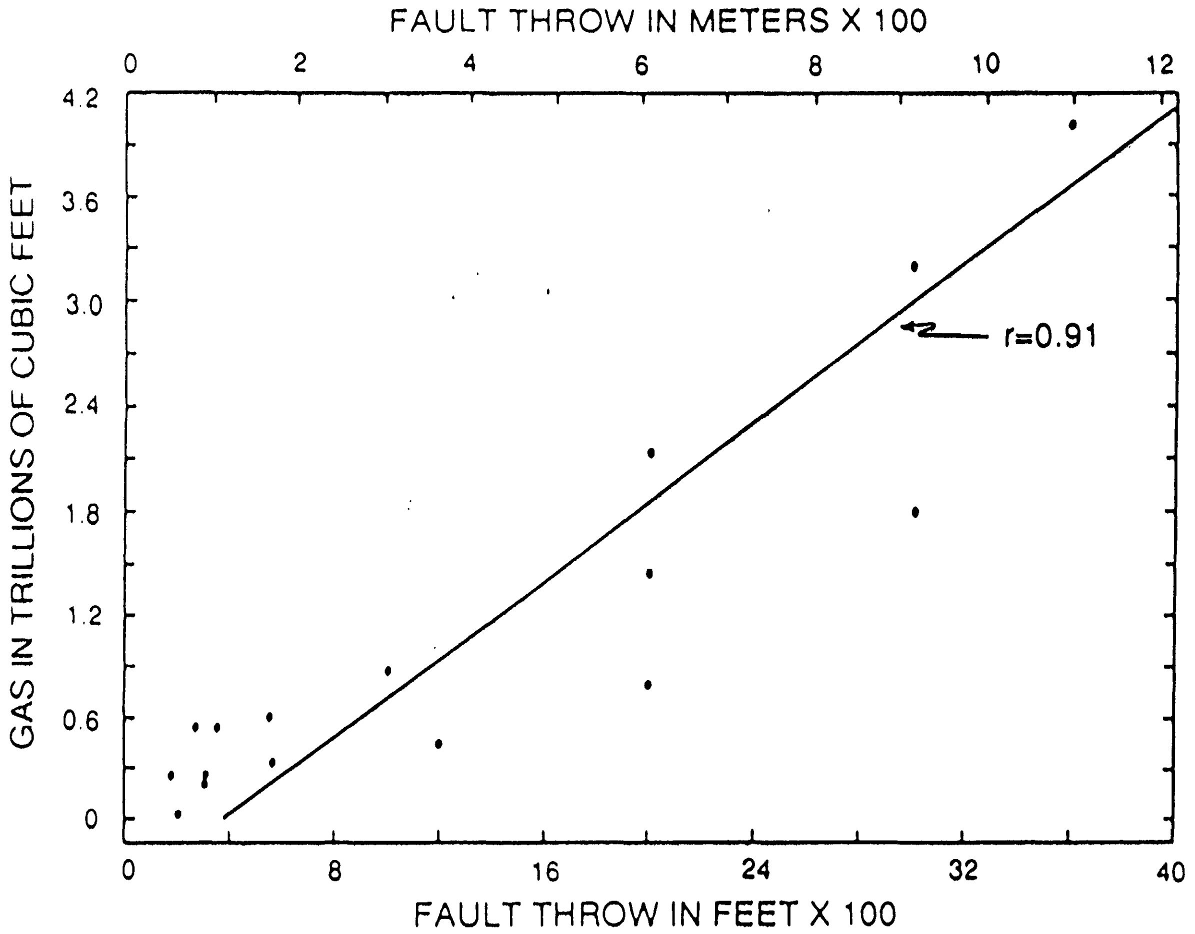

Figure 19. Plot of fault throw versus reserves (EUR) for the 16 southern Louisiana gas fields discussed in Lafayette and New Orleans Geological Societies (1968). Cumulative production data to 12/30/83 (International Oil Scouts, 1986) were used for the Lake Raccourci field (Lafourche and Terrebonne Parishes) because of a low, erroneous original EUR estimate. The solid line results from linear regression analysis of the data and has a correlation of r = 0.91 to the data. Oil was converted to gas at the ratio of one barrel equals 15,000 cubic feet.

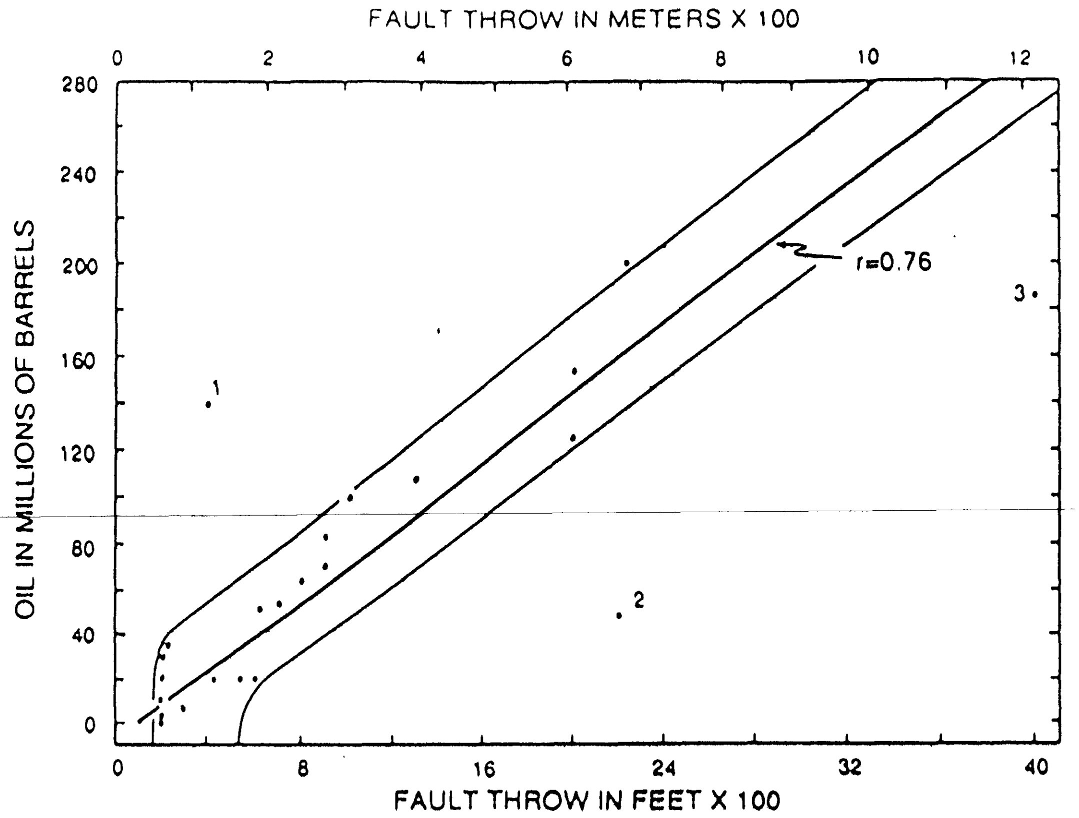

Figure 20. Plot of fault throw versus reserves (EUR) for the oil and gas fields discussed in Lafayette Geological Society (1964, 1970) where EUR's were given for the fields. The four following fields were plotted in figure 20 because their CP's as of 12/31/83 were significantly larger than their EUR's: Gillis-English Bayou, Calcasieu Pa.; Patterson, Saint Mary Pa.; Vermillion Block 39, offshore; and West Lake Verret, Saint Martin Pa. The solid line results from linear regression analysis of the data and has a correlation of r = 0.76 to the data. The two thin curved lines define the principal population field. The numbers 1-3 represent three fields which lay far off the regression line and out of the principal population field: 1 is Krotz Springs, St. Landry Pa.; 2 is North Ossum, Lafayette Pa.; and 3 is Erath, Vermillion Pa. Gas was converted to oil at the ratio of one barrel equals 15,000 cubic feet.

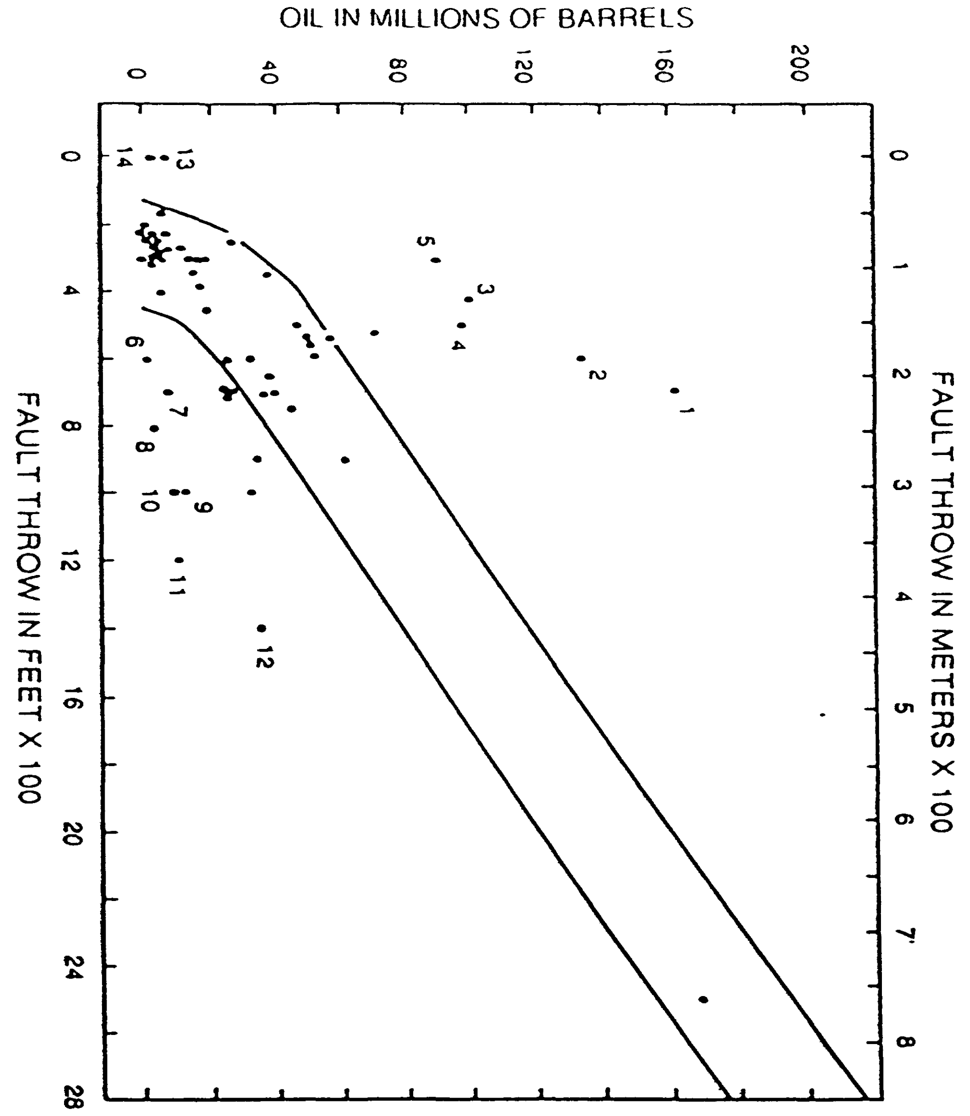

Figure 21. Plot of fault throw versus reserves (CP) for oil and gas fields discussed in Layfayette Geological Society (1964, 1970) and whose EUR's were not given. The two curved lines define the principal population field. the numbers 1-12 represent fields which lay significantly out of that population field: 1 is Vermillion Block 39, offshore; 2 is West Lake Verret, St. Martin Pa.; 3 is Patterson, St. Mary Pa.; 4 is Belle Isle, St. Mary Pa.; 5 is Ville Platte, Evangeline Pa.; 6 is East Cameron Block 4, offshore; 7 is Happytown, St. Martin Pa.; 8 is Intracoastal City, Vermillion Pa.; 9 is Savoy, St. Landry Pa.; 10 is Riceville, Vermillion Pa.; 11 is South Lake Charles-Coulee Hippolyte, Calcasieu Pa.; and 12 is Cameron Meadows, Cameron, Pa. Fields 1-5 have reserves large for their fault throw and fields 6-12 have reserves small for their fault throw. Gas was converted to oil at the ratio of one barrel equals 15,000 cubic feet. Bayou White, Pointe Coupee Pa., (13) and Glenmora, Rapids, Pa., (14) had no faults in direct association. Linear regression analysis of the data resulted in a line (not shown) with a correlation coefficient of r = 0.548 to the data.

throw. Further, in all three figures, a minimum throw of about 61 m (200 ft) appears necessary for any reserves to be present.

One might attribute such correlations between fault throw and reserve size to the hypothesis that the larger faults are associated with larger structures, which would be expected to have larger reserves. However, as stated, in the Gulf Coast, structure size has no correlation to size of reserves. Large fault throws allow two possibilities: 1) The fault has been active for a longer period of geologic time than a fault with small throws, and therefore has had more HC migrational pulses. 2) Faults with larger throws extend to greater depths and thus tap more mature source rocks than do faults with small throws.

These geologic correlations should not be restricted only to the Gulf Coast but should be present in all oil-bearing deltaic depositional sinks. For example, because of the absence of complicating salt tectonics in the Niger delta, even stronger correlations should be present there than in the Gulf Coast, between size of HC reserves and both fault throw and especially the depth at which the growth fault soles out. In the Niger delta, roll-over anticlines in the downthrown blocks of major growth faults constitute the preponderance of traps, with fault traps and stratigraphic traps being minor. Weber and Daukorn (1976) studied the association of production with faulting in the Niger Delta, and found, among other things, that production was only in the traps associated with faults of at least 131 m (429 ft) of throw. Yet the traps associated with faults of smaller throws were identical in all other respects with the productive traps.

Exploration Implications of Vertical Oil Migration in the Gulf Coast

The scenario of deeper origin and vertical migration of Neogene oils in the Gulf Coast as presented here is given only as a hypothesis, and many investigators and explorationists would no doubt disagree with the concept. However, if such a scenario is correct, then the most important element in Gulf Coast exploration becomes the fault zone. Timing, trap formation, structure, source rock considerations and so on would assume a secondary importance. For example, certainly a trap is necessary to contain HC's; however, the HC's will move vertically up a major fault whether or not a conventional trap is associated with, or adjacent to, the fault at shallower depths. If such a trap is not present, the oils will migrate off the fault and updip until some type of trap prevents further migration. Certainly source rocks are also important. However, from the amount of oil and gas discovered and produced thus far in the Gulf Coast, at least one adequate, and no doubt multiple, source rocks are present in the basin, although we have not yet recognized them. Further, if the source rocks are generally, or always, deeper than, and buried vertically under the oil fields they source, we may simply never obtain samples of such rocks. Thus study of such rocks becomes, to some extent, academic, and the old argument of some explorationists results: "Who cares what the source rock is, the oil is obviously there."

Essentially every HC field in the Gulf Coast, including the fields of the interior Gulf Coast, is either directly associated with or updip from a major fault; and generally the larger the fault, the greater the size of the field. Many structures have been drilled and found to be barren in the Gulf Coast, but not all the major fault zones in the Gulf Coast have been "drilled". If Gulf Coast HC's do originate and vertically migrate from depth, major unexplored fault zones should be identified and the first possible traps off the fault zone would be prospective, no matter how unlikely the trap appears to be.

Fluid entry pressures of shallower sandstones at the time HC's are migrating enter heavily into accumulation considerations (Price, 1980a, p. 356). Deep-basinal, vertically-migrating fluids cannot enter abnormally-pressured sandstones, which are closed fluid systems, or the sands would not be abnormally-pressured in the first place. Such deep-basinal fluids must bypass abnormally-pressured sands and can only be emplaced into rocks with hydrostatic, or near hydrostatic, fluid pressures. Thus, in the case of a growth fault with a roll-over anticline on the downside of the fault, fluids migrating vertically up the fault would be focused into the first transmissive, hydrostatically-pressured rocks on the downside of the fault block, if the rocks on the upside of the fault block at the same depth were abnormally-pressured (Price, 1980a; Fig. 2). If the rocks on the upside of the fault block were also normally pressured, the vertically-migrating fluids could enter transmissive rocks in the upthrown block at the same depth (Price, 1980a, Fig. 7). However, this does not mean that HC deposits should not be expected in abnormally-pressured sandstones in the Gulf Coast. HC's may be emplaced in normally-pressured rocks, and then with further burial, those deposits may become abnormally pressured. Also, the depths at which abnormally-pressured rocks are first encountered may shift upward or downward during geologic time due to fluid-pressure changes. Further, the actual emplacement of the HC's, and other deep basinal fluids, may cause abnormal pressuring of the previously transmissive unit.

Several specific plays may be expected in the Gulf Coast, if a deeper origin and vertical migration of HC's is common there. First, ultra-deep, high-rank ($R_o \geq 1.35$) oil may be expected in some areas of the Gulf Coast in structures associated with buried fault zones, i.e. - fault zones which die out at depth, far below the earth's surface. The lack of fault extension to shallower depths prevents oil in a deep, fault-associated structure to escape to shallower depths from deep-basinal compaction processes. A second expected play is regional stratigraphic trapping updip from large regional faults along which production has already been established on the downthrown side of the fault. In the interior South Texas Gulf Coast, the 322 km (200 mi) long Jackson trend, updip from the oil-productive Vicksburg fault zone fields (Price, 1980, p. 363-364), is an example of this play. In the Gulf Coast, much exploration thinking tends to be lateral, i.e. - "the Vicksburg play", "the Frio play", "the Wilcox play", and so on. Yet vertically-stacked reservoirs, such as those at Caillou Island are not unusual. In many established Gulf Coast fields associated with major faults, possible deeper production in vertically-stacked reservoirs may have been overlooked because of the bias of lateral exploration thought patterns.

CONCLUSIONS

1) The location of oil at Caillou Island and Timbalier Bay (largely on the north side of the Caillou Island-Bay Machand salt ridge), the extensive faulting associated with this salt ridge which prohibits lateral oil migration around the ridge, and oil compositions of each compartmentalized reservoir, all argue strongly against an updip lateral migration from an undefined source to the south of the salt ridge. At the same time, these facts suggest a local oil origin from three possible sources: A) shales interbedded with the oils, B) rocks in the southern limb of the syncline to the north of the salt ridge, or C) rocks at depth beneath the oil fields.

2) The Neogene, fine-grained rocks at Caillou Island have utlra-poor source-rock characteristics (T.O.C. = 0.3-0-.5%, HI's = 60-100, and $S_1 + S_2$ = 200-600 ppm). Also, the only primary migration mechanism which seems applicable to the organic-poor, Gulf Coast Tertiary shales is gaseous solution. However, this mechanism actually acts as a HC sink because of the need for a

free-gas phase at critical gas saturation levels with this migration mechanism.

3) Shales interbedded with the oil sands at Caillou Island (and other Gulf Coast oil fields) are improbable oil sources because: A) of their ultra-poor organic nature, B) of their limited volume from geometric considerations, C) of their low maturation rank, D) of the lack of a viable primary migration mechanism, and E) the shale bitumen is different than the oil.

4) For the same reasons as above (number 3), the shales of the southern limb of the snycline to the north of the salt ridge at Caillou Island are improbable oil source rocks. Further, lateral stratigraphic change in these rocks to more organic-rich rocks is unlikely.

5) Organic richness appears to increase with depth and/or age in the fine-grained rocks of the Gulf Coast, and possibly in all deltaic depositional systems, which may be due to the nature of deltaic deposition itself. In some cases (such as the Miocene shales at Caillou Island), although these increases in organic richness are significant, the rocks are still incapable of generating significant amounts of oil. In other cases (such as the Upper Cretaceous Gulf Series shales of the Jacobs-1 wellbore and the Eocene-Paleocene shales on which Sassen and Chinn (1990) report), thick sections of moderately organic-rich (T.O.C. = 2-6%, HI's = 250-500) rocks may be adequate source sections. These shifts in organic richness do not appear to be constant, with respect to either geologic age or geographic location, throughout the Gulf Coast.

6) Three possible sources for Gulf Coast Neogene oils exist at depth: A) these thick sections of moderately organic-rich Eocene to Upper Cretaceous (or older) shales with hydrogen-rich (Types I and II) OM, B) widespread Eocene-Paleocene coals and carbonaceous shales, and C) Lower Cretaceous-Jurassic, organic-rich, "black shale" type source rocks, which have high T.O.C. contents and high HI's, and which may floor the Tertiary sediment package throughout the Gulf Coast. However, a call upon any one of these as a source for Neogene oils will involve maturation ranks moderately to significantly greater than $R_o = 1.35$.

7) The call for an origin of the Caillou Island oils from any pre-Oligocene fine-grained rock at depth would generally be considered unlikely because of the hypothesis of the thermal extinction of C_{15}+ HC's by $R_o = 1.35$. However, the three principal lines of evidence which support this hypothesis can be explained by other causes, and a large body of data contradicts this hypothesis. Although it is firmly entrenched in petroleum geochemistry, I believe this hypothesis to be in error.

8) A large body of data from both nature and the laboratory suggests that the different OM Types have different reaction kinetics due to different bond strengths. Thus the specific reaction kinetics of the kerogen under consideration may enter heavily into models of HC generation, migration, and accumulation for the Gulf Coast. Type III OM undergoes the first detectable HC generation at $R_o = 0.6$, and intense HC generation and primary migration commence by $R_o \doteq 0.8$. Intense HC generation and primary migration occur from $R_o = 0.8$ to about 1.8, with thermal burnout (loss of all HC generation potential) by $R_o = 2.0$ in Type III OM. Types I and II OM apparently undergo intense HC generation and migration at more elevated (and yet undefined) maturation ranks, with kerogen burnout occurring only at ranks far above $R_o = 2.0$. As the original HI's of hydrogen-rich OM increase, apparently so do the maturation ranks required for intense HC generation.

9) Strong convictions exist among many Gulf Coast geologists and geochemists that coals cannot be oil source rocks. However: A) The three principal arguments against coals being source rocks can be replied to.

B) Persuasive lines of logic and evidence exist that hydrogen-rich coals can be oil source rocks. C) In other parts of the world, it is taken for granted that coals are oil source rocks. In my opinion, thick sections of hydrogen-rich Eocene-Paleocene coals in the Gulf Coast may represent a very significant oil source section.

10) With a model of deeper origin and vertical migration of oil in the Gulf Coast the fault zone becomes the most important exploration consideration, and specific exploration targets can be predicted by this model.

11) Except for fault throw, depth to salt in the interdomal salt basin area, and especially the sole-out depth of faults, no other known geologic parameters exhibit correlation with amount of oil reserves in the Gulf Coast, including the size and/or gathering area of anticlines. The correlation of fault throw (and probably sole-out depth of faults) exhibits correlation to oil reserve size in other petroleum-bearing delta systems also.

12) The "something from nothing" propositions for the organic-poor shales of the Gulf Coast (and other basins) do not take into account vast HC sinks which may negate the validity of these propositions.

13) A possible recoverable, natural-gas based, alternate resource of staggering proportions may exist in the hard-geopressure zone in parts of the Gulf Coast (and other basins) as a consequence of primary migration by gaseous solution. This resource, and its recovery, differ greatly from the geopressure resource under study by the Department of Energy research program.

REFERENCES

Barker, C., 1977, Aqueous solubility of petroleum as applied to its origin and primary migration: Discussion: Bulletin of American Association of Petroleum Geologists, v. 61, p. 2146-2149.

Bertrand, P., 1984, Geochemical and petrographic characterization of humic coals considered as possible oil source rocks: Organic Geochemistry, v. 6, p. 481-488.

Bissada, K. K., Katz, B. J., Barnicle, S. C,, and Schunk, D. J., 1990, On the origin of hydrocarbons in the Gulf of Mexico basin - A reappraisal: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 163-171.

Bustin, R. M., 1988, Sedimentology and characteristics of dispersed organic matter in Tertiary Niger delta: Origin of source rocks in a deltaic environment: Bulletin of American Association of Petroleum Geologists, v. 72, p. 277-298.

Clementz, D., 1979, Effect of oil and bitumen saturation on source rock pyrolysis: Bulletin of American Association of Petroleum Geologsits, v. 63, p. 2227-2232.

Dow, W. G., 1984, Oil source beds and oil prospect definition in the Upper Tertiary of the Gulf Coast: Transactions of Gulf Coast Association of Geological Societies, v. 34, p. 329-339.

Dow, W. G., Mukhopadhyay, P. K., and Jackson, T., 1988, Source rock potential and maturation of deep Wilcox from south-central Texas: Bulletin of American Association Petroleum Geologists, v. 72, p. 179.

Durand, B., 1982, Oil potential of coals - a geochemical approach: Journal of Petroleum Geology, v. 5, p. 209.

Durand, B., and Oudin, J. L., 1979, Exemple de migration des hydrocarbures dans une serie deltaique: Le delta de la Mahakam, Kalimantan, Indonesie, in, Proceedings of the Tenth World Petroleum Congress: Heyden, London, v. 2, p. 3-11.

Durand, B., and Paratte, M., 1983, Oil potential of coals: A geochemical approach: in, J. Brooks, ed., Petroleum Geochemistry and Exploration of Europe: Blackwell Scientific Publications, London, p. 255-264.

Fertl, W. H., and Timko, D. J., 1971, Salinity plots evaluate subsurface formations: World Oil, July, p. 93-98.

Frey, M. G., and Grimes, W. H., 1970, Bay Marchand-Timbalier Bay-Caillou Island salt complex, Louisiana: in, M. T. Halbouty, ed., Geology of giant petroleum fields: American Association of Petroleum Geology, Tulsa, p. 277-291.

Gussow, W, C., 1954, Differential entrapment of oil and gas- A fundamental principle: Bulletin of American Association of Petroleum Geologists, v. 38, p. 816-853.

Holcomb, C. W., 1971, Hydrocarbon potential of Gulf Series of Western Gulf basin: in I. H. Cram, ed., Future petroleum provinces of the United States - Their geology and potential: American Associaton of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 887-900.

Horsefield, B., Yordy, K. L., and Crelling, J. C., 1988, Determining the petroleum-generating potential of coal using organic geochemistry and organic petrology: Advances in Organic Geochemistry, 1987, Organic Geochemistry, v. 13, p. 121-129.

Huc, A. Y., and Hunt, J. M., 1980, Generation and migration of hydrocarbons in offshore South Texas Gulf Coast sediments: Geochimica et Cosmochimica Acta, v. 44, p. 1081-1089.

Huc, A. Y., Durand, J., Roucachet, J., Vandenbroucke, M., and Pittion, J. L., 1985, Comparison of three series of organic matter of continental origin: Organic Geochemistry, v. 10, p. 73-84.

Hvoslef, S., Larter, S. R., and Leytheuser, D., 1988, Aspects of generation and migration of hydrocarbons from coal-bearing strata of the Hitra Formation, Haltenbanken area, offshore Norway: Advances in Organic Geochemistry 1987, Organic Geochemistry, v. 13, p. 525-536.

International Oil Scouts, 1983, International Oil and Gas Development Yearbook 1984 (Review of 1982-1983), v. 53-54, Part 2, International Oil Scouts Association, Austin, Texas.

Jones, P. H., 1969, Hydrodynamics of geopressure in the northern Gulf of Mexico basin: Journal of Petroleum Technology, v. 21, p. 803-810.

Jones, R. W., 1978, Some mass balance and geologic constraints on migration mechanisms: in, W. H. Roberts, III, and R. J. Cordell, eds., Physical and chemical constraints on petroleum migration: American Association of Petroleum Geologists Continuing Education Course Note Series #8, p. A-1 to A-43.

Jones, R. W., 1980, Some mass balance and geological constraints on migration mechanisms: in, W. H. Roberts, and R. J. Cordell, eds., Problems of petroleum migration: American Association of Petroleum Geologists Studies in Geology, no. 10, Tulsa, Oklahoma, p. 47-68.

Jones, R. W., 1983, Origin and migration of petroleum in the Mesozoic and Cenozoic of the Gulf Coast: Habitat of oil and gas in the Gulf Coast, Fourth Annual Research Conference, Gulf Coast Section SEPM, Programs with Abstracts.

Jones, R. W., 1990, Conference highlights: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 1-8.

Katz, B. J., 1983, Limitations of 'Rock Eval' pyrolysis for typing organic matter: Journal of Organic Geochemistry, v. 4, p. 195-199.

Kaufman, R. L., Ahmed, A., and Elsinger, R. J., 1990, Gas Chromatography as a development and production tool for fingerprinting oils from individual reservoirs: Applications in the Gulf of Mexico: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 263-282.

Kennicutt, M. C., and Brooks, J. M., 1990, Seepage of gaseous and liquid petroleum in the northern Gulf of Mexico: in D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 309-310.

Kontorovich, A. E., and Trofimuk, A. A., 1976, Lithogenez i neftegazoobrazoveniye (lithogenesis and formation of oil and gas): in, N. B. Vassoyevich, et al., eds., Goryuchiye Iskopayeme - Problemy Geologii i Geokhimii Noftidov i Bituminoznykh Porod, Mezhdunarodnyy Geologicheskiy kongress XXV sessiya, Doklady Sovetskikh Geologov, p. 19-36, Nauka Press, Moscow.

Korashani, G. K., 1987, Oil-prone coals of the Wallon Coal Measures, Surat basin, Australia: in, A. C. Scott, ed., Coal and coal bearing strata: Recent advances, Geological Society Special Publication No. 32, p. 303-310.

Lafayette Geological Society, 1964, Typical oil and gas fields of southwestern Louisiana: in, J. C. McCampbell, and J. W. Sheller, eds., v. 1, Third Printing, Lafayette, Louisiana.

Lafayette Geological Society, 1970, Typical oil and gas fields of southwestern Louisiana: in F. W. Harrison, R. K. Jones, and L. C. Searles, eds., v. 2, Lafayette, Louisiana.

Lafayette and New Orleans Geological Societies, 1968, Geology of natural gas in south Louisiana: in, B. W. Beebe, and B. F. Curtis, eds., Natural gases in North America: American Association Petroleum Geologists Memoir 9, Vol., p. 840-855.

Landrum, J. H., Sutton, C., and Sofer, Z., 1988, Organic geochemical analysis of oils from coastal plain along Gulf of Mexico: Bulletin of American Association Petroleum Geologists, v. 72, p. 209.

Law, B. E., 1984, Relationships of source-rock, thermal maturity, and overpressuring to gas generation and occurrence in low-permeability Upper Cretaceous and Lower Tertiary rocks, greater Green River basin, Wyoming, Colorado, and Utah: in, J. Woodward, F. F. Meissner, and J. L. Clayton, eds., Hydrocarbon source rocks of the greater Rocky Mountain region: Rocky Mountain Association of Geologists, Denver, p. 469-490.

Lofton, C. L., and Adams, W. M., 1971, Possible future petroleum provinces of Eocene and Paleocene, Western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 855-886.

McAuliffe, C., 1966, Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cyclo-olefin and aromatic hydrocarbons: Journal of Physical Chemistry, v. 70, p. 1267-1275.

McAuliffe, C., 1969, Solubility in water of normal C_9 and C_{10} Alkane Hydrocarbons: Science, v. 163, p. 478-479.

Moses, P. L., 1961, Geothermal gradients: Drilling and Production Practice: American Petroleum Institute, New York, p. 57-63.

Newkirk, T. F., 1971, Possible future potential of Jurassic, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 927-953.

Palacas, J. G., 1984, South Florida basin - A prime example of carbonate source rocks of petroleum: in, J. G. Palacas, ed., Petroleum geochemistry and source rock potential of carbonate rocks: American Association of Petroleum Geologists Studies in Geology 18, Tulsa, Oklahoma, p. 71-97.

Phillipi, G. T., 1965, On the depth, time, and mechanism of petroleum generation: Geochimica et Cosmochimica Acta, v. 29, p. 1021-1051.

Pittion, J. L. and Gouadain, J., 1985, Maturity studies of the Jurassic 'Coal Unit' in three wells from the Haltenbanken area: in, B. M. Thomas, et al., eds., Petroleum geochemistry in exploration of the Norwegian Shelf: Graham and Trotman for the Norwegian Petroleum Society, Stavanager, Norway, p. 205-211.

Powell, L. D. and Woodbury, H. O., 1971, Possible future petroleum potential of Pleistocene, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 831-823.

Price, L. C., 1976, Aqueous solubility of petroleum as applied to its origin and primary migration: Bulletin of American Association of Petroleum Geologists, v. 60, p. 213-244.

Price, L. C., 1977, Aqueous solubility of petroleum as applied to its origin and primary migration: Reply: Bulletin of American Association of Petroleum Geologists, v. 61, p. 2149-2156.

Price, L. C., 1980a, Utilization and documentation of vertical oil migration in deep basins: Journal of Petroleum Geology, v. 2, p. 353-387.

Price, L. C., 1980b, Shelf and shallow basin oil as related to hot-deep origin of petroleum: Journal of Petroleum Geology, v. 3, p. 91-116.

Price, L. C., 1980c, Crude oil degradation as an explanation of the depth rule: Chemical Geology, v. 28, p. 1-30.

Price, L. C., 1981a, Aqueous solubility of crude oil to 400°C and 2,000 bars pressure in the presence of gas. Journal of Petroleum Geology, v. 4, p. 195-223.

Price, L. C., 1981b, Primary petroleum migration by molecular solution: Consideration of new data: Journal of Petroleum Geology, v. 4, p. 89-101.

Price, L. C., 1982, Organic geochemistry of core samples from an ultradeep hot well (300°C, 7 km): Chemical Geology, v. 37, p. 215-228.

Price, L. C., 1983, Geologic time as a parameter in organic metamorphism and vitrinite reflectance as an absolute paleogeothermometer. Journal of Petroleum Geology, v. 6, P. 6-38.

Price, L. C., 1986, A critical oveview and proposed working model of surface geochemical exploration: in, J. J. Davidson, ed., Unconventional methods in exploration for petroleum and natural gas IV: Dallas, Southern Methodist University Press, p. 245-304.

Price, L. C., 1988, The organic geochemistry (and causes thereof) of high-rank rocks from the Ralph Lowe-1 and other well bores: U.S. Geological Survey Open-File Report 88-651, 48p.

Price, L. C., 1989a, Louisiana oil-oil correlation by iso-cyclic, aromatic, and gasoline-range hydrocarbons, with an appendix of organic-geochemical rock data from selected wells in the Gulf Coast: U.S. Geological Survey Open-File Report 89-358, 90p.

Price, L. C., 1989b, Hydrocarbon generation and migration from Type III kerogen as related to the oil window: U.S. Geological Survey Open-File Report 89-194, 41p.

Price, L. C., 1989c, Primary petroleum migration from shales with oxygen-rich organic matter. Journal of Petroleum Geology, v. 12, p. 289-324.

Price, L. C., 1990, Crude-oil characterization at Caillou Island, Louisiana, by "generic" hydrocarbons: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 219-261.

Price, L. C., Clayton, J. L. and Rumen, L. L., 1979, Organic goechemistry of a 6.9-kilometer deep well, Hinds County, Mississippi: Gulf Coast Association of Geological Society Transactions, v. 29, p. 352-370.

Price, L. C., Clayton, J. L. and Rumen, L. L., 1981, Organic geochemistry of the 9.6 km Bertha Rogers No. 1 well, Oklahoma: Organic Geochemistry, v. 3, p. 59-77.

Price, L. C., Wenger, L. W., Ging, T. and Blount, C. W., 1983, Solubility of crude oil in methane as a function of pressure and temperature: Organic Geochemistry, v. 4, p. 201-221.

Price, L. C., Ging, T., Daws, T., Love, A., Pawlewicz, M. and Anders, D., 1984, Organic metamorphism in the Mississippian Devonian Bakken Shale North Dakota portion of the Williston Basin: in, J. Woodward, F. F. Meissner, and J. L. Clayton, eds., Hydrocarbon source rocks of the greater Rocky Mountain region: Rocky Mountain Association of Geologists, Denver, Co., p. 83-134.

Price, L. C. and Barker, C. E., 1985, Suppression of vitrinite reflectance in amorphous rich kerogen - A major unrecognized problem: Journal of Petroleum Geology, v. 8, p. 59-84.

Price, L. C. and Clayton, J. C., 1990, Reasons for and signfiicance of deep, high-rank hydrocarbon generation in the South Texas Gulf Coast: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 219-235.

Price, L. C., and Wenger, L. M., 1990, The influence of pressure on petroleum generation and maturation as suggested by hydrous pyrolysis: American Association of Petroleum Geologists Bulletin, v. 74, p. 743.

Prikryl, J. D., 1990, Origin of limestone cap rock at the Damon Mound Salt dome: A petrographic and geochemical model: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 219-235.

Radke, M., Schaefer, R., Leythaeuser, D. and Teichmüller, M., 1980, Composition of soluble organic matter in coals: Relation to rank and liptinite fluorescence: Geochimica et Cosmochimica Acta, 44, p. 1787-1800.

Rainwater, E. H., 1971, Possible future petroleum potential of lower Cretaceous, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 901-926.

Requejo, A. G., and Halpern, H. I., 1990, A geochemical study of oils from the South Pass 61 Field, Offshore Louisiana: in, Schumacher, D., and Perkins, B. F., eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 219-235.

Rice, D. D., Clayton, J. L., and Pawlewicz, M., 1989, Characterization of coal-derived hydrocarbons and source rock potential of coal beds, San Juan basin, New Mexico and Colorado, U.S.A.: International Journal of Coal Geology, v. 13, p. 597-626.

Roberts, H. H., Carney, R., and Aharon, P., 1990, The role of hydrocarbons in creating sediment and small-scale topography on the Louisiana continental slope: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 311-324.

Roe, G. D. and Polito, L. J., 1979, Source rocks for oils in the Ardjuna sub-basin of the Northwest Java basin, Indonesia: UN/ESCAP, CCOP Tech. Pub. 6, Bangcock, p. 180-194.

Rogers, M. A., Mcalary, J. D., and Bailey, N. J. L., 1974, Significance of reservoir bitumens to thermal maturation studies, western Canada basin: Bulletin of American Association of Petroleum Geologists, v. 58, p. 1806-1824.

Sagjó, Cs., 1980, Hydrocarbon generation in a super-thick Neogene sequence in south-east Hungary. A study of the extractable organic matter: in, A. G. Douglas, and J. R. Maxwell, eds., Advances in Organic Geochemistry 1979: Pergamon Press, London, p. 103-113.

Sassen, R. 1990, Geochemistry of carbonate source rocks and crude oils in Jurassic salt basins of the Gulf Coast: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 11-22.

Sassen, R., and Chinn, E. W., 1990, Implications of lower Tertiary source rocks in South Louisiana to the origin of crude oil, offshore Louisiana: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases:

Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 175-179.

Schmidt, G. V., 1971, Interstitial water composition and geochemistry of deep Gulf Coast shales and sands: Masters Thesis, Unviersity of Tulsa.

Schoell, M., Teschner, M., Wehner, H., Durand, B., and Oudin, J. L., 1983, Maturty-related biomarker and stable isotope variations and their applications to oil/source rock correlation in the Mahakam Delta, Kalimantan, in, Bjorøy, M., et al., eds., Advances in Organic Geochemistry 1981: Wiley, Chichester, p. 156-163.

Shinn, A. D., 1971, Possible future petroleum potential of upper Miocene and Pliocene, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 824-835.

Teichmüller, M., 1974, Generation of petroleum-like substances in coal seams as seen under the microscope: in, B. Tissot, and F. Bienner, eds., Advances in Organic Geochemistry 1973: Editions Technip., p. 379-407.

Teichmüller, M., and Durand, B., 1983, Fluorescence microscopial rank studies on lipinites and vitrinites in peats and coals and comparison with results of the ROCK EVAL pyrolysis: International Journal of Coal Geology, v. 2, p. 197-230.

Thomas, B. M., 1982, Land plant source rocks for oil and their significance in Australian basins: Journal of Australian Petroleum Exploration Association, v. 22, p. 166-178.

Thompson, K. F. M., and Kennicutt, M. C., 1990, Nature and frequency of occurrence of non-thermal alteration processes in Gulf of Mexico offshore oils: in, D. Schumacher, and B. F. Perkins, eds., Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference Society of Economic Paleontologists and Mineralogists Foundation, p. 199-218.

Thompson, S., Cooper, B. S., Morley, R. J., and Barnard, P. C., 1985, Oil-generting coals: in, B. M. Thomas, et al., eds., Petroleum geochemistry in exploration of the Norwegian Shelf: Graham and Trotman for the Norwegian Petroleum Society, Stavanger, Norway, p. 59-73.

Tipsword, H. L., Fowler, W. A., and Sorrell, B. J., 1971, Possible future petroleum potential of lower Miocene-Oligocene, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 835-854.

Tissot, B., 1984, Recent advances in petroleum geochemistry applied to hdyrocarbon exploration: Bulletin of American Assocation of Petroleum Geologists, v. 68, p. 545-563.

Tissot, B., and Welte, D., 1978, Petroleum formation and occurrence, Springer Verlag, New York, 538 p.

Tissot, B. P., Pelet, R., and Ungerer, PH., 1987, Thermal history of sedimentary basins, maturation indices, and kinetics of oil and gas generation: Bulletin of American Association of Petroleum Geologists, v. 71, p. 1445-1466.

Vandenbroucke, M., Durand, B., and Oudin, J. L., 1983, Detecting migration phenomena in a geological series by means of C_1-C_{35} hdyrocarbon amounts and distributions: in, M. Bjorøy, et al., eds., Advances in Organic Geochemistry 1981: John Wiley and Sons, New York, p. 147-155.

Vernon, R. C., 1971, Possible future petroleum potential of pre-Jurassic, western Gulf basin: Future petroleum provinces of the United States - Their geology and potential: American Association of Petroleum Geologists, Memoir 15, v. 2, Tulsa, p. 954-979, Wallace, W. E., 1970, Water production from abnormally pressured gas reservoirs, Part 2: Second Symposim Abnormal Subsurface Pore Pressure, Baton Rouge, Louisiana, Preprint SPE 2225, p. 63-86.

Waples, D., 1981, Organic geochemistry for exploration geologists: Burgess, Minneapolis, 151p.

Weber, K. J., and Daukorn, E., 1976, Petroleum geology of the Niger Delta: Proceedings Ninth World Petroleum Congress, Tokyo, v. 4, p. 209-221.

Wenger, L. M., 1987, Variations in organic geochemistry of anoxic-oxic black shale-carbonate sequences in the Pennsylvanian of the midcontinent, U.S.A.: Ph.D. dissertation, Department of Geology, Rice University, Houston, Texas.

Wenger, L. M., and Baker, D. R., 1987, Variations in vitrinite reflectance with organic facies - Examples from Pennsylvanian cyclotherms of the Midcontinent U.S.A.: Organic Geochemsitry, v. 11, p. 411-416.

Wilson, R. D., Monaghan, P. H., Osanik, A., Price, L. C., and Rogers, M. A., 1974, Estimate of annual input of petroleum to the marine environment from natural marine seeapge: Transactions of Gulf Coast Association Geological Societies, v. 23, p. 182-193.