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The organic geochemistry (and causes thereof) of high-rank rocks
from the Ralph Lowe-1 and other well bores

by

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ABSTRACT

High C_{15+} bitumen coefficients, 40-154 mg/g organic carbon (O.C.) and moderate values (34-157 mg/g O.C.) for the ROCK EVAL S_2 pyrolysis peak are present in the deepest rocks of the Ralph Lowe-1 well bore, West Texas. These data are unexpected considering the maturation ranks ($R_o = 3.5$ to 5.0), ages (Mississippian-Devonian to Ordovician), present-day equilibrium burial temperatures (216°-246°C), and burial depths (7.1-8.2 km) of the rocks. These data correlate with a change in organic matter (OM) type in the deepest rocks of the well bore, from oxygen-rich to an inferred originally hydrogen-rich OM. This OM change is documented by maceral analysis and kerogen hydrogen/carbon atomic ratios. At the depth where this change in OM type takes place, sharp increases occur in the concentration of C_{15+} HC's and bitumen, and in the values of the S_2 pyrolysis peak from zero S_2 values in the shallower, but high-rank, rocks with oxygen-rich OM. In this well, what appears to be a high-rank ($R_o > 3.5$), deep hydrocarbon (HC) generation zone in point of fact is due to the change in OM type at depth.

In the rocks of the Ralph Lowe-1 with oxygen-rich OM, loss of C_{15+} HC generation potential occurs by $R_o = 1.8-2.0$ which agrees with the results of other studies. However, unlike other situations of some high-rank rocks with oxygen-rich OM (such as in the Douala basin or in coal suites), the rocks of the Ralph Lowe-1 with oxygen-rich OM still retain measurable to moderate amounts of C_{15+} HC's at maturation ranks in excess of $R_o = 1.35$, in fact to ranks as high as $R_o = 3.5$. These unexpectedly high C_{15+} HC concentrations are believed to be due to inefficient primary migration. Standard organic-geochemical maturation indices do not show the expected trends versus depth, R_o , or each other in the rocks of the Ralph Lowe-1. Most, or all, of these results have been duplicated in high-rank ($R_o = 2.0-5.0$) rocks from other deep well bores. The rocks of this (and the other) studies have been buried for hundreds of millions of years at minimal burial temperatures of 200°-300°C.

The organic-(and inorganic-) geochemical data from the deeply-buried, high-rank rocks of the Ralph Lowe-1, and other deep, well bores, other published data, and accepted precepts from other disciplines all contradict some aspects of conventional wisdom in petroleum-organic geochemistry regarding HC generation, maturation, and eventual thermal destruction: 1) The threshold of intense HC generation (TIHG) occurs in fine-grained rocks by $R_o = 0.6$ or present-day (maximal) burial temperatures of 120°C. 2) C_{15+} HC's are thermally destroyed by $R_o = 1.35$, or burial temperatures of 110°-250°C (depending on burial time). 3) Greenschist metamorphism and graphite formation occur by burial temperatures of 200°-250°C.

Four principal reasons are hypothesized for these contradictions: 1) A possible erroneous assignation of geologic time as the principal factor responsible for high levels of organic metamorphism found in geologically-old rocks at shallow-burial depths and/or at low-burial temperatures. Erosion, and/or brief-geologic periods of highly-elevated paleogeothermal gradients, can explain the elevated levels of organic maturation found in these rocks. 2) A possible erroneous assignation of the thermal destruction of C_{15+} HC's as being the factor responsible for the decrease (over the maturation rank range $R_o = 0.8-1.35$) and disappearance (at $R_o = 1.35$) of C_{15+} HC's in some rocks with oxygen-rich OM (such as at Douala). Four separate lines of evidence suggest

that this disappearance and loss of C_{15+} HC's may not be due to their thermal destruction. Primary migration by gaseous solution is hypothesized as the parameter responsible for this feature. 3) Lack of recognition that high static fluid (confining) pressures may suppress all aspects of, and thus also be a dominant controlling parameter of, organic (and inorganic) metamorphism. Pervasive shearing, which relieves high static fluid pressures, appears to promote both inorganic and organic metamorphism. 4) A lack of recognition that OM type is a probable dominant controlling parameter of organic metamorphism. Oxygen-rich (Type III) OM undergoes the TIHG by $R_o = 0.6$ (present-day, maximal burial temperatures of 120°C) and loses all HC generation potential by $R_o = 1.8$ to 2.0 . Hydrogen-rich (Types I and II) OM apparently undergo the TIHG at present-day, maximal burial temperatures only in excess of 210°C ($R_o \geq 1.2$) and still retain moderate C_{15+} HC generation potential to maturation ranks of at least $R_o = 5.0$. All aspects of organic metamorphism appear to be suppressed in hydrogen-rich OM compared to what the maturation levels would be in oxygen-rich OM buried under the same conditions.

GEOLOGY AND STRATIGRAPHY

The asymmetric Permian basin in west Texas and southeastern New Mexico (Fig. 1) is bounded on the south by the Marathon-Ouachita thrust, on the west by the Diablo platform and the Pedernal uplift, on the north by the Matador Arch, and on the east by the Bend Arch. The main structural features of the Permian basin are the Delaware and Val Verde depocenters (sediment thicknesses in excess of 9 km), the Central Basin Platform--a fault block high to the east-northeast of the Delaware basin, and the Midland Basin, to the east-northeast of the Central Basin Platform. Most of the sediments in the Delaware and Val Verde depocenters are Paleozoic.

From Cambrian through Mississippian time, the area underwent only mild structural deformation, which produced local unconformities and structures of low, broad relief. From Early Pennsylvanian through Early Permian time, strong structural deformation and orogenic movement resulted in the present-day structural framework of the region. In Permian time, thick sediments were deposited in the Delaware and Val Verde depocenters and in the shallower Midland Basin. In Middle to Late Permian time, tectonic activity was greatly reduced and reefs formed on the shelf and platform areas. Throughout the Triassic to Late Cretaceous, at different times, different basinal areas underwent uplift and erosion, or marine transgression. Significant igneous activity took place, in the early Tertiary, in the Marathon thrust belt and at the southern boundaries of the Delaware and Val Verde basins (Weisman, 1971). The Ralph Lowe #1 (University 17) well bore was drilled on the axis of the Val Verde-Delaware basins near the center of Pecos County, Texas, about 15 km southeast of Fort Stockton. A partial stratigraphy of the well bore is given in table 1, and it was typical of the area with one exception: The stratigraphy of the 6.5 km Pan American "CS" well bore, 4.8 km due southeast, indicated that the top of the Pennsylvanian should have been encountered at about 5.6 km. Instead from 5,627 to 6,565 m, conglomerates and giant boulder beds were interbedded between arkosic sandstones and minor shales. Exotic boulders up to 29 m thick composed of Ordovician Simpson, Ordovician Montoya, and Mississippian-Devonian Woodford rocks were present in the boulder beds. Dips of these strata ranged from 17° to 40° , and the operators of the well interpreted this section as fan deposition off the Fort Stockton high (see Guinan, 1971). The well encountered gas (84 percent methane and 10 percent carbon-dioxide) in the Cambro-Ordovician

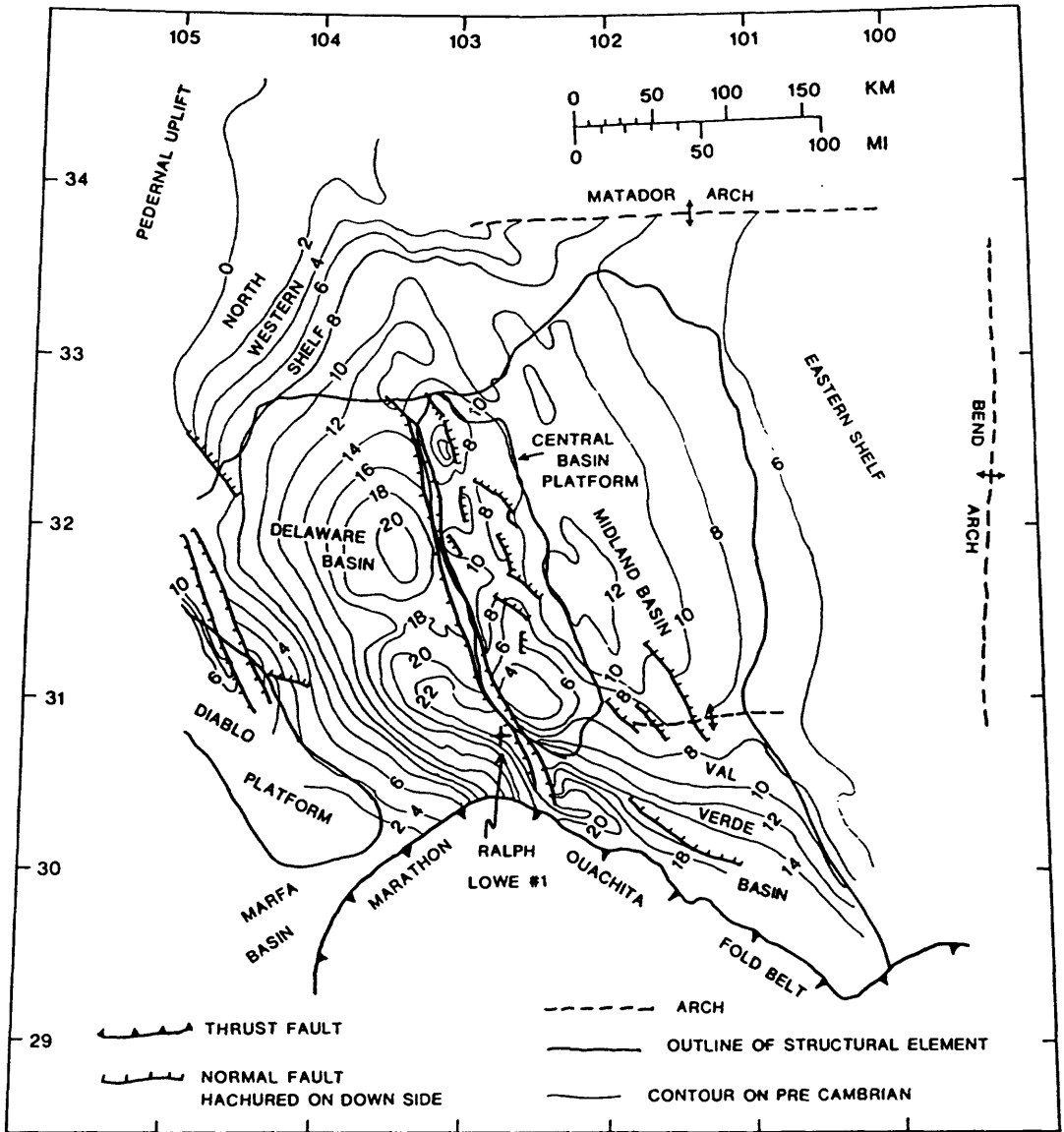


Figure 1. Sediment thickness on crystalline basement in thousands of feet for the West Texas Permian basin. Estimates over basin troughs are conservative. Location of the Ralph Lowe-1 is shown by the cross. Modified from Dolton and others (1979).

Table 1.--Stratigraphic units and the depth to the top of each unit in km for the Ralph Lowe-1 well bore.
 (Data supplied by Hugh Freznel, Chief Geologist, Ralph Lowe-1 drilling venture, written communication, 1975).

Geologic Age	Stratigraphic Unit	Depth to Stratigraphic Top in Km
Permian	Ochoa Series	0.394
	(Rustler)	
	Guadalupe Series	0.608
	(Tansil)	
	Delaware Sand	1.195
	(Lower Guadalupian)	
	Leonard Series	1.797
	Wolfcamp Series	2.354
Pennsylvanian	Pennsylvanian	6.565
Mississippian	Barnett Shale	7.009
	Mississippian Lime	7.116
Mississippian-	Woodford Shale	7.319
Devonian		
Devonian	Devonian Chert	7.406
Silurian	Silurian	7.776
Ordovician	Lower Ordovician	8.314
	Ellenburger Dolomite	

Ellenburger formation. However, due to extensive formation damage during attempted completion, the well was non commercial.

This previous discussion was based on Hills (1968), Salisbury (1968), Dolton and others (1979), and on an extensive written communication from Hugh Freznel (1976) who was the chief geologist of the Ralph Lowe-1 well bore.

SAMPLES AND METHODS

Samples were drill cuttings in paper packets of 10 or 20 ft (3.05-6.10 m) intervals. A contamination test (Price, and others, 1979) showed no contamination from migrated hydrocarbons (HC's) or organic-based drilling fluids. The characteristics of the gas chromatograms of the C₁₅₊ saturated and aromatic HC's confirmed this. Caving represents another possible source of contamination, especially because of the small sample intervals. However, the well was cased at 0.614, 3.339, 5.624 and 7.169 km (Hugh Freznel, written communication, 1976). The significant organic-geochemical data of this well were derived from samples between the depths of 7.324 to 8.191 km. Therefore, any caving would have originated from rocks buried to at least 7.169 km and such caving would not significantly change the conclusions of this study.

WELL BORE TEMPERATURES

The Ralph Lowe #1, after completion, had a logged temperature of 212°C at total depth (8.692 km). The well was then shut in and re-entered over a month later, at which time a bottom hole temperature of 260°C was measured (Drilling, DCW, 1972). This latter temperature is taken as the correct (equilibrated) bottom hole temperature for the bore hole which results in a present-day geothermal gradient of 2.74°C/100 m for this area of the basin.

KEROGEN ANALYSES

Kerogen isolations were carried out by Core Laboratories, Dallas, Texas and by Alonza Love, U.S. Geological Survey, Denver, CO. Kerogen elemental analyses were carried out by Alonza Love. R_o analyses (Table 2) were performed by Robertson Research, Houston, Texas. In this paper, all R_o values carry an inferred percent sign. R_o values (Fig. 2) increase uniformly with depth to a maximum value of R_o = 4.04. The solid line in the R_o plot of figure 2 was generated by linear regression analysis of the R_o data and has a correlation coefficient of r = 0.992 to the data. The R_o histograms for the data of figure 2 are shown in figure 3. The range of the R_o values in any one sample increases with increase in maturation rank and becomes quite large at the highest maturation ranks. This same trend was observed in the R_o histograms of Paleozoic rocks from another ultra-deep well bore (Price and others, 1981). Hunt (1979, p. 332) noted that R_o histograms broaden with rank increase above R_o = 1.0, and broaden even more above R_o = 2.0 to 3.0. This feature is largely due to an increase in anisotropy in the reflectance of vitrinite with increase in maturation rank (Stach and others, 1982).

Maceral analyses (Fig. 2) show that at shallower depths the organic matter (OM) is largely (60 to 80 percent) composed of vitrinite (an oxygen-rich maceral) and inertinite. In the deepest samples, the percentage of amorphous (assumed originally hydrogen-rich) macerals increases from 5 percent to 55-60 percent. The hydrogen to carbon (H/C) atomic ratio of the kerogen (Fig. 2)

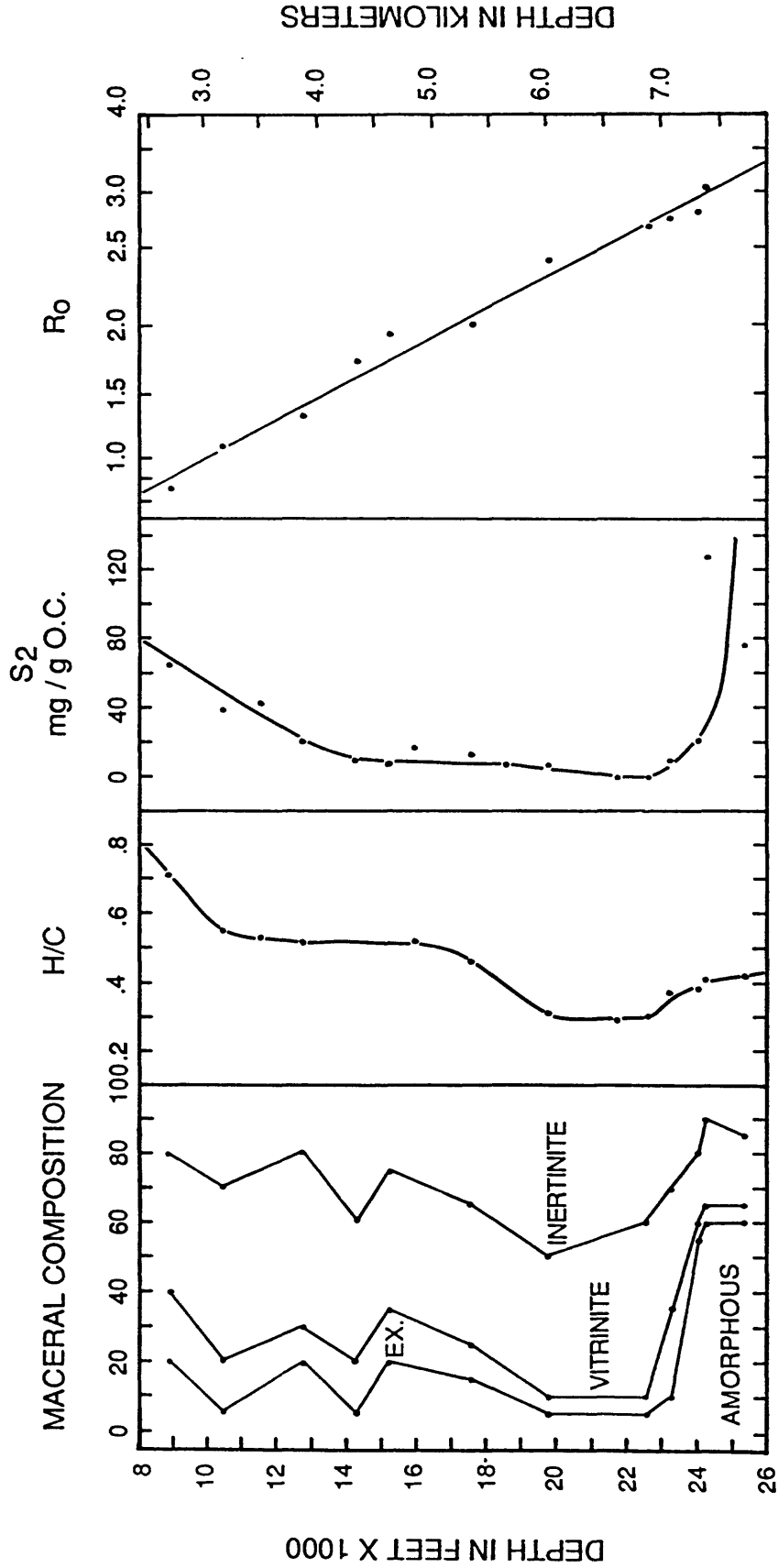


Figure 2. Plot of maceral composition in percent, atomic hydrogen/carbon (H/C) ratio for isolated kerogen, the S₂ pyrolysis peak (mg/g O.C.) for Soxhlet-extracted rocks, and R_o, all versus depth, for rock samples from the Ralph Lowe-1. EX. refers to exinite. Data from tables 2, 3 and 5.

Table 2.--Maceral and R_o analyses of kerogen isolates from rocks of the Ralph Lowe-1 well bore.

Depth in Kilometers	Organic Matter Type in Percent				R_o
	Amorphous	Exinite	Vitrinite	Inertinite	
2.706-2.713	20	20	40	20	0.86 ± 0.11
3.185-3.194	5	15	50	30	1.07 ± 0.09
3.889-3.901	20	10	50	20	1.25 ± 0.11
4.346-4.359	5	15	40	40	1.66 ± 0.11
4.633-4.639	20	15	40	25	1.91 ± 0.26
5.358-5.364	15	10	40	35	2.02 ± 0.19
6.026-6.032	5	5	40	50	2.79 ± 0.27
6.882-6.888	5	5	50	40	3.33 ± 0.28
7.080-7.087	10	5	55	30	3.47 ± 0.37
7.324-7.330	55	5	20	20	3.59 ± 0.37
7.391-7.398	60	5	25	10	4.04 ± 1.17
7.718-7.724	60	5	20	15	NA

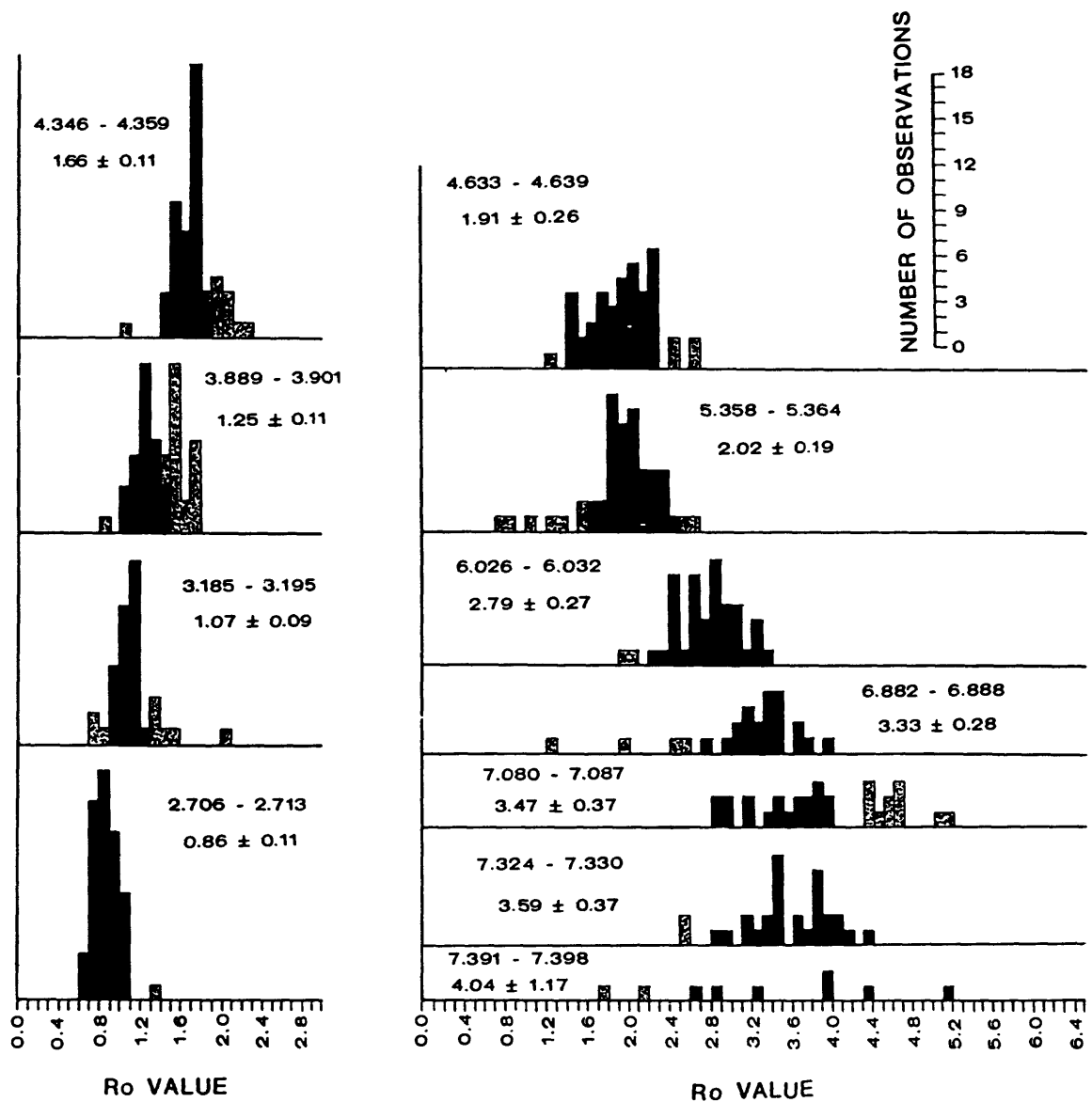


Figure 3. R_o histograms for kerogen isolates from rock samples of the Ralph Lowe-1. Upper numbers are depth interval for each sample in km. Lower numbers are mean R_o values with standard deviation. Each horizontal line is zero number of observations for that sample. Bars with stippled patterns represent reworked or non-indigenous vitrinite populations, as interpreted by the analyst. Analyses by Robertson Research, Houston, Texas.

Table 3.--Elemental analyses and atomic H/C ratios of kerogen isolates from the Ralph Lowe-1 well bore.

Depth in Kilometers	Elemental Analyses (normalized percent)				Atomic Ratios		
	C	H	N	O	H/C	N/C	O/C
2.706 - 2.713	75.10	4.46	2.13	18.32	0.71	0.024	0.18
3.185 - 3.194	76.60	3.53	1.95	17.92	0.55	0.022	0.18
3.505 - 3.517	80.16	3.55	1.68	14.61	0.53	0.018	0.14
3.889 - 3.901	80.02	3.46	1.72	14.79	0.52	0.018	0.14
4.346 - 4.359	NA	NA	NA	NA	NA	NA	NA
4.633 - 4.639	NA	NA	NA	NA	NA	NA	NA
4.868 - 4.874	83.82	3.66	1.47	11.05	0.52	0.015	0.10
5.358 - 5.364	83.08	3.18	1.19	12.55	0.46	0.012	0.11
5.654 - 5.660	NA	NA	NA	NA	NA	NA	NA
6.026 - 6.032	86.17	2.20	1.05	12.02	0.31	0.010	0.10
6.629 - 6.635	84.71	2.04	0.68	12.57	0.29	0.007	0.11
6.882 - 6.888	82.73	2.11	0.72	14.43	0.30	0.007	0.13
7.080 - 7.087	81.26	2.54	1.11	15.09	0.37	0.012	0.14
7.324 - 7.330	83.73	2.63	1.40	12.26	0.38	0.014	0.11
7.391 - 7.398	83.00	2.87	1.14	12.98	0.41	0.012	0.12
7.718 - 7.724	82.77	2.89	1.26	13.08	0.42	0.013	0.12

decreases with increase in depth from 0.72 in the 2.706-2.713 km sample to values around 0.30 at depths of 6.0 to 6.8 km. However, in the deepest samples, which contained high percentages of amorphous OM, the trend of the kerogen H/C atomic ratio reverses and increases to values of 0.37 to 0.42. The changes in both the kerogen H/C atomic ratio and in the maceral composition are proposed to reflect a change from mainly oxygen-rich (Type III) OM to an inferred originally hydrogen-rich (Type I or II) OM in the deepest rocks of the well. Important organic-geochemical changes in these deep rocks also reflect this OM type change.

SOXHLET EXTRACTIONS-SILICA GEL CHROMATOGRAPHY

The methods employed in Soxhlet extraction, silica gel chromatography, and gravimetric determinations of the various fractions are described in Price and others (1979, p. 353). With the exception of small aliquants for C_{15+} bitumen determinations, the solvent extracts of the two deepest samples were destroyed in a large fire at the Denver Federal Center in 1976. Thus, silica gel chromatography data are not available for these two samples (Table 4). The C_{15+} bitumen coefficient (mg/g O.C.), for samples with T.O.C. contents of at least 0.50 percent (Fig. 4), exhibits a slight decrease from 2.7 km to the 4.633-4.639 km sample and from 4.6 to 5.6 km exhibits a bell shaped curve. In the deepest samples, the C_{15+} bitumen coefficient dramatically increases to maximum of about 150 mg/g O.C.

C_{15+} bitumen (Fig. 5) ranges from 109 to 500 ppm from 2.7 to 6.9 km, and increases dramatically in the deepest rocks to values ranging between 1,410 to 3,590 ppm. The amount of C_{15+} bitumen, and the values for the C_{15+} bitumen coefficient, are extraordinary in these deep rocks, considering their burial depth (7.080-8.191 km), age (Mississippian-Devonian to Ordovician), and present day burial temperatures (224° to 246°C). The HC coefficient (mg C_{15+} HC's/g O.C., Fig. 6) and the amounts of C_{15+} HC's in ppm (Fig. 7), when plotted versus depth, show the same trends as does C_{15+} bitumen.

The deep C_{15+} HC and bitumen data would seem to indicate that a deep generation zone had been encountered in the Ralph Lowe-1. However, the increases in C_{15+} bitumen and HC's in the rocks at burial depths in excess of 6.9 km correspond with a change in the OM type of these rocks, from oxygen rich to originally hydrogen-rich OM. Thus, it is hypothesized here that the quantitative changes in the solvent extractable OM at depth are not the result of a HC generation zone but are due solely to the change in OM type in the deep rocks of these well. The reasons for the bell shaped curves in the C_{15+} bitumen and HC coefficients between 4.6 to 5.6 km are discussed below.

The maturation rank equated to the thermal deadline for C_{15+} HC's ($R_o = 1.35$) is reached at a depth of 3.97 km in the Ralph Lowe #1 well bore. Yet, the rocks from 4.3 to 8.2 km have C_{15+} bitumen contents ranging from 109 to 3,590 ppm, C_{15+} bitumen coefficients ranging from 12 to 154 mg/g O.C., and the C_{15+} HC's show similar trends. In the Ralph Lowe #1, C_{15+} HC's and bitumen are surviving in moderate to high concentrations to maturation ranks of $R_o = 4.0-5.0$, which are far above the hypothesized thermal deadline for C_{15+} HC's at $R_o = 1.35$.

Table 4. RESULTS OF SOHXLLET EXTRACTIONS AND SILICA GEL CHROMATOGRAPHY

[T.O.C., total organic carbon in weight percent; CaCO₃ %, weight percent calcium carbonate; C₁₅+ BIT ppm, C₁₅+ bitumen in ppm (dry rock weight); mg BIT/gOC, milligrams of C₁₅+ bitumen per gram of organic carbon; SAT HC and ARO HC ppm, saturated and aromatic hydrocarbons in ppm; Total HC ppm, C₁₅+ saturated plus aromatic hydrocarbons in ppm; mg HC/gOC, milligrams of C₁₅+ hydrocarbons per gram of organic carbon; NSO ppm, resins and asphaltenes in ppm; SAT/ARO, the ratio of saturated to aromatic hydrocarbons; HC/NSO, the ratio of total hydrocarbons to resins and asphaltenes; NA, not available]

Depth km	T.O.C.	CaCO ₃ %	C ₁₅ +BIT ppm	mg BIT gOC	SAT HC ppm	ARO HC ppm	Total HC ppm	mg HC gOC	NSO ppm	SAT ARO	HC NSO	Pristane Phytane	Geologic Age (and stratigraphic unit)
2.706 - 2.713	0.80	14.5	239	30	60	46	106	13	133	1.30	0.80	2.57	Permian - (Upper Wolfcamp)
3.185 - 3.194	0.78	13.2	134	17	59	20	79	10	55	2.95	1.43	2.25	Do.
3.505 - 3.517	0.60	12.5	133	22	72	16	88	14	45	4.50	1.96	2.18	Do.
3.889 - 3.901	0.84	9.4	113	13	56	15	71	9	42	3.73	1.69	1.82	Do.
4.346 - 4.359	0.85	8.7	112	13	60	13	73	9	39	4.62	1.87	2.13	Do.
4.633 - 4.639	0.91	28.2	109	12	42	10	52	6	57	4.20	0.91	1.89	Do.
4.868 - 4.874	0.52	36.7	146	28	60	33	93	18	53	1.82	1.75	1.76	Do.
5.358 - 5.364	0.38	33.9	194	51	75	23	88	23	106	3.26	0.83	1.39	Do.
5.654 - 5.660	0.68	8.2	136	20	45	14	59	9	77	3.21	0.77	1.75	Do.
6.026 - 6.032	1.39	7.3	358	26	126	53	179	13	179	2.38	1.00	1.79	Do.
6.629 - 6.635	1.34	14.6	500	37	273	59	332	25	168	4.63	1.97	2.03	Pennsylvanian
6.882 - 6.888	3.08	12.4	451	14	161	90	251	8	200	1.79	1.26	2.08	Do.
7.080 - 7.087	3.46	23.7	1,410	41	790	240	1,030	30	380	3.31	2.71	1.60	Mississippian (Barnett Shale)
7.324 - 7.330	4.32	10.5	1,650	38	1,140	240	1,380	32	270	4.79	5.10	1.74	Mississippian (Woodford Shale)
7.391 - 7.398	2.37	9.6	3,590	151	1,150	460	1,610	68	1,980	2.49	0.81	1.19	Do.
7.718 - 7.724	2.68	60.8	2,420	90	NA	NA	NA	NA	NA	NA	NA	NA	Ordovician (Simpson)
8.181 - 8.191	1.36	36.2	2,100	154	NA	NA	NA	NA	NA	NA	NA	NA	Ordovician (Oil Creek)

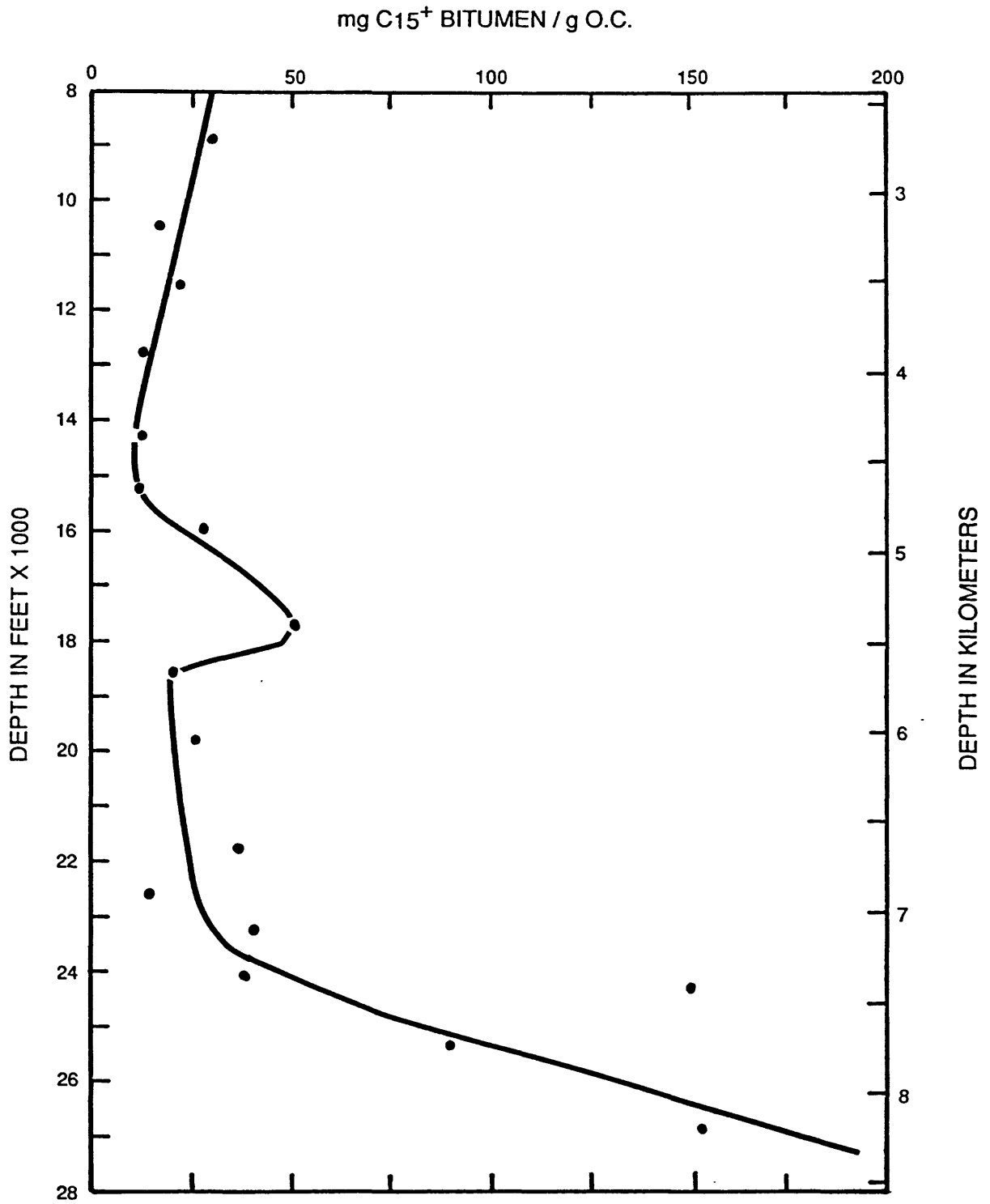


Figure 4. Plot, versus depth, of the C₁₅⁺ bitumen coefficient (mg C₁₅⁺ bitumen/g O.C.) for Soxhlet-extracted rocks of the Ralph Löwe-1. Data from table 4.

C₁₅⁺ BITUMEN IN ppm

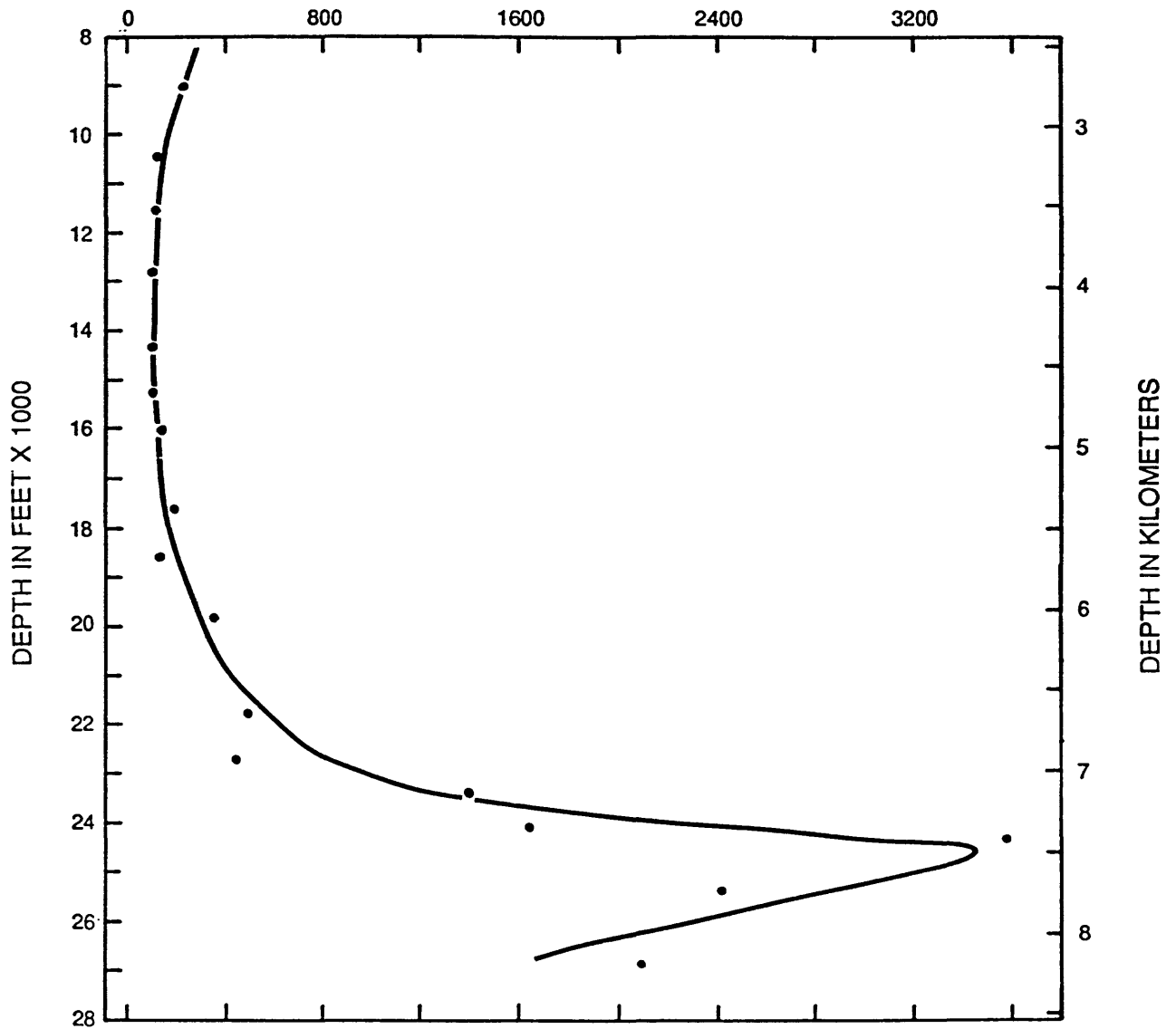


Figure 5. Plot, versus depth, of C₁₅⁺ bitumen in ppm (by weight) for Soxhlet-extracted rocks of the Ralph Lowe-1. Data from table 4.

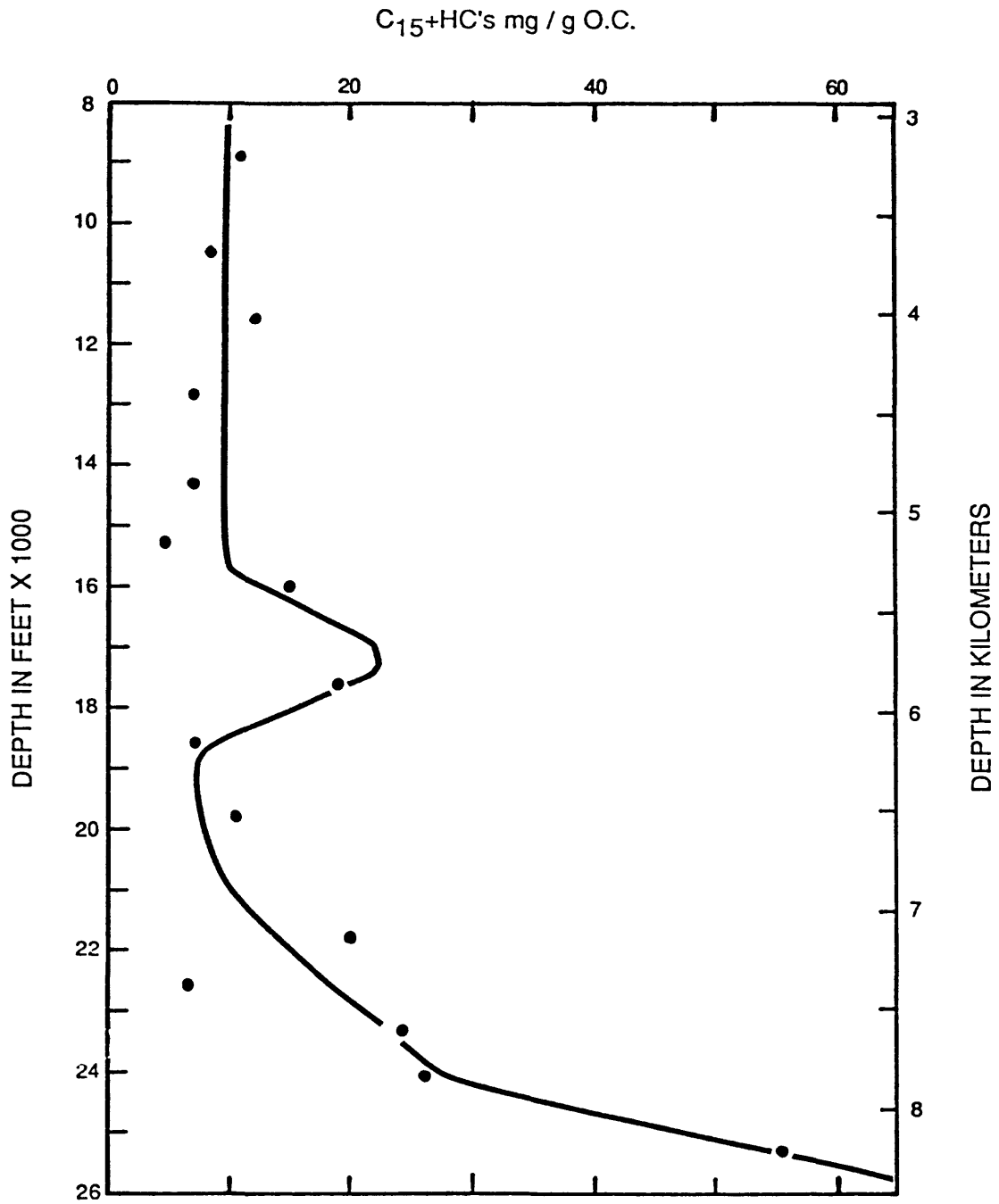


Figure 6. Plot, versus depth, of the C₁₅+ HC coefficient (mg C₁₅+ HC's/g O.C.) for Soxhlet-extracted rocks of the Ralph Lowe-1. Data from table 4.

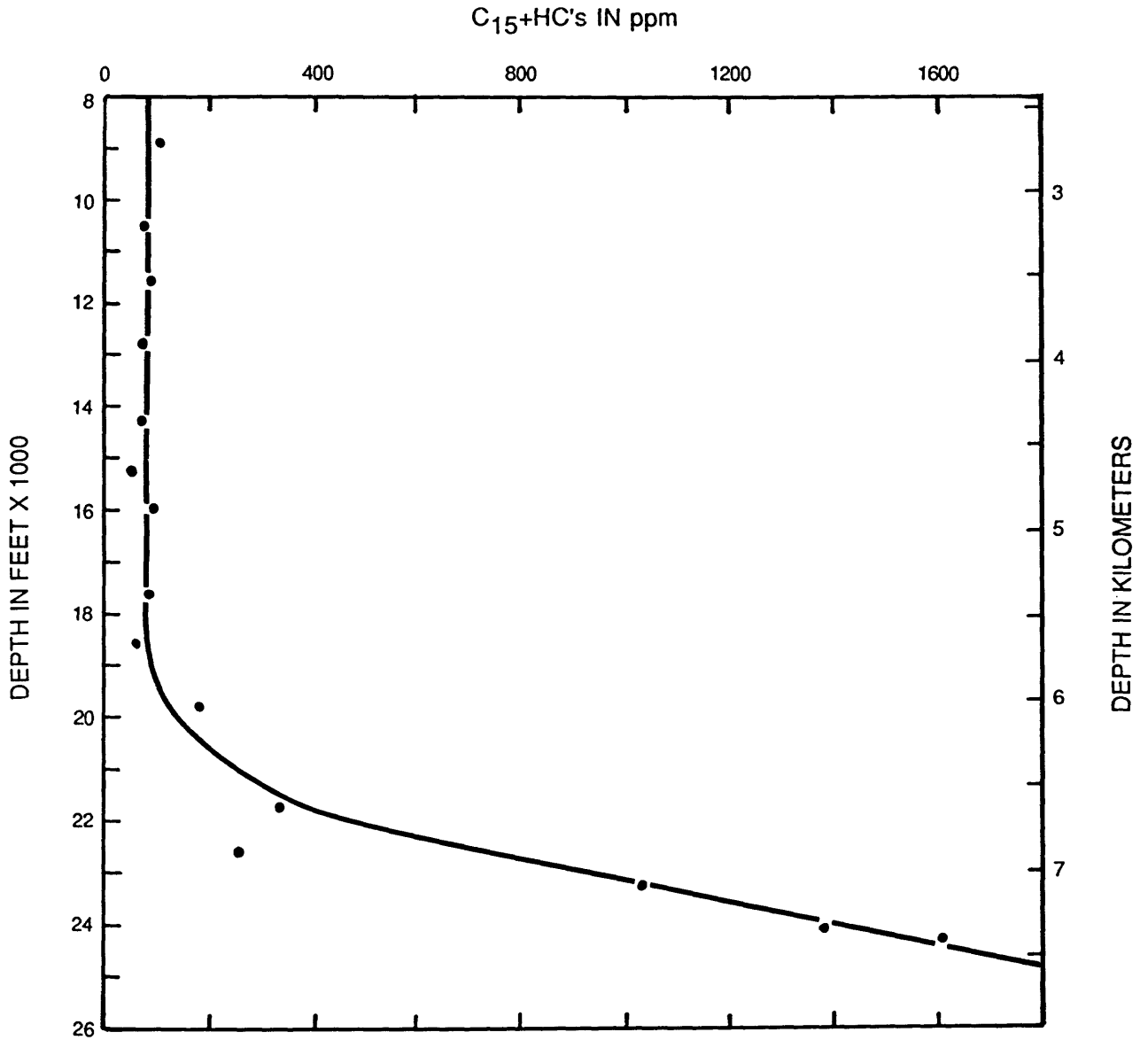


Figure 7. Plot, versus depth, of C₁₅+ HC's in ppm (by weight) for Soxhlet-extracted rocks of the Ralph Lowe-1. Data from table 4.

From table 4, the calcite content of the rocks, the ratio of saturated to aromatic C_{15+} HC's, and the ratio of C_{15+} HC's to NSO bearing compounds (HC/NSO ratio) show no meaningful correlation with each other, with other organic geochemical parameters, or with depth.

ROCK EVAL PYROLYSIS

ROCK EVAL pyrolysis was performed on splits of rock samples which had been Soxhlet extracted, as well as on unextracted samples (Fig. 8). The S_1 pyrolysis peak, when normalized to organic carbon (mg/g O.C.), is an approximation of the C_{15+} HC coefficient as determined by Soxhlet extraction. In figure 8, the S_1 peak decreases from a value of 94.7 mg/g O.C. in the 2.706-2.713 km sample ($R_o = 0.86-0.91$) to a minimum value of 10.8 mg/g O.C. by 4.35 km ($R_o = 1.55$). This is the expected trend by the hypothesis of a C_{15+} HC thermal deadline by $R_o = 1.35$, and a trend which has been documented in previous studies: a decrease in C_{15+} HC's from a maximum at $R_o = 0.8$ to low or zero concentrations by $R_o = 1.35$. This trend was observed at Douala by Albrecht and others (1976), and Durand and Espitalié (1976); in coals by Hood and Castanõ (1974), and by Teichmüller and Durand (1983); in the Mahakam delta by Vandenbroucke and others (1983); in offshore Texas Gulf Coast rocks by Huc and Hunt (1980); and in many other localities. In the past, most investigators have attributed such decreases in C_{15+} HC's, or in the S_1 ROCK EVAL pyrolysis peak values, over the maturation rank range $R_o = 0.8$ to $1.35+$, to HC thermal destruction. Price (1989) suggested that such HC concentration decreases were not necessarily due to C_{15+} HC thermal destruction, but instead could be explained by intense primary petroleum migration (by gaseous solution). The data of figures 4-8 do not support the hypothesis of a thermal destruction of C_{15+} HC's by $R_o = 1.35$, in the rocks of the Ralph Lowe-1. Further, similar data have been reported from rocks of other deep well bores (Price and others, 1979, 1981; Price, 1982; Price, 1983, table 1; and Sajgó, 1980).

The moderate to high values of C_{15+} HC's and/or of the S_1 pyrolysis peak found in the rocks of the Ralph Lowe #1 at maturation ranks in excess of $R_o = 1.5$ are proposed as due to two causes. First, an inefficiency of primary migration by gaseous solution from the rocks with oxygen-rich OM over the 4.5-7.0 km depth interval. As such, all C_{15+} HC's were not stripped from the rocks at maturation ranks of $R_o > 0.9$ as has been observed in other studies (Hood and Castanõ, 1974; Albrecht and others, 1976; and Teichmüller and Durand, 1983). (Other examples exist of moderate to high concentrations of C_{15+} HC's in rocks with oxygen-rich OM at ranks of $R_o = 1.0$ to 2.0 - see Law, 1984). The second cause for the high amounts of C_{15+} HC's, in some rocks of the Ralph Lowe #1, is thought to be due to the change of OM type from oxygen-rich to hydrogen-rich in rocks deeper than 7.0 km. Evidence has been advanced that HC generation from hydrogen-rich OM and the thermal burnout of hydrogen-rich OM may require significantly higher maturation ranks than HC generation from, and kerogen burnout of, oxygen-rich OM (Price and others, 1984; and Price and Barker, 1985).

The cause of the bell-shaped curves in the plots of C_{15+} bitumen and HC coefficients (Figs. 4 and 6, respectively) between 4.6-5.6 km is believed due to primary migration by gaseous solution. Over this depth range, T.O.C. values exhibit an inverse relationship with the C_{15+} bitumen and HC coefficients. As discussed in Price (1988), all other things being equal, decreases in T.O.C. contents decrease the effectiveness of primary migration by gaseous solution, as less gas is available per unit of rock to act as a migration agent. Although

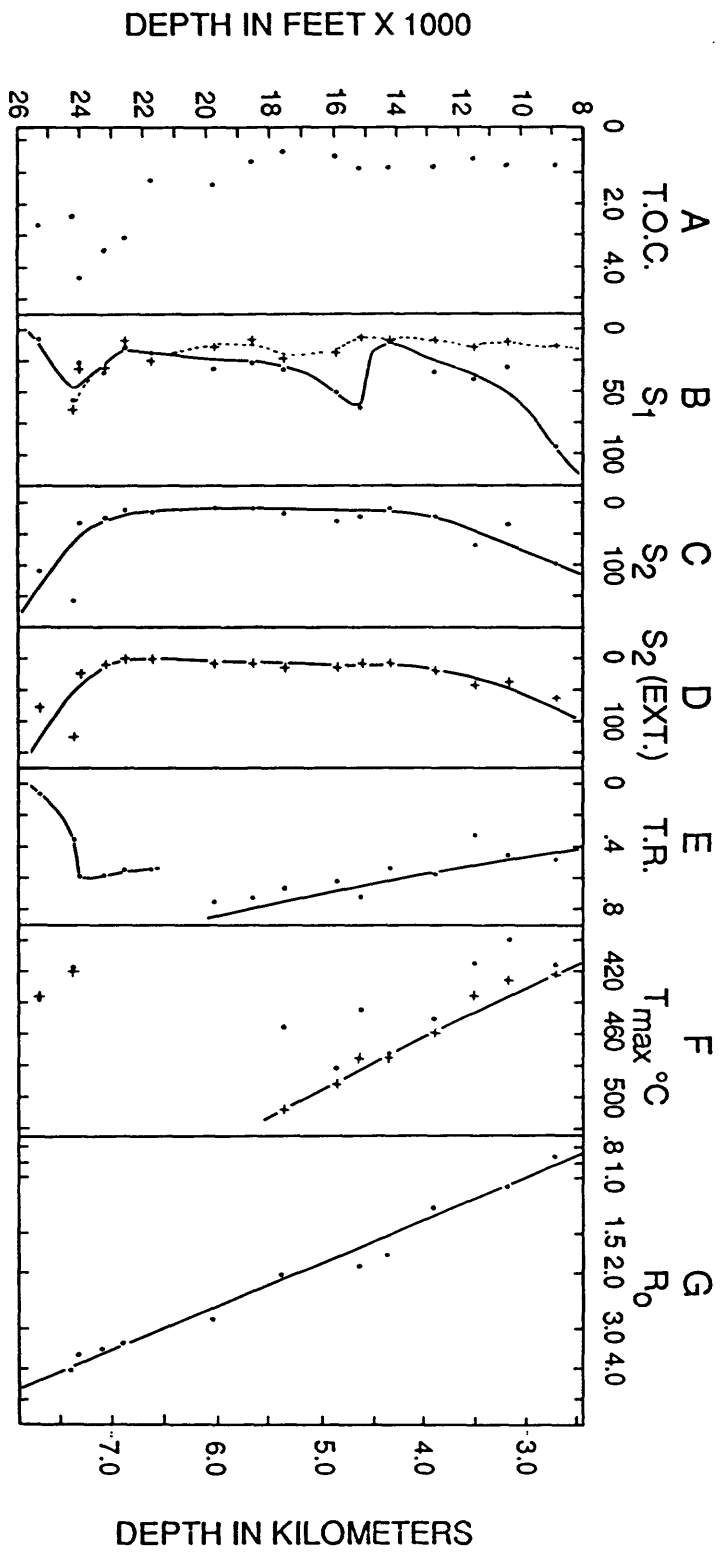


Figure 8. Plot, versus depth, of (A) T.O.C.; (B) the ROCK EVAL S₁ pyrolysis peak (mg/g 0.C., shown by dots and solid line) and the C₁₅⁺ Soxhlet-extracted HC's (mg/g 0.C., shown by crosses and dashed line); the ROCK EVAL S₂ pyrolysis peak for both (C) unextracted (dots) and (D) Soxhlet-extracted samples (crosses); (E) T.R.; (F) T_{max} for both unextracted samples (dots) and Soxhlet-extracted samples (crosses); and (G) R₀. Data from tables 2, 4 and 5.

this is the preferred hypothesis to explain the bell-shaped curves of figures 4 and 6 between 4.6-5.6 km, there is no incontrovertible evidence to prove or even support this hypothesis. Other hypotheses also certainly could be advanced to explain these bell-shaped curves.

Oxygen-rich OM has been documented (Price, 1989) as losing its HC generation potential by $R_0 = 1.8-2.0$ due to thermal burnout. In the Ralph Lowe #1, the hydrogen index⁰ values (normalized to organic carbon-mg/g O.C.), for both Soxhlet-extracted and unextracted samples, are approaching zero by $R_0 = 2.0$ (Fig. 8, Table 5). Obviously, the expected S_1 value for Soxhlet-extracted samples is also zero. However, Soxhlet extraction was inefficient in removing all the C_{15+} bitumen from these samples, as evidenced by the values for the S_1 pyrolysis peak for the extracted samples (Table 5). High molecular weight C_{15+} bitumen is eluted in the S_2 pyrolysis peak in ROCK EVAL pyrolysis (Clementz, 1979; and Price and others, 1984). Thus, the high molecular weight C_{15+} bitumen which remained in the Soxhlet-extracted samples, could be responsible for the small hydrogen index values, as opposed to the expected zero values, in the samples over the 5.0 to 7.0 km depth range. The inefficiency of Soxhlet extraction in this case was likely due to inadequate grinding of the rock samples, which left grain sizes too large. Another reason for the small, but not zero, hydrogen index values over the 5.2-5.9 km depth range, could be small amounts of originally hydrogen-rich OM in some of the rocks of this interval.

Hydrogen index values for Soxhlet-extracted samples are zero in the 6.6-6.9 km depth range, which correlates with minimum values (0.29-0.31) in the H/C atomic ratio of the OM over this depth range (Table 3). In passing from the rocks with oxygen-rich OM to rocks which were assumed to originally have hydrogen-rich OM, hydrogen index values increase to as high as 125 mg/g O.C. However, the HC generation potential in these deep samples is remnant generation potential. The majority of the original generation potential in these samples was assuredly lost at lower maturation ranks. On the other hand, the final thermal destruction of hydrogen-rich OM in the rocks of this well, and in other wells with rocks at high maturation ranks (Price, 1983), appears to take place at maturation ranks greater than $R_0 = 5.0$. In this light, the jump in the values of the S_1 pyrolysis peak and C_{15+} HC's in samples deeper than 7.0 km in the Ralph Lowe #1, is attributed to the fact that the hydrogen-rich OM of those rocks still has the capacity to generate C_{15+} HC's, as opposed to the oxygen-rich OM in the shallower rocks which lost its HC generation potential at lower maturation ranks.

The plot of C_{15+} HC's and the S_1 pyrolysis peak (mg/g O.C.) of figure 8B shows that eight samples have relatively poor agreement between the S_1 pyrolysis peak and C_{15+} HC's, including most samples shallower than 6.5 km. The greater values of the S_1 pyrolysis peak, compared to the values for the Soxhlet-extracted C_{15+} HC's, could be explained by the inefficiency of Soxhlet extraction. The measurable S_1 values for the Soxhlet-extracted samples (Table 5) show that Soxhlet extraction did not remove all the C_{15+} HC's. By adding the value of the S_1 pyrolysis peak of the Soxhlet-extracted samples to the value of C_{15+} HC's as determined by Soxhlet extraction, a closer agreement would result with the S_1 value for the unextracted samples. Another likely reason for the disagreement could be that significant amounts of C_8-C_{14} HC's are present in the rocks. Such HC's would be seen by pyrolysis analysis but missed by gravimetric C_{15+} HC determination. Although excellent agreement is possible between the

Table 5.--Results of ROCK-EVAL Analyses

T.O.C. is total organic carbon in weight percent; S₁, S₂ and S₃ ppm are the S₁, S₂ and S₃ pyrolysis peaks in ppm (weight percent); S₁, S₂ and S₃ mg/g OC are the S₁, S₂ and S₃ pyrolysis peaks normalized to organic carbon; T.R. is the transformation ratio (S₁/S₁+S₂); T_{max} °C is the temperature at the maximum of the S₂ pyrolysis peak in °C; and Sox HC's/S₁ is the ratio of the C₁₅+ saturated and aromatic HC's as determined by Soxhlet extraction to the S₁ pyrolysis peak, both normalized to organic carbon.

Depth in Kilometers	T.O.C.	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	T.R.	T _{max} °C	Comments	Sox HC's
		ppm	ppm	ppm	mg/g OC	mg/g OC	mg/g OC				S ₁
2.706-2.713	0.80	758	796	453	94.7	99.5	56.6	.488	416	Unextracted	0.140
	0.78	116	502	835	14.3	64.4	107	.182	423	Extracted	
3.185-3.194	0.78	289	279	522	30.6	35.8	66.9	.461	400	Unextracted	0.330
	0.77	78	301	840	10.1	39.0	109	.205	426	Extracted	
3.505-3.517	0.60	241	415	476	40.1	69.5	79.3	.366	415	Unextracted	0.365
	0.59	73	251	664	12.3	42.5	112	.378	436	Extracted	
3.889-3.901	0.84	281	199	365	33.5	23.7	43.4	.585	451	Unextracted	0.253
	0.83	79	168	480	9.6	20.2	57.8	.321	460	Extracted	
4.346-4.359	0.85	92	78	372	10.8	9.2	43.7	.540	473	Unextracted	0.793
	0.84	50	77	495	5.9	9.2	59.0	.392	475	Extracted	
4.633-4.639	0.91	572	211	522	62.9	23.2	57.4	.730	445	Unextracted	0.091
	0.90	51	63	544	5.7	6.9	60.4	.449	476	Extracted	
4.868-4.874	0.52	265	161	403	50.9	31.0	77.5	.622	482	Unextracted	0.351
	0.51	115	87	385	22.5	17.1	75.5	.568	491	Extracted	
5.358-5.364	0.38	125	62	316	32.8	16.4	83.1	.667	456	Unextracted	0.704
	0.37	62	50	394	16.7	13.5	106	.552	523	Extracted	
5.654-5.660	0.68	185	69	406	27.2	10.2	59.8	.727	450	Unextracted	0.319
	0.67	69	48	521	10.3	7.2	77.7	.586	461	Extracted	
6.026-6.032	1.39	447	140	397	32.2	10.1	28.5	.762	410	Unextracted	0.400
	1.35	400	94	372	29.6	7.0	27.6	.810	405	Extracted	
6.629-6.635	1.34	255	208	444	19.0	15.5	33.2	.551	330	Unextracted	1.30
	1.29	52	0	560	4.1	0	43.4	1.00	-	Extracted	
6.882-6.888	3.08	440	362	695	14.3	11.8	22.6	.548	328	Unextracted	0.570
	3.04	43	0	460	1.41	0	15.1	1.00	-	Extracted	
7.080-7.087	3.46	1,220	858	297	35.4	24.8	8.6	.588	335	Unextracted	0.844
	3.32	42	306	727	1.25	9.2	21.9	.112	353	Extracted	
7.324-7.330	4.32	1,070	1,460	613	27.1	33.8	14.2	.445	340	Unextracted	1.29
	4.15	101	1,010	670	2.43	24.3	16.1	.037	338	Extracted	
7.391-7.398	2.37	2,070	3,710	775	87.2	157	32.7	.358	419	Unextracted	0.778
	2.01	125	2,550	497	6.21	127	24.7	.047	420	Extracted	
7.718-7.724	2.68	200	2,940	1,190	7.46	110	44.4	.064	446	Unextracted	NA
	2.48	26	1,920	990	1.05	77.4	39.9	.013	447	Extracted	

values of the S_1 pyrolysis peak and C_{15+} HC's as determined by Soxhlet extraction under optimum circumstances (Fig. 2 of Price and others, 1984), such instances are not the usual situation. Normally, in the cases where I have compared the relationship, agreement has been poor.

The transformation ratio (T.R. - S_1/S_{1+S_2}) shows a fairly tight increase, with increase in depth (Fig. 8), to a maximum value of 0.762 in the 6.026-6.635 km sample. With further increase in depth, due to probable influence by primary migration and OM type changes, the T.R. decreases. The values for the temperature in $^{\circ}C$ at the maximum of the S_2 pyrolysis peak (T_{max}) for unextracted samples (shown by dots) exhibit significant scatter, versus depth. However, T_{max} values for the solvent-extracted samples (shown by crosses) exhibit a much more regular increase, versus depth. This contrast is because in the solvent-extracted samples, much or most of the resins and asphaltenes have been removed, and thus these compounds do not elute and interfere with the S_2 pyrolysis peak. Therefore, the S_2 pyrolysis peak of the Soxhlet-extracted samples, for the most part represents the thermal breakdown of kerogen.

At maturation ranks of $R_o > 2.0$, T_{max} values show sharp declines from values of $520^{\circ}C$ to values as low as $330^{\circ}C$ (table 5, not shown in figure 8). In the deepest samples with hydrogen-rich OM, T_{max} values again increase to higher values. I have observed such a decrease in T_{max} values at maturation ranks of $R_o > 2.0$ in rocks with oxygen-rich OM from other deep well bores. In my opinion, T_{max} values of 300° to $400^{\circ}C$ at maturation ranks of $R_o > 2.0$ are meaningless numbers which are probably due to the ROCK-EVAL instrument mistaking small concentrations of solvent-extractable HC's for generation potential on kerogen.

In all but one of the rock samples shallower than 6.0 km, the S_3 pyrolysis peak has higher values, and in most cases, substantially higher values, in the Soxhlet-extracted samples compared to unextracted samples (Table 5). I have noticed this same feature in studies of rocks from other well bores. This behavior is hypothesized as being due to active sites on kerogen. These sites are electrically satisfied by resins and/or asphaltenes being loosely bound to them. When these compounds are removed by solvent extraction, some or all of these active sites on the kerogen bind with carbon dioxide. Subsequent ROCK EVAL pyrolysis records this atmospheric gas as increased values of the S_3 pyrolysis peak. It would be expected with increasing maturation rank and the subsequent condensation of the aromatic rings in kerogen, that these active sites would be eliminated; and thus, this behavior should be reduced or disappear. This seems to be the case in the deep rocks of the Ralph Lowe-1. However, the shift from oxygen-rich to hydrogen-rich OM at depth in this well could also be responsible for the disappearance of this behavior.

GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Gas chromatography (GC) was carried out on the C_{15+} saturated HC fractions isolated from the rocks of this well. Two primary observations from these analyses were: the gross similarity of the GC patterns at all depths (Fig. 9), and the lack of any "maturation" changes over the 5.2 km depth interval studied.

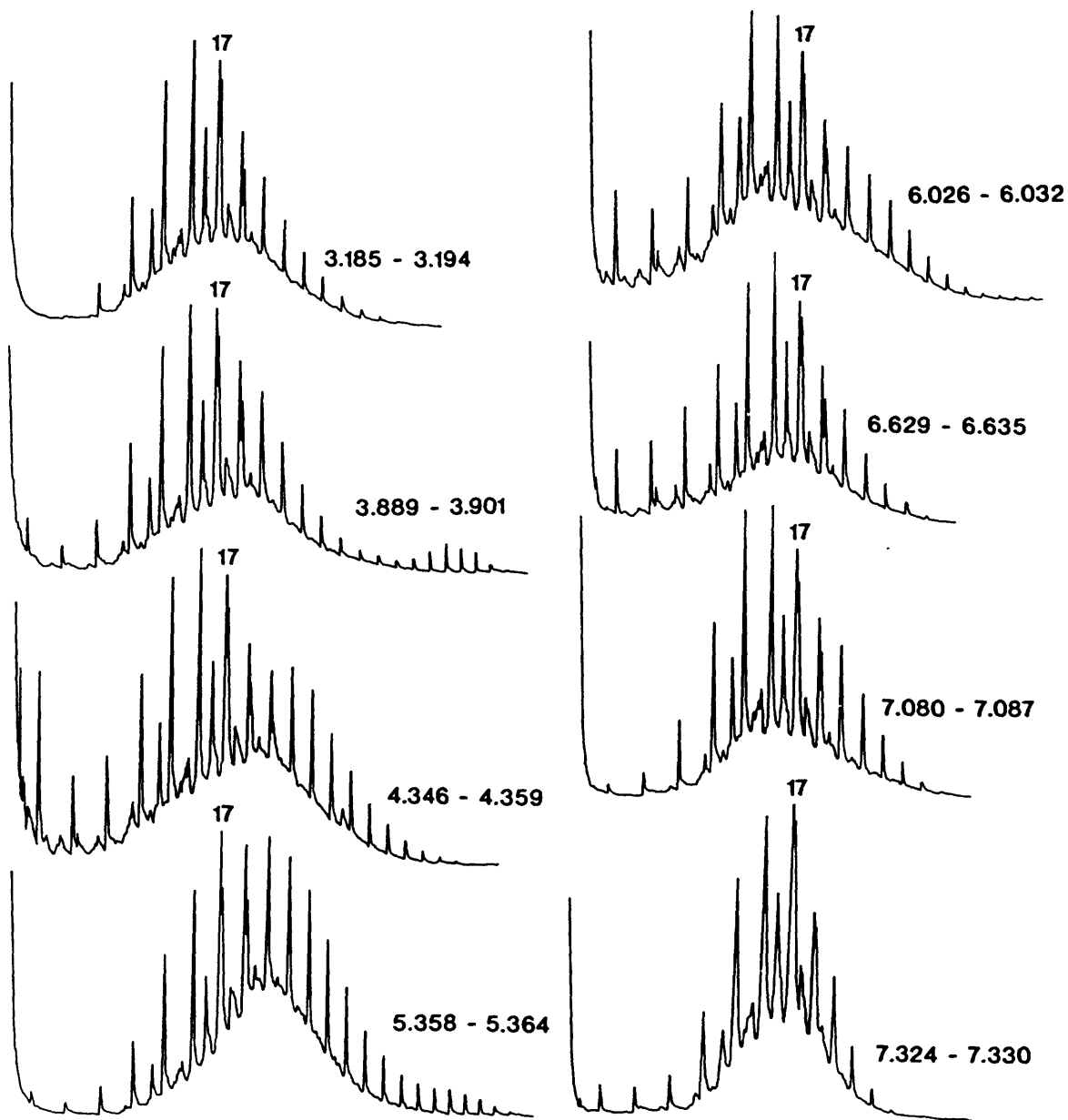


Figure 9. Gas chromatograms of $C_{15}+$ saturated HC's from rock extracts of the Ralph Lowe-1. Numbers on each chromatogram are sample depths in km. The C_{17} n-paraffin is labeled in each chromatogram. Column conditions were 1/8" by 6' column packed with 100 to 120 mesh Chromsorb coated with 3 percent SE-30. After a 2-minute post injection interval, the oven was programmed at $10^{\circ}\text{C}/\text{minute}$ from 80° to 200°C and at $10^{\circ}\text{C}/\text{minute}$ from 200° to 300°C . The upper temperature limit interval was 10 minutes, the injection block temperature was 250°C , and the detector block (FID) temperature was 300°C .

All chromatograms had mature appearances with abundant n-paraffins, odd-even preferences near unity, and symmetrical well-rounded naphthene envelopes. The pristane-phytane ratio (Table 4) showed no trends versus depth.

The saturated HC gas chromatograms of figure 9 are very similar, or even identical, to saturated HC gas chromatograms from rocks at high maturation ranks from other deep well bores (Price and others, 1979, 1981; Price, 1982). All these chromatograms: 1) are composed predominantly of C₁₅ to C₂₁ HC's, 2) have low amounts or even no C₂₅⁺ HC's, 3) have well rounded mature appearances, and 4) have low amounts of C₁₃⁻ HC's. The low contents of C₁₃⁻ HC's could be due to the fact that no steps were taken in the analytical procedure to recover these HC's. However, their absence also could be due to a marked preference of primary petroleum migration by gaseous solution to remove newly generated C₁₅⁻ HC's from rocks (Price, 1988). Many reasons are possible for the other three characteristics, however, no one reason is preferred here.

Mass spectrometry was carried out on nine of the saturated HC fractions of the rock extracts (Fig. 10). Disregarding the 2.706-2.713 km sample, the relative amounts of the different compound classes remain roughly constant versus depth to the 6.026 to 6.032 km sample. The amounts of paraffins increase in the deepest samples (with hydrogen-rich OM) at the expense of decreases in all the naphthene fractions. An increase in the percentage of paraffins and one-ring naphthenes in the saturated HC fraction, with decreases in the 3- to 5-ring naphthenes, has been attributed as a characteristic of both thermal maturation and of the principal zone of oil formation (Phillipi, 1965; Staplin, 1969; Hood and Castanõ, 1974; Tissot and Welte, 1978; and Hunt, 1979). However, in this well, it can also be explained by a change in OM type.

Gas chromatography was also carried out on all the C₁₅⁺ aromatic HC fractions (Fig. 11) from the rocks of this well. Individual compound (peak) identification was made by mass spectrometry (Fig. 12). No compositional trends versus depth were obvious from the chromatograms; and with the exception of five of the chromatograms, all were compositionally similar, the 3.505 to 3.517 and 6.629 to 6.635 km samples (Fig. 11) being examples. These two chromatograms are dominated by peaks representing naphthalene, methyl and dimethyl-naphthalenes, with lesser contents of biphenyl, methyl and dimethyl biphenyls, and tri-methyl-naphthalenes. Three- and four-ring aromatic compounds are present in low concentrations and there are small or no envelopes ("humps") of unresolved compounds. Five of the samples had chromatograms with higher contents of tri-methyl naphthalenes, biphenyls, three- and four-ring aromatic compounds, and significant envelopes of unresolved compounds. The chromatograms of the 4.346 to 4.350, 5.358 to 5.364, 7.324 to 7.330, and 7.391 to 7.398 km samples (Fig. 11) are examples. There was also a notable lack of any indications of maturation versus depth in the chromatograms of the aromatic HC's of this well.

DISCUSSION

Introduction

The principal organic-geochemical conclusions from the rocks of the Ralph Lowe-1, conclusions which also have been made from other studies, including studies of rocks from other deep well bores, are:

1) A loss of HC generation potential occurs in rocks with oxygen-rich OM by maturation ranks of R_o = 1.8 to 2.0. This loss of HC generation potential may,

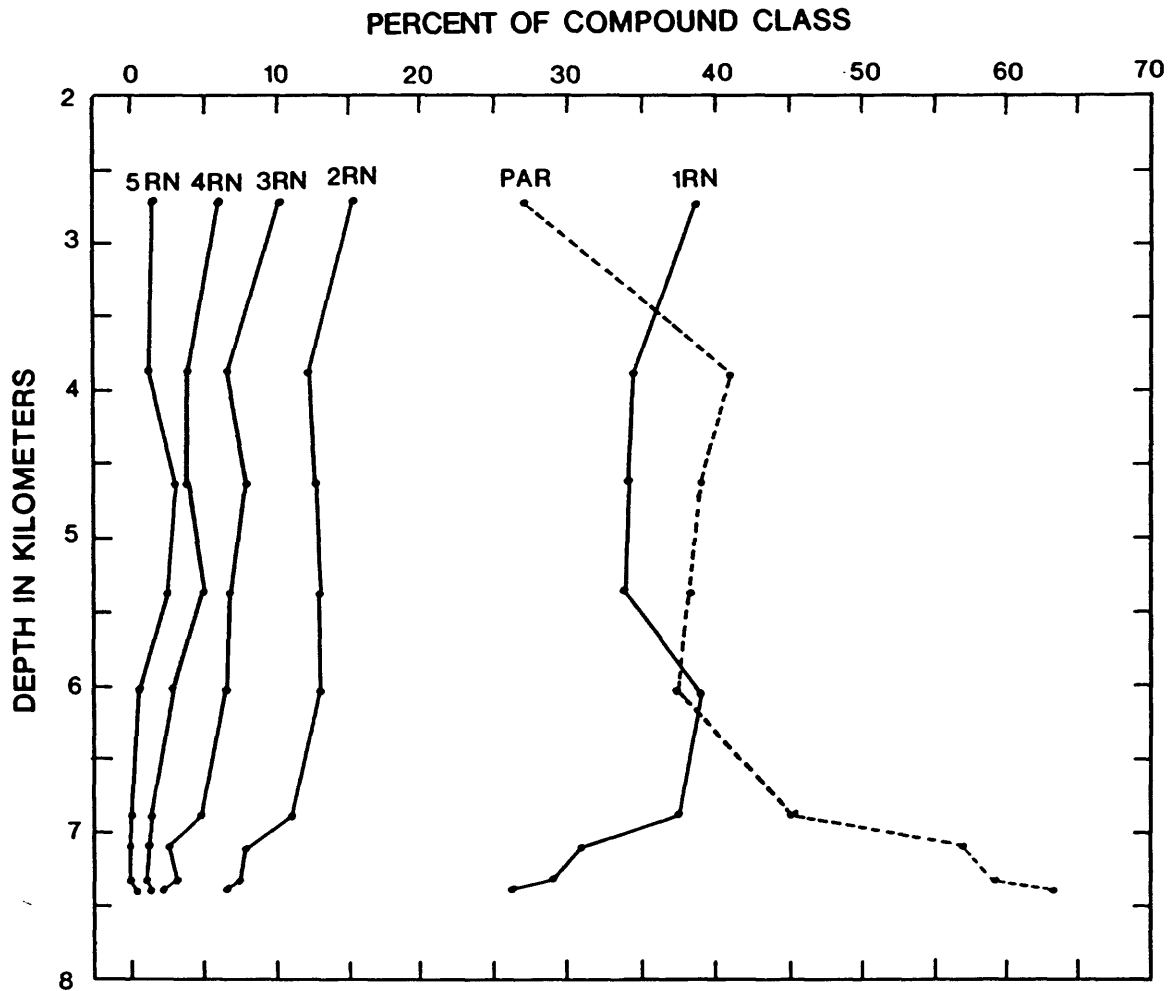


Figure 10. Mass spectrometric analyses of $C_{15}+$ saturated HC's from rock extracts of the Ralph Lowe-1. PAR are paraffins (dashed line); 1RN are one-ring naphthenes; 2RN are two-ring naphthenes, etc. Analyses by Dave King, U.S. Geological Survey, Denver, Colorado. Data from table 6.

Table 6.--Compositional analyses of the C₁₅+ saturated HC's from rock extracts of the Ralph Lowe-1 well bore. Analyses by J. David King, United States Geological Survey, Denver, Colorado.

Sample Depth in Km	Weight Percent					
	Paraffins	One-Ring Naphthenes	Two-Ring Naphthenes	Three-Ring Naphthenes	Four-Ring Naphthenes	Five-Ring Naphthenes
2.706-2.713	27.1	38.7	15.4	10.2	7.1	1.7
3.889-3.901	41.1	34.6	12.3	6.7	4.0	1.3
4.633-4.639	39.2	34.2	12.7	7.9	4.0	3.1
5.358-5.364	38.3	33.8	13.1	6.9	5.1	2.7
6.026-6.032	37.5	39.2	13.0	6.6	3.0	0.7
6.882-6.888	45.1	37.7	11.0	4.8	1.5	0
7.080-7.087	57.0	31.0	8.0	2.8	1.3	0
7.324-7.330	59.2	29.1	7.5	3.1	1.1	0
7.391-7.398	63.4	26.1	6.5	2.3	1.3	0.4

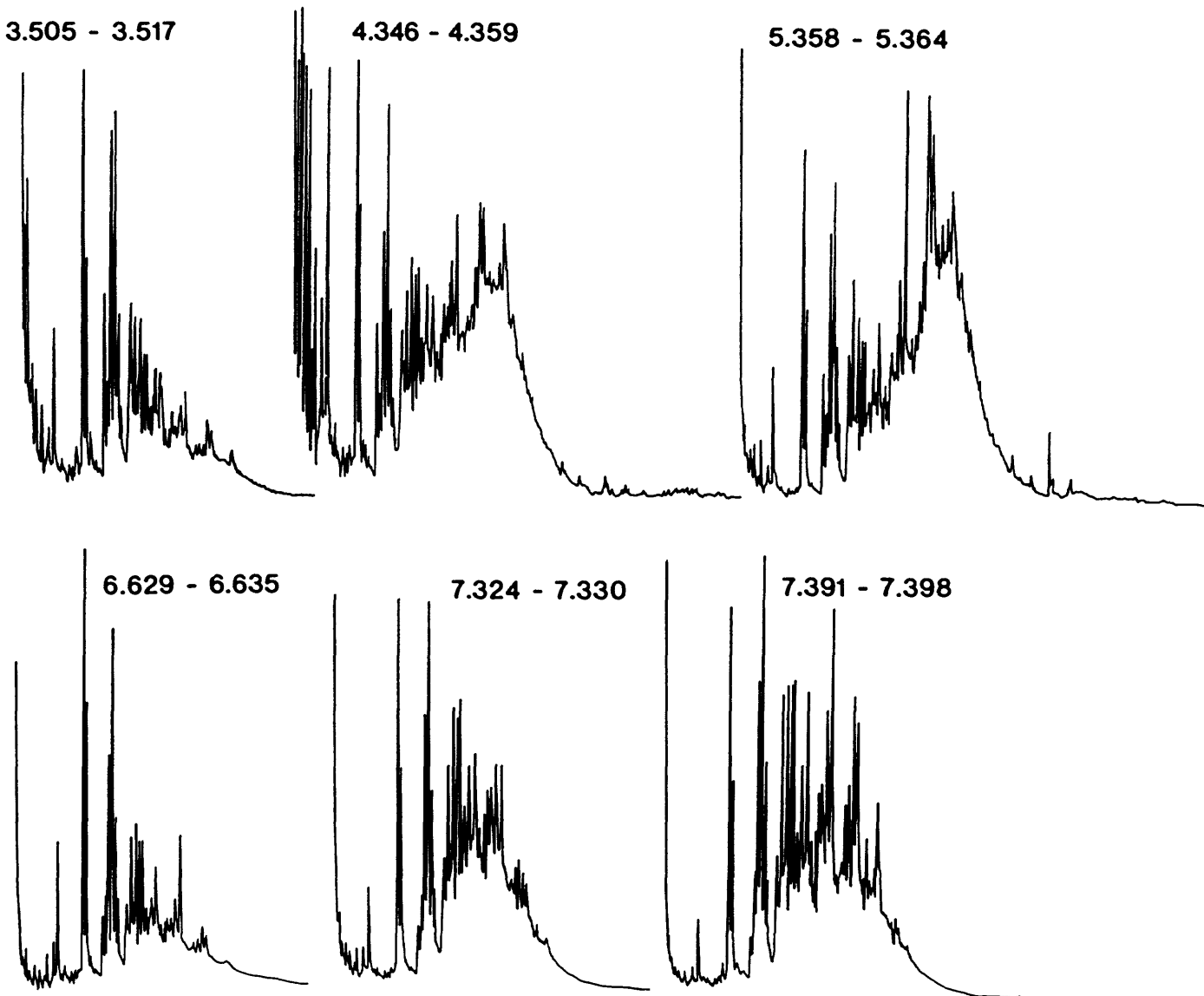


Figure 11. Gas chromatograms of C_{15}^+ aromatic HC's from rock extracts of the Ralph Lowe-1. Numbers on each chromatogram are sample depths in km. Column conditions were 0.25 mm I.D. x 25m open column, coated with SE-52. After a 20 minute post-injection interval, the oven was programmed from 80° to 250° at $8^{\circ}\text{C}/\text{minute}$ with a 30-minute upper temperature limit interval. The injection block temperature was 250°C , and the detector block (FID) temperature was 300°C .

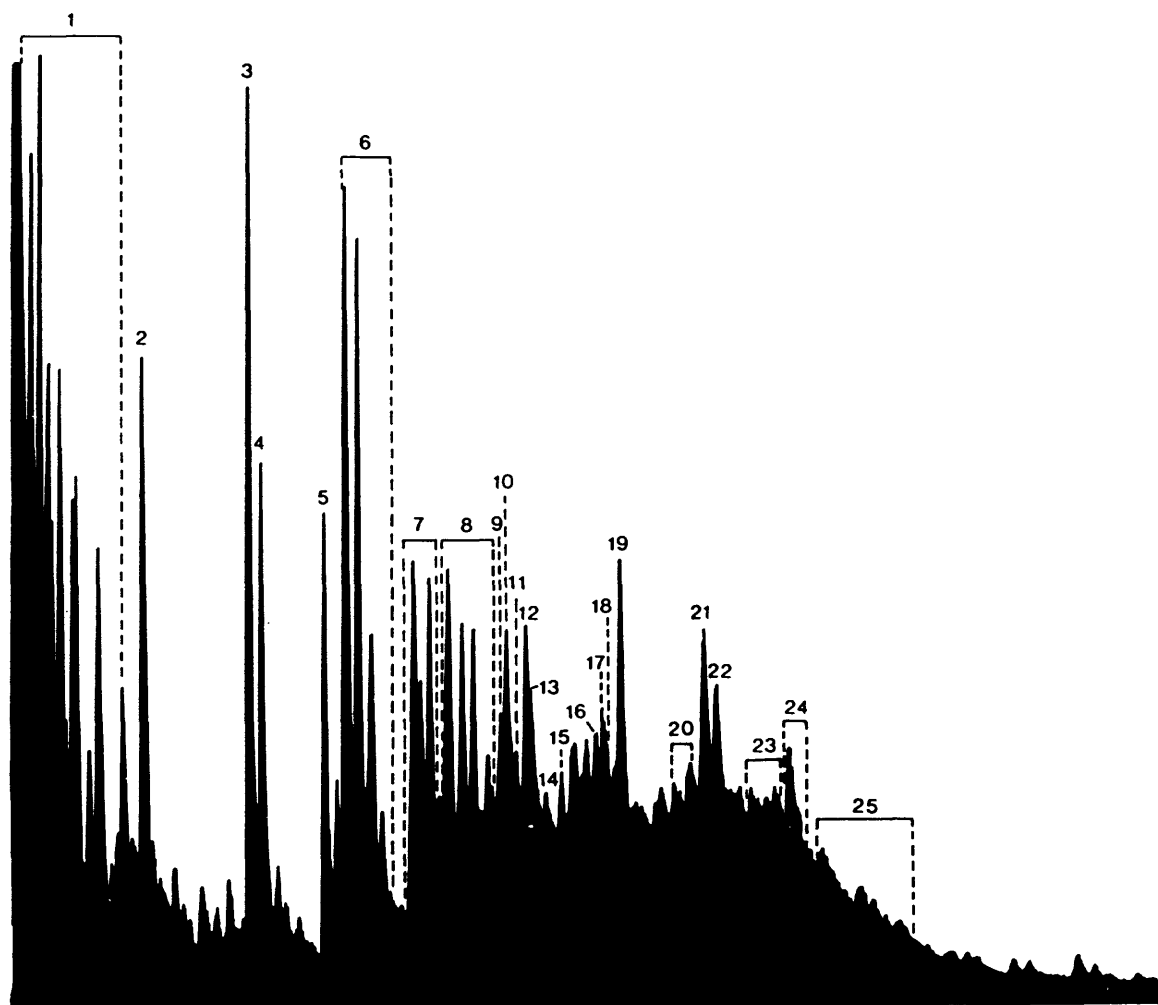


Figure 12. Mass spectrometric analysis of the $C_{15}+$ aromatic HC fraction from the 3.889 to 3.901 km rock sample of the Ralph Lowe-1. Numbers refer to compound class types: 1, normal-alkyl-substituted benzenes; 2, naphthalene; 3, and 4, methyl-naphthalenes; 5, biphenyl; 6, dimethyl-naphthalenes; 7, 10, 12, methyl-biphenyls; 8, trimethyl-naphthalenes; 9, 11, 13, dimethyl-biphenyls; 14, methyl-diethyl-naphthalene; 15, unknown naphthalene compound; 16, 18, trimethyl-biphenyls; 17, indane; 19, anthracene or phenanthrene; 20, unidentified condensed unsubstituted four ring aromatic compounds; 21 and 22, unidentified methyl-substituted condensed three ring aromatic compounds; 23, unidentified methyl-substituted condensed four ring aromatic compounds; 24, 25 dimethyl-phenantherenes. Mass spectrometric analyses of aromatic fractions from other sediment intervals in this well showed identical compound distributions. Thus, figure 12 can be used as an index for the chromatograms of figure 11. Analyses by Dave King, USGS, Denver, Colorado.

or may not, be accompanied by low or zero values for either the S_1 ROCK EVAL pyrolysis peak and/or for C_{15+} solvent-extractable HC's.

2) Profound organic-geochemical changes occur in both the kerogen and solvent-extractable HC's from high-rank rocks ($R_o = 2.0$ to 5.0) due to shifts in OM type of the rocks from oxygen-rich to hydrogen-rich.

3) Measurable to moderate amounts of both solvent-extractable C_{15+} HC's and HC generation potential remain in rocks with hydrogen-rich OM at maturation ranks ($R_o = 2.0$ to 5.0) far above the hypothesized thermal deadline for C_{15+} HC's ($R_o = 1.35$).

4) In the rocks of some well bores, some maturation indices are distinctly invariant over large ranges of maturation rank.

5) These findings suggest that problems may exist with some accepted precepts of organic metamorphism.

In this section, some of these accepted precepts are reviewed, as are contradictions which exist to these precepts. Hypotheses to explain these contradictions are also advanced.

Accepted Precepts in Organic Maturation

The threshold of intense HC generation--As Tissot and Welte (1978, p. 201) note, by consensus of published studies, "The threshold corresponding to the beginning of significant oil generation varies with the geothermal gradient, the depth and duration of burial. The related temperature ranges from 50°C in basins of Paleozoic age to 115°C in Mio-Pliocene sediments." The TIHG, from many studies of oxygen-rich OM (including: Hood and Castanõ, 1974; Albrecht and others, 1976; Durand and Espitalié, 1976; Durand and Oudin, 1979; Huc and Hunt, 1980; Teichmüller and Durand, 1983; and Vandenbroucke and others, 1983) has been documented as occurring at a maturation rank of $R_o = 0.6$.

The thermal destruction of HC's--Petroleum organic geochemists generally maintain that C_{15+} HC's are thermally destroyed between 100° to 250°C . Hunt (1979) puts the thermal stability limit of oil between 110° to 150°C and that for gas as between 180° to 225°C (Fig. 13). Hood and Castanõ (1974, p. 102) noted, "Pusey pointed out that 99+ percent of the world's oil is found in reservoirs at temperatures less than 300°F (149°C) and that liquid hydrocarbon destruction is dominant at greater temperatures." Landes (1967), Andreev and others (1968), Kartsev and others (1971), Pusey (1973a), Stahl (1974), Hunt (1974, 1975), and Barker (1977) have all made similar statements. Because HC generation is held to be a first order reaction (Welte, 1972; Dow, 1977; Tissot and Welte, 1978; and Hunt, 1979), it has been proposed that the reaction rate will double for each 10°C rise in burial temperature (Lopatin, 1971; Hood and Castanõ, 1974; Erdman, 1975; Hood and others, 1975; and Hunt, 1979). Thus, the same reaction extent will be reached in old-cold rocks as in young-hot rocks. This concept was succinctly stated in Connan's (1974) time-temperature diagram of HC generation (Fig. 13), as later modified by Hunt (1979). From figure 14, which is a compilation of the accepted scheme for the thermal evolution of HC's, it is apparent that oil is thought to be thermally destroyed by $R_o = 1.35$, and wet gas by $R_o = 2.00$, leaving only methane.

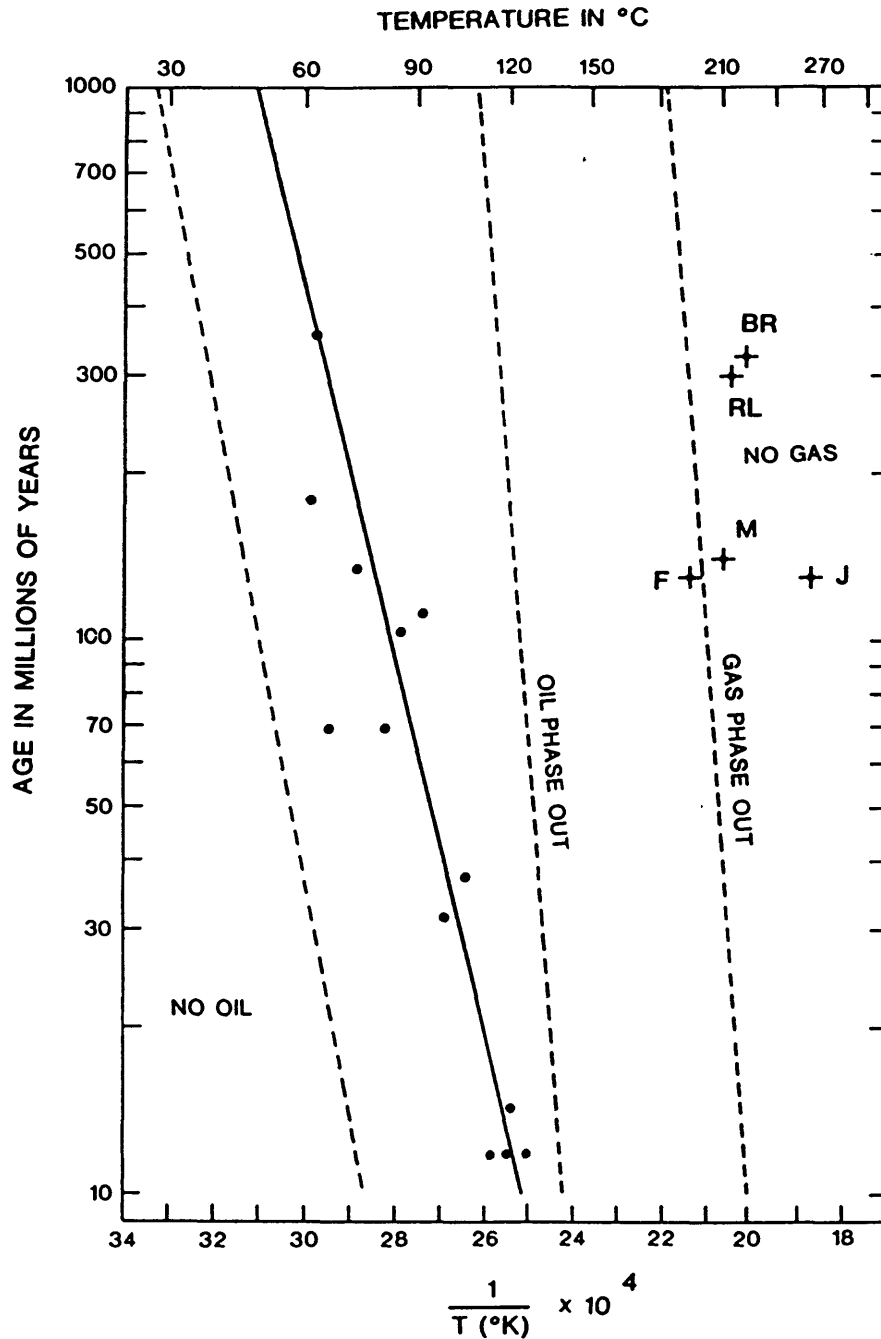


Figure 13. Time-temperature locus for the TIHG (solid line) from Connan (1974). Dashed lines are from Hunt (1979) from left to right representing: "oil phase in", "oil phase out", "gas phase out". Connan's (1974) original points were: AM, Amazon basin; PAR, Paris basin; A, Aquitaine basin (2 points); RDO, El Aaiun, Rio de Oro; D, Douala; OFF T, Offshore Taranaki basin, New Zealand; ON T, Onshore Taranakai basin, New Zealand; C, Camargue basin, France; S, Sulu basin; V, Ventura basin; LA, Los Angeles basin. Crosses are deep or double HC generation zones from various studies: BR, Bertha Rogers-1, Anadarko basin, Price and others (1981); RL, Ralph Love-1, this paper; M, McNair-1, Mississippi Salt basin, Price and others (1979); F, Pan Am Foerster-1, South Texas, (Unpublished data of L. C. Price and J. L. Clayton). J, J.R.G. Jacobs-1, South Texas, Price (1982); ST, South Texas offshore (corrected well-log temperatures), Huc and Hunt (1980); and H, Hungarian (Pannonian) basin (two points), Sagjó (1980).

Greenschist metamorphism--Hunt (1979, p. 550) defines metamorphism as, "The transformation of preexisting rocks into new types by the action of heat, pressure, stress, and chemically active migrating fluids. Metamorphism usually begins at temperatures above 200°C (392°F). At such temperatures, the organic matter is already reduced to a low-hydrogen carbon residue capable of yielding only small amounts of gas." Tissot and Welte (1978, p. 470) note, "Metamorphism (greenschist facies) appears at about $R_o = 4\%$ ". R_o values of 4.0 are thought to correspond to burial temperatures of 200°C to 250°C (Fig. 14; or Pusey 1973b, his Fig. 2). It is widely accepted among petroleum organic geochemists that with greenschist metamorphism, all C_2+ HC's are thermally destroyed.

Maturation progression--Between the TIHG and the assumed destruction of C_{15+} HC's by $R_o = 1.35$, a suite of organic-geochemical changes, attributed to organic maturation, have been proposed to take place in a regular and repeatable fashion. For example, Tissot and Welte (1978, p. 172) noted that, "In the principal zone of oil formation, substantial amounts of new alkanes are generated with less or no odd preference, thus causing the progressive disappearance of the odd/even predominance by dilution. Thus, the CPI is lowered to about 1. In addition, alkanes of low molecular weight are favored. This causes a shift of the maximum in the n-alkane distribution curve towards a smaller number of carbon atoms per molecule." Besides changes in CPI values and a trend to maturity of saturated HC gas chromatograms, changes in the molecular composition of the saturated HC's (increases in paraffins and one-ring naphthenes with concurrent decreases in three- to five-ring naphthenes) are expected from burial-maturation (Hood and Castaño, 1974; Tissot and Welte, 1978; Hunt, 1979; and others). Changes in biomarker compound ratios have also been proposed to result from burial maturation. Progressive changes in ROCK EVAL maturation indices are also subscribed to burial maturation, such as: 1) continuous increases in T_{max} , 2) continuous increases in the transformation ratio, 3) a regular and continuous decrease in the values of the S_2 pyrolysis peak at R_o values >0.6 , and 4) a continuous decrease in the values of the S_3 pyrolysis peak.

Graphite formation--The end point of organic metamorphism is the formation of graphite, and most petroleum organic geochemists hold that exposure of OM to 150°C to 200°C in the natural system over geologic time will result in methane and graphite. "High temperatures ($>350^\circ\text{F}$, 177°C) or long exposure to moderate temperatures will ultimately destroy oil yielding mainly graphite and methane", (Hunt, 1974, p. 103). "As kerogen is heated in the eometamorphism range, it chars and eventually becomes graphite", (Pusey, 1973a, p. 196). His eometamorphism range is between 66°C and 249°C. Stahl (1974), Barker (1977) and others have made similar statements.

Contradictions to Accepted Precepts

The threshold of intense HC generation--As discussed, it is well documented that the TIHG in oxygen-rich OM occurs by $R_o = 0.6$ (as measured in oxygen-rich OM), or by present day (maximal) burial temperatures of 120°C, which correspond to $R_o = 0.6$. On the basis of the first detectable decrease in the values of the S_2 pyrolysis peak (which would occur at the commencement of intense HC generation), Price (1989) suggested that the TIHG spans a rather wide maturation range ($R_o = 0.6$ to 0.8), and that intense HC generation actually commences at $R_o = 0.81$. However, this is more of a point of interpretation than a contradiction to accepted thought.

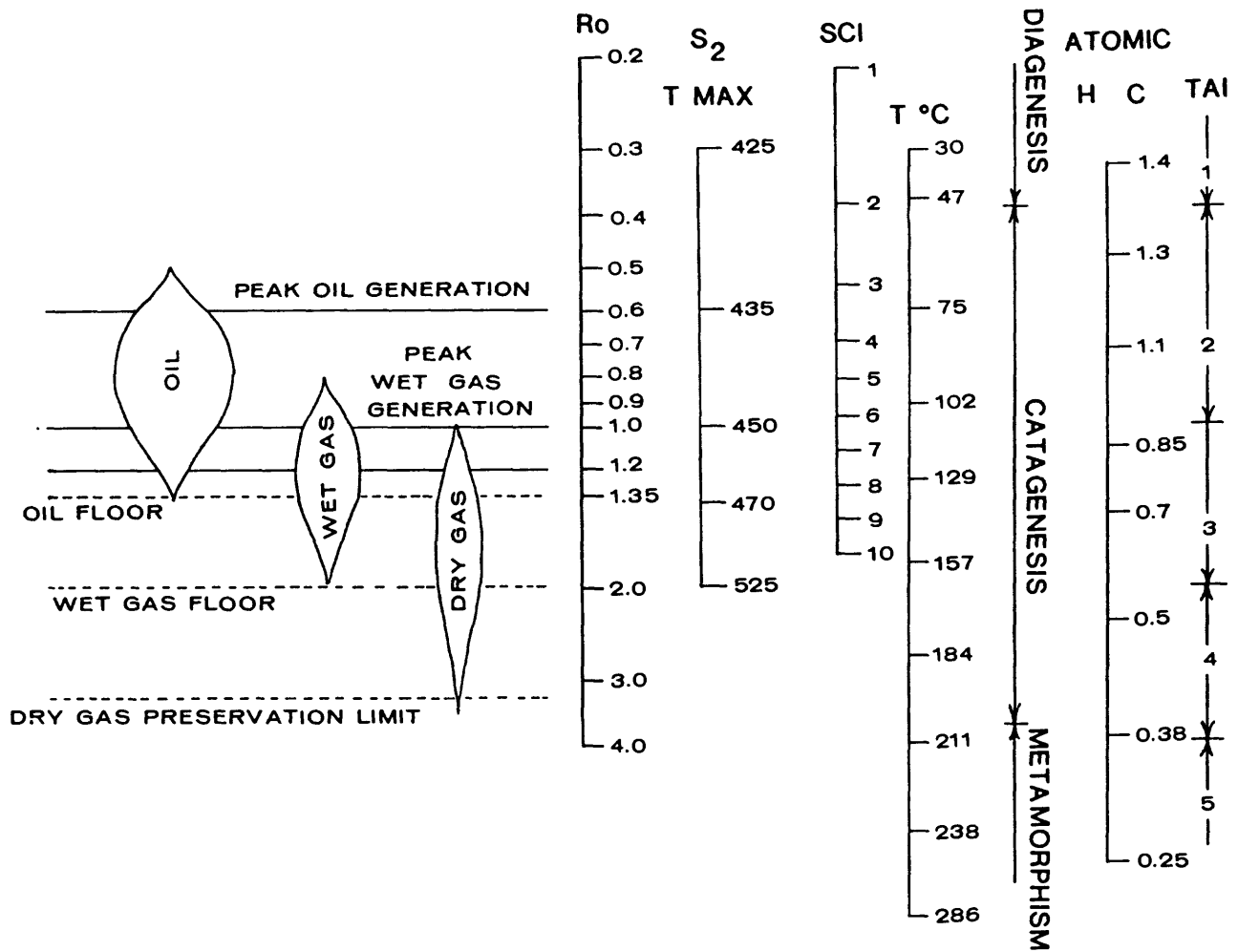


Figure 14. Chart for the correlation of commonly used maturation indices. S_2 TMAX is the temperature in $^{\circ}\text{C}$ at the maximum of the ROCK EVAL S_2 pyrolysis peak. SCI is the spore coloration index. $T^{\circ}\text{C}$ is burial temperature in $^{\circ}\text{C}$. ATOMIC HC is the atomic hydrogen/carbon ratio of kerogen. TAI is the thermal alteration index. Modified from Dow (1977) and Hunt (1979).

A real and serious contradiction to accepted thought appears to exist with hydrogen-rich OM. It has generally gone unrecognized that significantly higher (but yet undefined) maturation ranks may be necessary to initiate intense HC generation in hydrogen-rich OM, compared to the rank necessary for the initiation of intense HC generation in oxygen-rich OM. In rocks with oxygen-rich OM in the Los Angeles-Ventura (and other California petroleum) basins, based on unpublished ROCK EVAL analyses of a very large sample base which I have carried out, the TIHG is attained at burial temperatures of 120^o-125^oC. These results agree well with Phillipi's (1965) conclusions regarding HC generation in the Los Angeles-Ventura basins. However, at the same time in these basins, in rocks with hydrogen-rich OM, not only is the TIHG not detected at 120^oC, this event is not detected up to present-day burial temperatures of 210^oC. (The following information for the Shell Taylor 653 well bore was supplied by John Castanõ in a personal communication 11/5/1985, who was then a research geologist with Shell Oil Co.). The Shell Taylor 653, a 6.553 km (21,500 ft) well bore drilled in the Ventura Avenue field of the Ventura basin, encountered the Miocene Santa Margarita formation (a stratigraphic equivalent of the Miocene Monterey formation) at about 4.993 km (16,000 ft). Throughout this formation to the bottom of the well, which is at a present-day burial temperature of 210^oC, the TIHG was never encountered in these high T.O.C. rocks with hydrogen-rich OM. In fact, all measured maturation indices in the rocks of the Santa Margarita formation were suppressed from the values expected for the high burial temperatures (155^o-210^oC) of the rocks. I have encountered the same results in the Los Angeles, Ventura, and Santa Maria basins. (For example, see Price, 1983, figs. 3 and 4).

Price and others (1984) determined that in the Williston basin, the TIHG first occurred in the Mississippian-Devonian Bakken Shale, a rock characterized by hydrogen-rich 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 oxygen-rich OM. Another example of the suppression of the TIHG, and other maturation indices, exists in Pennsylvanian black shales with hydrogen-rich OM in the midcontinent region, U.S.A. (Wenger, 1987).

Main-phase HC generation is recognized by increases in the ratio of solvent-extractable bitumen normalized to organic carbon (mg/g O.C.) from normal values of 10 to 50 to maximum values of 100 to 300 (dependent on OM type and other parameters). Based on this widely accepted definition, examples of high-rank ($R_o = 2.0$ to 4.5) generation zones or "double generation" profiles within the same well bore exist, and these examples would contradict the hypothesis that the TIHG always occurs at $R_o = 0.6$. An example of such an apparent high-rank generation zone occurs over the 7.0-8.1 km depth range in the Ralph Lowe-1 well bore. This and other high-rank (and double) generation zones are plotted on Hunt's (1979) modification of Connan's (1974) time-temperature plot (Fig. 13). All the data points representing these apparent high-rank generation zones lie outside Hunt's (1979) thermal stability field for oil, and five points lie outside his thermal stability field for methane. These data are serious contradictions to conventional wisdom concerning both the maturation rank necessary for the TIHG and the rank necessary for C₁₅+ HC thermal destruction. Further, these anomalous results have been duplicated by other investigators (Sajgó, 1980; and Kontorovich and Trofimuk, 1976, as noted by Sajgó, 1980, p. 109).

The thermal destruction of C₁₅+ HC's--A large body of evidence has been presented (Price and others, 1979, 1981; Price, 1982, 1983, table 1; Sajgó, 1980; and the data from this paper) which does not support the hypothesis of a thermal deadline for C₁₅+ HC's by R_o = 1.35 and/or burial temperatures of 200°C. This evidence suggests that significant concentrations of C₁₅+ HC's have remained thermally stable in high maturation rank (R_o = 2.0-5.0) rocks buried for hundreds of millions of years at minimum burial temperatures of 200° to 300°C. Further, in all but one of these cases, maximum burial paleotemperatures were probably higher than present-day burial temperatures. The kerogen of these rocks has measurable, and sometimes moderate, amounts of C₁₅+ HC generation potential. The Soxhlet-extraction and ROCK EVAL data of the deep rocks of the Ralph Lowe-1 (Tables 4 and 5) serve as examples.

Maturation progression--In rock sequences with oxygen-rich OM, the expected progression of organic maturation changes usually is present over maturation rank ranges of R_o = 0.3 to R_o = 2.0 or greater. Furthermore, the different maturation indices always show moderate, and many times good, cross correlations with each other and/or depth, such as good linear cross plots of R_o with T_{max}, or regular continuous increases of R_o, T_{max}, T.R. etc. with increase in depth. However, when one passes from such rocks into rocks containing hydrogen-rich OM, such good continuous cross correlations and/or increases of maturation indices with depth disappear.

Price and Barker (1985) discussed and gave examples of significant suppression of R_o in rocks with hydrogen-rich OM compared to the R_o values in rocks with oxygen-rich OM which were at the same maturation rank or which had had the same burial history and burial temperatures. Actually, all organic maturation indices, and not just R_o, appear to be suppressed in rocks with hydrogen-rich OM compared to the values found in rocks buried under the same conditions but containing oxygen-rich OM. This suppression is believed to be due to hydrogen-rich OM following different reaction kinetics (and therefore requiring substantially higher burial temperatures for reaction) than oxygen-rich OM. Examples of this exist in the organic-geochemical data of the Ralph Lowe #1: 1) The ROCK EVAL S₂ pyrolysis peak, which had approached and/or reached zero values by R_o >2.0 (Fig. 8), increased significantly in the rocks with hydrogen-rich OM at the bottom of the well, to maximum values of 150 mg/g O.C. 2) The T.R., which had exhibited a continuous increase versus depth (Fig. 8), fell off to much lower values in the rocks with hydrogen-rich OM at depth. 3) T_{max} values which had increased continuously with depth to 523°C by R_o ~2.0 (Fig. 8), fell back to values of 420°-447°C in the deep rocks with hydrogen rich OM. 4) The gas chromatograms of the saturated HC's from all rocks of the Ralph Lowe #1 were very similar in appearance and showed no trend of increasing maturity with increase in depth. Thus: A) The chromatogram from the 3.185-3.194 km sample (R_o = 1.1) was for all intents and purposes equal in appearance to the chromatogram from the 7.324-7.330 km sample (R_o = 4.1). B) The CPI did not change with depth (values near 1.0 for all samples). C) The maximum of both the n-alkane distribution and of the naphthene envelope remained at C₁₆ to C₁₉ for all samples.

Similar reversals of maturation trends were also encountered in rocks with hydrogen-rich OM in the Bertha Rogers well bore (Price and others, 1981), in the McNair well bore (Price and others, 1979) and in the Foerster-1 well bore (unpublished data of L. C. Price and J. L. Clayton). In the California petroleum basins, profound reversals in maturity trends occur in going from

rocks with oxygen-rich OM to rocks with hydrogen-rich OM at the same maturation rank. Other investigators have also reported situations where the OM in hydrogen-rich rocks is too immature (suppressed) for the burial temperature and age of the rocks: the Cook Inlet (Magoon and Claypool, 1979) the Hungarian Pannonian Basin (Sajgó, 1980), and the midcontinent United States (Wenger and Baker, 1987).

Greenschist metamorphism and graphite formation--Precepts among petroleum organic geochemists concerning the conditions necessary for the onset of greenschist metamorphism and graphite formation do not agree with the conclusions of metamorphic petrologists on the subjects. Winkler (1976) has noted that no noticeable mineralogic changes (greenschist metamorphism) take place in thick geosynclinal pelitic sequences until temperatures of 400°C or greater. C. Weaver, after a detailed clay mineralogical study in the southeastern United States, concluded that greenschist metamorphism begins at temperatures of 375° to 425°C (personal communication, Santa Fe, N.M., Sept. 16, 1981).

Figure 15 shows X-ray diffraction patterns for kerogen isolates from the rocks of the Ralph Lowe-1. Kerogen from the deep rocks of this well bore are not graphite, nor is there any visible tendency towards graphitization, versus depth, in this well bore. Identical results were obtained by X-ray diffraction of kerogen isolates from the Shell McNair-1 well bore (Price and others, 1979) and the Bertha Rogers-1 well bore (Price and others, 1981). These results support the conclusions of metamorphic petrologists, who from many analyses of metamorphic rocks, have concluded that graphite does not form in nature until minimum temperatures of 600°C. Grew (1974, p. 69) after studying metasediments of the New England Narragansett basin concluded that, "A temperature of at least 660°-690°C appears to be necessary for the development of well ordered graphite....". Miyashiro (1973, p. 53) noted that, "Black carbonaceous matter in metamorphic rocks has usually been called graphite in the geologic literature. Recent investigations have shown, however, that the carbonaceous matter in low-temperature metamorphic rocks are organic materials comparable to semi-anthracite and anthracite. Their composition and atomic structure change gradually with increasing metamorphism until graphite is formed in the amphibolite facies (Izawa, 1968)."

Reasons for Contradictions

Introduction--In past (and this) publications (Price 1977, 1978, 1980, 1982, 1983, 1985, 1988, 1989; Price and others, 1979, 1981, 1984; and Price and Barker, 1985), I have presented a large body of data which do not support all aspects of accepted models concerning the generation and eventual thermal destruction of HC's. This body of data implies that facets of these models may be in error and, therefore, may require at least some degree of modification. At this point reasons can be advanced for these contradictions, which may serve to increase the overall understanding of this area of study. There are five principal reasons why I believe the contradictions to some aspects of the accepted models of organic metamorphism, as enumerated above, exist:

- 1) A possible erroneous assignation of geologic time as the factor responsible for high levels of organic metamorphism found in some geologically-old rocks currently buried at shallow depths. The factor

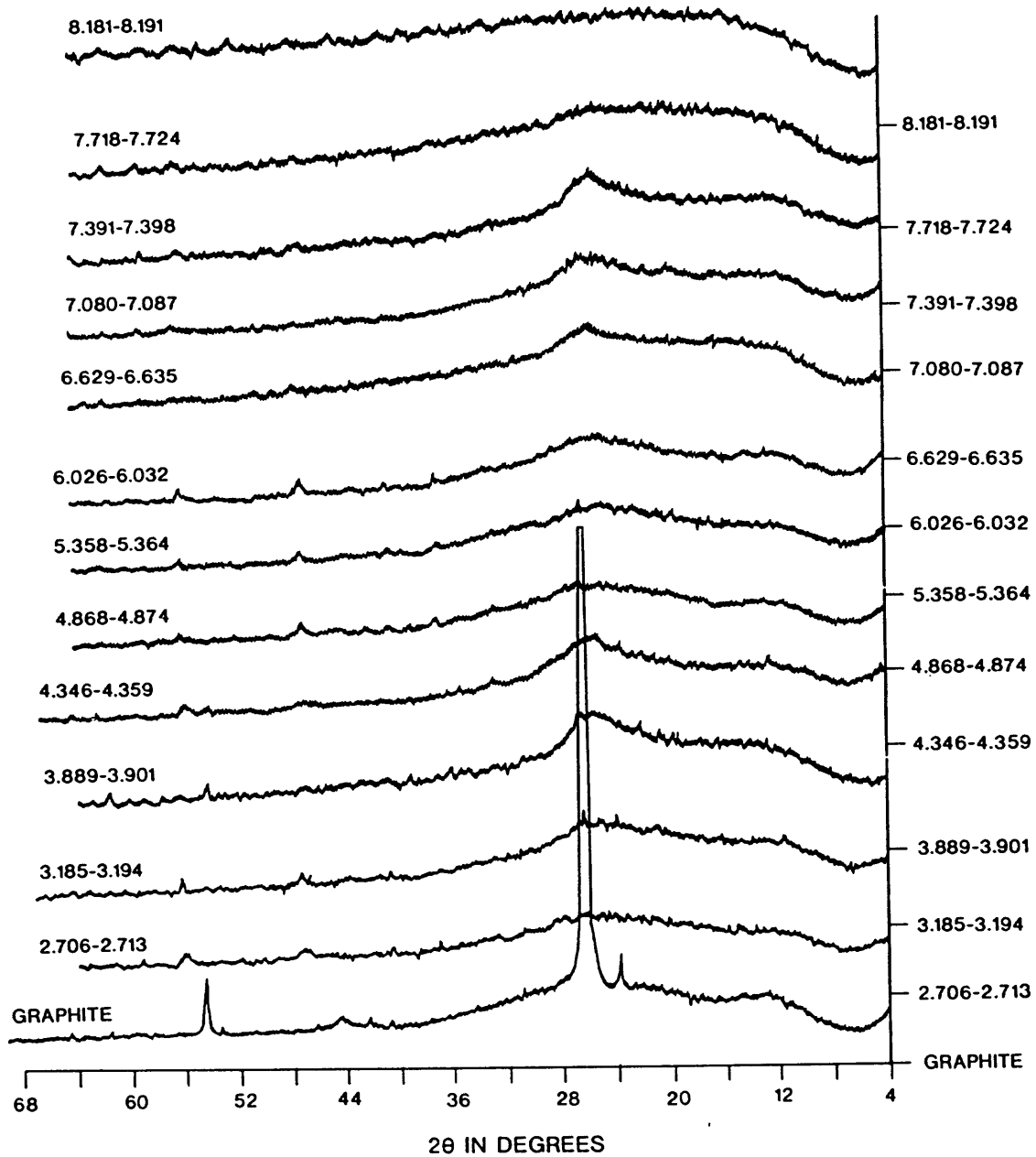


Figure 15. X-ray diffraction analyses of kerogen isolates from rock samples of the Ralph Lowe #1 and from a sample of Ceylon graphite. The numbers over and on the left side of each sample are sample depths in km. Tick marks and numbers to the right of the figure are zero response for each sample. Ceylon graphite is full scale response.

responsible for these levels could have been erosion and/or high paleo heat flows. This point has been covered in detail in Price (1983, 1985) and will not be discussed further here.

2) A possible erroneous assignment of the thermal destruction of C_{15+} HC's being responsible for the decrease, over $R_o = 0.8$ to 1.35 , and disappearance, at $R_o = 1.35+$, of C_{15+} HC's in some rocks with oxygen-rich OM, when primary petroleum migration (by gaseous solution) could be the factor responsible for this decrease and disappearance.

3) The lack of previous recognition of the importance of OM type as one of the dominant controlling parameters of organic metamorphism.

4) The lack of previous recognition of high, static, fluid pressure as one of the possible dominant controlling parameters of organic metamorphism.

5) The role of shearing, as related to the disruption of closed or semi-closed chemical systems, with the concurrent release of high, static, fluid pressures in Nature and the resultant promotion of both organic and inorganic metamorphism.

C_{15+} HC destruction at $R_o = 0.8-1.35$ --The origins of the assignment of the thermal destruction of C_{15+} HC's as being responsible for the loss of C_{15+} HC's in some rocks with oxygen-rich OM over $R_o = 0.8$ to 1.35 lie in the studies of the Cretaceous Logbaba shales (Fig. 16), Douala basin, Cameroons (Albrecht and others, 1976; Durand and Espitalié, 1976; and Vandenbroucke and others, 1976), and are discussed in detail in Price (1989). Discussing the C_{15+} HC data of these studies, Albrecht and others (1976, p. 792) stated, "Deeper than 2,200 m the chloroform extract decreases rapidly, reaching very small values below 3,000 m. This decrease is mainly due to thermal cracking, leading to light material which is not analyzed by our procedure." Thus, an assumption was made that the concentration decrease of C_{15+} HC's in figure 16 at maturation ranks of $R_o \geq 0.9$ was due to HC thermal destruction by carbon-carbon bond breakage. An alternate hypothesis, that this decrease in the concentrations of C_{15+} HC's could have been due to their loss by primary migration was not considered. Many other organic-geochemical studies of rocks with oxygen-rich OM have found the same trends in the C_{15+} HC's as were found at Douala. Thus, a thermal destruction of C_{15+} HC's by $R_o = 1.35$ (and hence, a thermal deadline for crude oil at $R_o = 1.35$) came to be accepted as an organic-geochemical law.

Figure 17, modified from Teichmüller and Durand (1983) for Tertiary to Paleozoic coals from different worldwide localities, is an example of a subsequent study apparently confirming the results of the Douala study. Here the ROCK EVAL S_1 pyrolysis peak (which is representative of C_{15+} solvent-extractable HC's) decreases to, and remains at, low concentrations by $R_o \geq 0.9$. However, at the same time, as shown by the high values of the S_2 pyrolysis peak, significant C_{15+} HC generation capacity remains in these coals to R_o values far in excess of 1.35 . Thus, the disappearance of C_{15+} HC's by $R_o = 0.9$ in figure 17 cannot be due to their thermal destruction, but must be due to another cause. Teichmüller and Durand (1983) also concluded that in these coals the decrease and disappearance of C_{15+} HC's were not due to their thermal destruction, but instead were due to their primary migration. Thus, the fact that oxygen-rich OM does not lose its capacity to generate C_{15+} HC's until $R_o =$

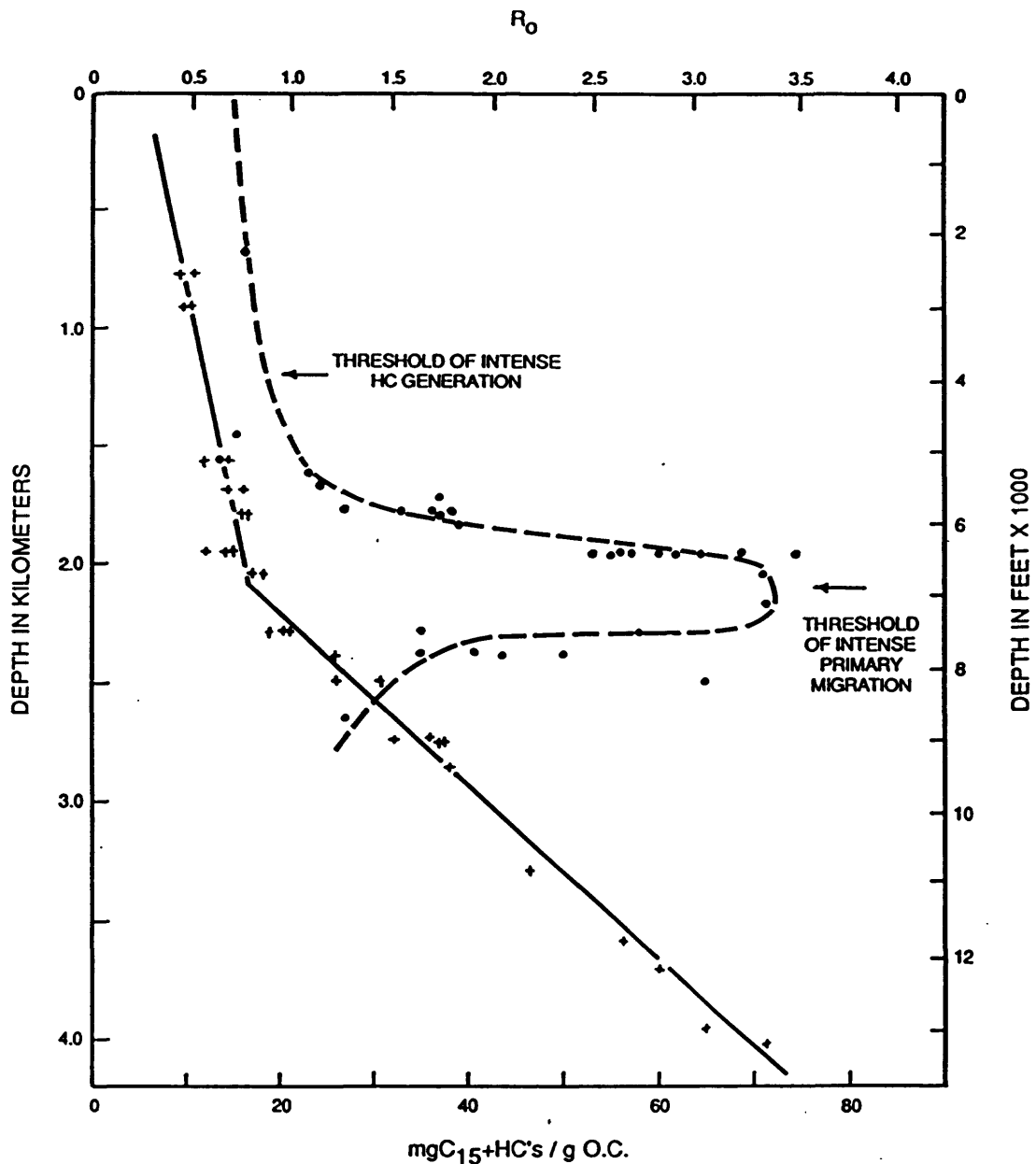


Figure 16. Plot of the $C_{15}+HC$ coefficient ($mg C_{15}+HC's/g$ organic carbon), as shown by the dashed line, and R_o , as shown by the solid line, versus depth, for the Upper Cretaceous Logbaba shales, Douala, Camerouns. The arrow at 1,200 m (3,940 ft) denotes the first detectable increase in $C_{15}+HC's$. The arrow at 2,050 m (6,726 ft) denotes the threshold of intense primary petroleum migration. Data from Albrecht and others (1976) and Durand and Espitalié (1976). It is assumed that the vitrinite reflectance data given by Durand and Espitalié (1976) were mean maximum vitrinite reflectance (R_m). These R_m values were converted to mean vitrinite reflectance values (R_o) by the formula $R_m = R_o (1.066)$.

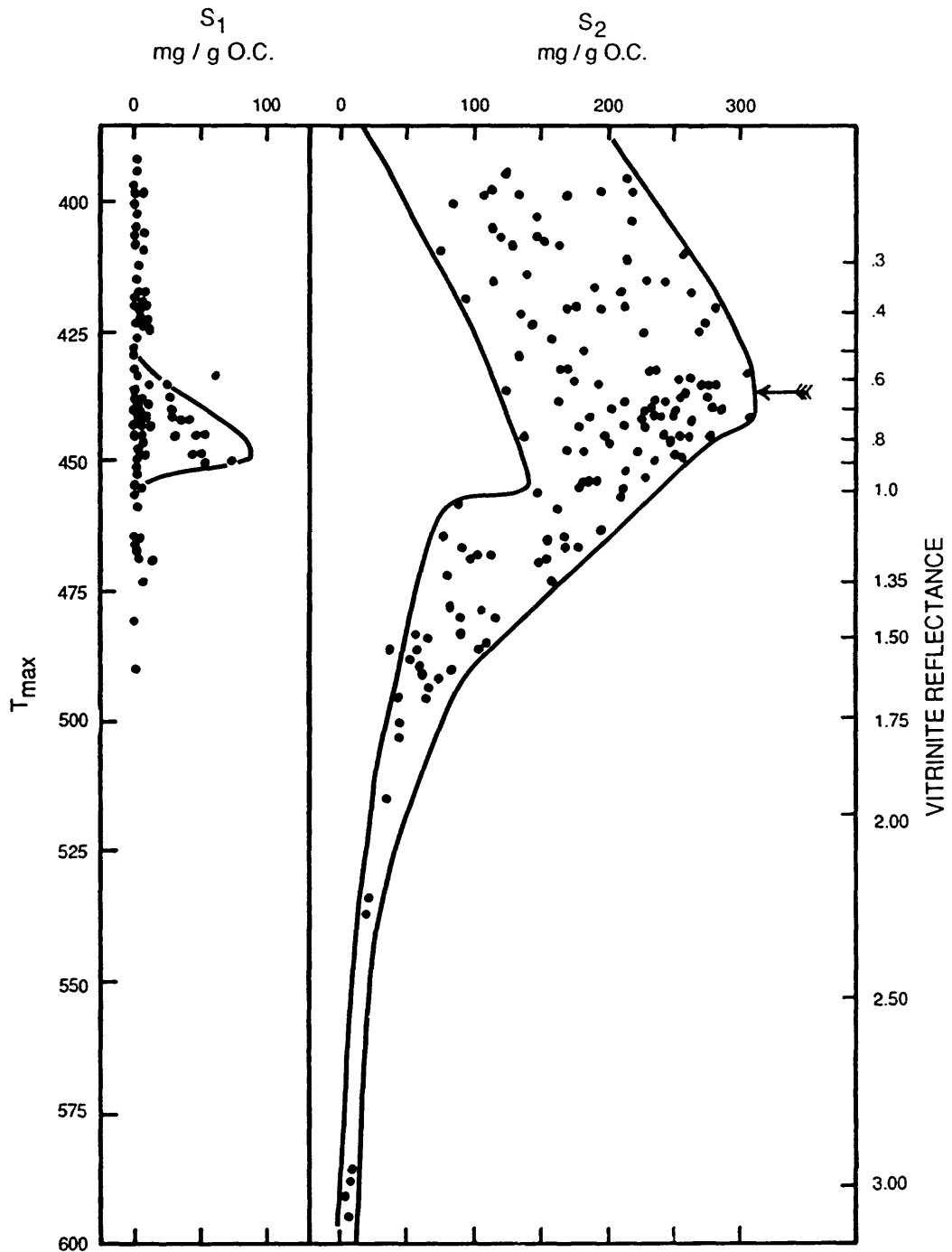


Figure 17. Plot of T_{\max} and R_o versus the ROCK EVAL S_1 and S_2 (hydrogen index) pyrolysis peaks (normalized to organic carbon-mg/g O.C.) for worldwide coals of Tertiary to Paleozoic age. The feathered arrow indicates the maximum in the hydrogen index data. T_{\max} was converted to R_o values by the use of Table 1 in Price (1989). Data from Teichmüller and Durand (1983).

1.8 to 2.0 does not support the hypothesis (which has come to be accepted as law) that C_{15+} HC's are thermally destroyed by $R_o = 1.35$.

Other lines of evidence do not support the hypothesis of a C_{15+} HC thermal deadline by $R_o = 1.35$. There are many cases of rocks with oxygen-rich OM where C_{15+} HC concentrations, or values for the ROCK EVAL S_1 pyrolysis peak, approach and remain at low or zero numbers by $R_o > 0.9$. However, at the same time, there are other cases of rocks with oxygen-rich OM where measurable or moderate concentrations of C_{15+} HC's, or the ROCK EVAL S_1 pyrolysis peak, exist to R_o values of 2.0, or even greater. The data from the Ralph Lowe #1 is such an example (Tables 4 and 5), and Law (1984) provided another example from the Green River basin. The presence of such elevated concentrations of C_{15+} HC's in rocks with oxygen-rich OM at high maturation ranks is hypothesized as due to inefficient primary migration (compared to similar cases where all C_{15+} HC's have been stripped from the rock at comparable maturation ranks.) Moderate concentrations of C_{15+} HC's apparently persist in some rocks with oxygen-rich OM past maturation ranks of $R_o = 2.0$, because this OM type loses all its capacity for HC generation, including methane generation, by $R_o = 1.8$ to 2.0. With no capacity left for HC gas generation, primary petroleum migration by gaseous solution is not possible. Thus, C_{15+} HC's which are present in the rock at this point, would remain in the rock until they are finally thermally destroyed, or are removed by another primary migration mechanism.

Another line of evidence which does not support a C_{15+} HC thermal deadline by $R_o = 1.35$ is moderate to high concentrations of C_{15+} HC's, and/or moderate to high ROCK EVAL S_1 pyrolysis peak values, coupled with high to moderate (remnant) C_{15+} HC generation capacity in fine-grained rocks with hydrogen-rich OM at maturation ranks far in excess of $R_o = 1.35$, or even $R_o = 2.0$. In fact, these characteristics have been encountered in rocks with hydrogen-rich OM at maturation ranks as high as $R_o = 4.0$ to 5.0. The solvent-extraction and ROCK EVAL pyrolysis data for the deep rocks with hydrogen-rich OM of the Ralph Lowe-1 well bore serve as an example of this point. Other examples also exist (Price and others, 1979, 1981; Price, 1982, 1983, Table 1; and Sajgó, 1980.) These data also suggest that the loss of HC generation potential by $R_o = 1.8$ to 2.0 in rocks with oxygen-rich OM may not be equivalent to the thermal destruction of C_{15+} HC's. This loss of HC generation potential rather could be due to a total expenditure of the relatively weak (compared to the bonds in hydrogen-rich OM) carbon-oxygen bonds in oxygen-rich OM.

One other line of evidence also does not support the hypothesized thermal destruction of C_{15+} HC's over the maturation rank range $R_o = 0.8$ to 1.35. If the decrease in C_{15+} HC's over this maturation rank range were due to carbon-carbon bond breakage, then this decrease in C_{15+} HC's should be accompanied by an increase in C_{14-} , and especially C_1-C_7 , HC's. However, in the cases (Durand and Oudin, 1979; Huc and Hunt, 1980; and Vandenbroucke and others, 1983) where the concentrations of these HC's have been measured, the concentrations of these lighter HC's also decrease over this maturation rank range (also presumably due to primary migration by gaseous solution, see Price, 1989).

OM type--OM type has been suspected of having only a minor effect, if any, on HC generation. Further, opinion is divided on which direction the effect is. Some investigators believe that hydrogen-rich (Types I and II) OM begins HC generation at lower maturation ranks than oxygen-rich (Type III) OM, including

Evans and others (1975), McCulloh (1979), and Walker and others (1983). Other investigators, including Tissot and Espitalié (1975), Tissot and others (1978), and Tissot and Welte (1978), have stated that based on their investigations in different sedimentary basins, the opposite is true. Empirically, the dominance of relatively weak carbon-oxygen bonds in oxygen-rich OM (and carbon-sulfur bonds in sulfur-rich OM), bonds which have low activation energies compared to those in hydrogen-rich OM, suggest that HC generation should occur at lower maturation ranks in oxygen-rich (and sulfur-rich) OM compared to hydrogen-rich OM. I have gathered a large amount of evidence (some of which has been discussed above and some of which has been published) both from Nature and the laboratory which suggests that this is the case. Furthermore, the effect is not subtle. Logically, wide variations in activation energies from the different reactions which result in HC generation would be expected. For example, probably the first major reaction which results in actual HC generation is the decarboxylation of fatty acids. Other reactions with higher activation energies than fatty acid decarboxylation, would be: de-oxygenation of other types of oxygen-bearing compounds such as ketones, esters, ethers, or alcohols; reactions involving loss of nitrogen or sulfur atoms; a breakdown of the molecular sieve properties of kerogen; the thermal conversion of asphaltenes and resins to HC's; and finally carbon-carbon bond rupture, which requires extreme burial temperatures because of the high activation energies involved (80 Kcal/mole; Tissot and Welte, 1978). Clearly, there are many different reactions with widely variable activation energies which can result in HC generation.

A substantial body of data has been presented that suggests: 1) HC generation from hydrogen-rich OM apparently requires much higher maturation ranks than HC generation from oxygen-rich OM. 2) Rocks with hydrogen-rich OM retain significant concentrations of C_{15+} HC's and remnant HC generation potential to much higher maturation ranks (up to at least $R_o = 4.0$ to 5.0) than do rocks with oxygen-rich OM ($R_o = 2.0$). 3) All organic maturation indices, including mainstage HC generation, appear to be suppressed in hydrogen-rich OM compared to the values which would be found in oxygen-rich OM buried under the same conditions.

The hypothesis advanced here, that OM type is a dominant controlling parameter in organic metamorphism, can be easily tested by experiments or investigations designed specifically to check the hypothesis. However, the maturation ranks at which the various stages of organic metamorphism take place in hydrogen-rich OM must be measured in, or tied to, maturation indices derived from oxygen-rich OM, due to the apparent suppression of all organic maturation indices in hydrogen-rich OM. For example, in the Mississippian-Devonian Bakken Shale (hydrogen-rich OM), the TIHG occurs at probable R_o values of 1.2 to 1.9 based on R_o analysis from the overlying Tertiary and Mesozoic shales (oxygen-rich OM). However, at the TIHG in the Mississippian-Devonian Bakken shales, the R_o values as read in these shales range between 0.24 to 0.38.

Pressure, system openness, and shearing--The effect of static (confining) pressure on HC generation is unclear. Consideration of basic chemical principals suggests that static pressure should play a significant role in organic metamorphism, as gases (organic and inorganic) are the major products in organic metamorphism (Price, 1988). "According to the principle of Le Chatelier, an increase in pressure on a reaction involving a gas or gases should cause the equilibrium to shift in the direction that will result in a decrease in volume.", Crockford and Knight (1959, p. 173). However, some investigators,

including Tissot and Welte (1978, p. 183, 196), and Hunt (1979, p. 467), have stated that static pressure plays no, or only a subordinate, role in HC generation. Other investigators including Rogers and others (1962), McIntyre (1972), Sengupta (1974), McTavish (1978), Cecil and others (1979), and Stach and others (1982) have stated, and provided evidence either from Nature or the laboratory, that pressure significantly retards organic maturation. I have carried out isothermal, hydrous-pyrolysis experiments as a function of increasing pressure using helium as the pressure medium. The yet unpublished results of these experiments demonstrated that increase in pressure severely retarded all aspects of organic metamorphism, including HC generation, in these experiments. If these hydrous-pyrolysis experiments mimic HC generation and organic metamorphism in Nature, as some investigators have claimed (Barker, 1983, p. 418; Durand, 1983; and Winters and others, 1983, p. 524), then these data would be strong evidence that pressure increases retard both HC generation and the eventual thermal destruction of $C_{15}+$ HC's in Nature.

Such a pressure retardation effect could be a dominant reason why significant concentrations of $C_{15}+$ HC's have been found in the high-rank rocks of deep well bores (Price and others, 1979, 1981; Price, 1982, 1983; and this paper). These rocks, presently at high burial temperatures, probably had significantly higher paleo burial temperatures, due to their high R_o values. My studies suggest that in addition to retardation of organic metamorphism in such deep rocks, retardation of inorganic (greenschist) metamorphism also has taken place, which has also been noted by other investigators. For example, Borak and Freidman (1981) examined the deep rocks of the Bertha Rogers #1 and Badden #1 well bores and found that little, or no, mineralogical-textural differences existed between sandstones and carbonates buried at 9.1 to 9.5 km, compared to similar units at much shallower depths in the same wells. In the Rogers and Badden wells, depths of 9.1 to 9.5 km would be equivalent to extrapolated R_o values of 6.25 to 6.85, R_o values thought to be characteristic of greenschist metamorphism. In my opinion, such retardation of inorganic (and organic) metamorphism could be due to the very high abnormal fluid pressures which most probably were present in these rocks at the time of their maximal burial temperatures. One of the key controls of mineralogical metamorphism is the circulation of chemically-active, hot waters through the system for the redistribution of elements, which requires a chemically open system. Closed chemical systems inhibit such an exchange, and therefore, inhibit metamorphism. Abnormally-pressured, deep rocks in petroleum basins are closed chemical systems as testified to by the presence of the abnormal fluid pressures.

High fluid pressures, besides retarding inorganic metamorphism and the thermal destruction of HC's, also prevent HC migration. However, shearing, from intense geologic structuring or other factors, opens such systems which: (1) causes large decreases in static fluid pressures, (2) allows element redistribution (with resulting inorganic metamorphism), and (3) allows HC migration. Concurrent large decreases in static fluid pressures in rocks at extreme burial temperatures would probably also result in the thermal destruction of $C_{15}+$ HC's. Goffé and Villey (1984, p. 81) recognized the controls that shearing and high static fluid pressure had on organic metamorphism in their study of metamorphic rocks in the French Alps, "In high-pressure, low-temperature metamorphic areas (6 kbar - 300°C) of the internal part of Briançonnais zone, organic matter-bearing metasediments contain hydrocarbon compounds (oils and wet gas) as inclusions in metamorphic minerals (quartz, lawsonite...). In contrast with the metamorphic conditions, the degree

of transformation of the organic matter is much less than that predicted by classical models of organic matter evolution during metamorphism. The textural study of solid organic matter in these metasediments indicates the coexistence of two phases: -- one has a structure similar to a kerogen of deep catagenesis. The degree of organisation is compatible with the existence of associated hydrocarbon compounds; -- the second has a structure similar to anthracite. Its degree of organisation is more compatible with the thermal conditions of metamorphism, but seems to result of shearing effects. An hypothesis is proposed: at a given temperature, the kinetics of organic matter evolution is considerably slowed by increasing static pressures (hydrostatic type). This inhibition effect of pressure is locally cancelled, in the case of carbonification, by shear stress, which promotes the transformation of kerogen."

Another example of the controls that high hydrostatic pressure, and the release of that pressure through shearing, have on organic and inorganic metamorphism comes from the highly-sheared rocks of the Salton Sea geothermal system, Southern California. Here, at burial temperatures as low as 200°C, classical greenschist metamorphism has taken place in these meta-sediments. Yet, the deep rocks in some sedimentary basins show absolutely no indications of greenschist metamorphism, and these deep rocks are currently at (and have been for hundreds of millions of years) burial temperatures far in excess of 200°C, and have probably been at even higher paleo temperatures for brief periods of geologic time. Furthermore, some of these rocks have not attained the expected levels of organic metamorphism according to accepted theory. The lack of shearing in such rocks, coupled with abnormal, static, fluid pressures, have, in my opinion, possibly played a dominant role in suppressing organic and inorganic metamorphism.

CONCLUSIONS AND SUMMARY

1) Measurable to moderate amounts of C₁₅⁺ HC's, and/or high values for the S₁ ROCK EVAL pyrolysis peak, were encountered in the rocks of the Ralph Lowe-1 well bore at maturation ranks of R_o = 1.0 to 4.5. These data do not support the hypothesis of the thermal destruction of C₁₅⁺ HC's by maturation ranks of R_o = 1.35. Two explanations are advanced for the moderate to high amounts of C₁₅⁺ HC's in the deep, high-rank rocks of the Ralph Lowe-1: A) inefficient primary migration by gaseous solution, and B) a change in OM type in the deep rocks of the well bore from oxygen-rich to an assumed originally hydrogen-rich OM as documented by maceral analysis and kerogen H/C atomic ratios.

2) In the deep rocks of the Ralph Lowe-1 with hydrogen-rich OM, sharp increases in C₁₅⁺ HC and bitumen coefficients (mg/g O.C.) and concentrations (ppm) took place in passing from the rocks with oxygen-rich OM. These sharp increases were unexpected, considering the maturation ranks (R_o = 3.5 to 5.0+), ages (Mississippian-Devonian to Ordovician), present-day burial temperatures (216°-246°C), and burial depths (7.1-8.2 km) of the rocks.

3) Values of the ROCK EVAL S₂ pyrolysis peak showed that kerogen burnout (loss of HC generation potential) occurred in the rocks with oxygen-rich OM of the Ralph Lowe-1 by maturation ranks of R_o = 1.8 to 2.0. This duplicated results of other studies of rocks with oxygen-rich OM at these maturation ranks.

4) In the Ralph Lowe-1, the values for the ROCK EVAL S₂ pyrolysis peak (normalized to organic carbon, mg/g O.C.) increased from zero (in the shallower

rocks with oxygen-rich OM) to values ranging from 24 to 127 mg/g O.C. in the deeper, high-rank rocks ($R_o = 3.5-4.2$) with assumed originally hydrogen-rich OM. This suggests that burnout^o of hydrogen-rich OM requires higher maturation ranks, than those ($R_o = 1.8$ to 2.0) required for burnout in oxygen-rich OM.

5) Standard organic-geochemical maturation indices (T_{max} , T.R., qualitative characteristics of the C_{15+} saturated HC gas chromatograms, the compound composition of the saturated HC's, the values of the S_2 pyrolysis peak, and the atomic H/C ratio of kerogen) in the rocks of the Ralph Lowe-1 did not exhibit the trends expected by conventional wisdom versus: R_o , burial depth, or each other.

6) Most, or all, of the above findings have been encountered in high-rank ($R_o = 2.0-5.0$) rocks with hydrogen-rich OM in other deep well bores. These rocks have been buried for hundreds of millions of years at $200^{\circ}-300^{\circ}\text{C}$ with probable brief geologic periods of much higher paleo burial temperatures.

7) The organic (and inorganic) geochemical data from the deeply-buried, high-rank rocks of the Ralph Lowe-1, and other deep wells bores, do not support some accepted precepts in petroleum organic geochemistry concerning HC generation, maturation, and thermal destruction: A) the thermal destruction of C_{15+} HC's by burial temperatures of $110^{\circ}-250^{\circ}\text{C}$ (depending on burial time) and/or by a maturation rank of $R_o = 1.35$, B) expected trends of maturation indices versus burial depth, and/or burial temperature, R_o , or versus each other, C) the onset of greenschist metamorphism and graphite formation in sedimentary rocks with burial temperatures of $200^{\circ}-250^{\circ}\text{C}$.

8) Some established "laws" in organic geochemistry are not supported by other published and unpublished data, nor by established precepts from other disciplines: A) The TIHG for rocks with hydrogen-rich OM appears to occur only at present-day (maximal) burial temperatures higher than 210°C and at R_o values far in excess of 0.6. B) Profound suppression of various organic-geochemical maturation indices appears to occur in rocks with hydrogen-rich OM compared to what the values for these maturation indices would be in rocks with oxygen-rich OM under the same burial conditions. C) High-rank, or double, HC generation zones have been documented in deeply-buried rocks. D) After decades of study, metamorphic petrologists have concluded that: (1) Greenschist metamorphism does not take place until minimum temperatures of 400°C are reached in pelitic, unshered rocks in the depocenters of deep sedimentary basins. (2) Graphite formation does not occur until temperatures of $600^{\circ}-660^{\circ}\text{C}$ are reached in Nature. These laws of metamorphic petrology correlate with the lack of any tendency towards greenschist metamorphism and/or graphite formation in the deeply-buried, high-rank ($R_o = 2.0$ to 5.0+), unshered rocks of sediment depocenters, where these rocks have been buried at temperature of $200^{\circ}-300^{\circ}\text{C}$ for hundreds of millions of years.

9) Four principal reasons are hypothesized for these contradictions to some aspects of accepted thought in petroleum organic geochemistry regarding organic metamorphism:

A) A possible erroneous assignation of geologic time as the factor responsible for the elevated organic-maturation ranks found in some geologically-old rocks currently at low burial temperatures and/or at shallow burial depths. Erosion and/or brief-geologic periods of highly-elevated

paleogeothermal gradients are more probably responsible for these heightened levels of organic maturation.

B) The lack of previous recognition that high static fluid pressures may retard, and that shearing may promote, all aspects of organic, and inorganic, metamorphism.

C) The lack of previous recognition that hydrogen-rich (Types I and II) OM may require much higher burial temperatures, and/or maturation ranks, for HC generation and thermal burnout, compared to oxygen-rich (Type III) and sulphur-rich OM.

D) A possible erroneous assignation of the thermal destruction of C_{15+} HC's as being the parameter responsible for the decrease (over the maturation rank $R_o = 0.8-1.35$), and disappearance (at $R_o = 1.35$), of C_{15+} HC's in some rocks with oxygen-rich OM (such as at Douala). Primary petroleum migration by gaseous solution is hypothesized as the factor more probably responsible for this decrease and disappearance of C_{15+} HC's, in those cases. Four different lines of evidence suggest that C_{15+} HC thermal destruction may not be the cause of this feature.

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