Organic Metamorphism in the California Petroleum Basins

Chapter A—Rock-Eval and Vitrinite Reflectance

By Leigh C. Price, Mark Pawlewicz, and Ted Daws

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Contents

Figures

Tables

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Abstract

The results of ROCK-EVAL and vitrinite reflectance analyses of a large sample base from more than 70 wells located in three oil-rich California petroleum basins are reported. The cores from these wells have a wide range of present-day burial temperatures (40° to 220°C). The rocks in these basins were deposited under highly variable conditions, sometimes resulting in substantially different organic matter (OM) types in rocks tens of meters vertically apart from each other in one well. The kinetic response of these different OM types to equivalent well-known burial histories is a pivotal point of this study.

In the Los Angeles and Ventura Basins, rock organic-richness significantly increased with depth, as did kerogen hydrogen content, and the percentage of fine-grained versus coarse-grained rocks. The shales in these basins are perceived as containing primarily hydrogen-rich amorphous OM. In actuality, the shallowest 2,000 to 3,000 m of rocks in the basins, and at least the upper 6,000 m of rocks in parts of the Los Angeles Basin central syncline, are dominated by type III/IV OM. In the Los Angeles Basin, mainstage hydrocarbon (HC) generation commences in the type III/IV OM at present-day burial temperatures of 85° to 110°C, most likely around 100°C, and is largely complete by 220°C. In the Southern San Joaquin Valley Basin, mainstage HC generation commences in type III/IV OM at 150°C and is also largely complete by 220°C. In the Ventura Basin, mainstage HC generation commences above 140°C in type III/IV OM. The apparent lower temperatures for commencement of HC generation in the Los Angeles Basin are attributed to the fact that parts of the basin were cooled from maximal burial temperatures by increased meteoric water flows during the last glaciations.

All aspects of organic metamorphism, including mainstage HC generation, are strongly suppressed in rocks with hydrogen-rich OM in these basins. For example, ROCK-EVAL data suggest that mainstage HC generation has not commenced in rocks with hydrogen-rich OM at present-day temperatures of 198°C. This observation is attributed to much stronger bonds in hydrogen-rich OM compared to types III and IV OM and, therefore, significantly higher burial temperatures are required to break these bonds. This difference in OM kinetics has profound ramifications for petroleum-geochemical exploration models.

Organic-matter characteristics inherited from original depositional conditions were overlaid on, and at times confused interpretation of, characteristics from organic metamorphism in all study areas. In all the basins examined in this study, immature fine-grained rocks occasionally had high to very high carbon-normalized concentrations of pre-generation indigenous bitumen. This unusual characteristic may be due to unique depositional conditions in these basins.

Introduction

Why this Study?

The Los Angeles Basin is the richest petroleum basin by sediment volume or area worldwide (Barbat, 1958; Yerkes and others, 1965; Wright, 1987; Price, 1994; and many other investigators). Moreover, the Ventura and Southern San Joaquin Valley Basins are among the richest basins worldwide. However, a paucity of published petroleum-geochemical data exists for these three basins. For example, Keller (1987, p. 30) in her resource assessment of the Ventura Basin noted, "For a mature province with a long and successful period of hydrocarbon exploration and development, very few data are available on geochemistry and thermal maturity of possible source rocks in the Ventura Basin assessment province." This conclusion also applies to the Los Angeles and Southern San Joaquin Valley Basins. For example, Phillipi's (1965) classic study of the Los Angeles Basin includes only 12 samples from two areas (the Dominguez and Seal Beach oil-fields). Moreover, vitrinite reflectance (R_o), ROCK-EVAL, and gas chromatographic analyses were not available at the time of the Phillipi (1965) study. The general lack of published petroleum-geochemical data contrasts with the fact that geologically, these are the, or among the, most thoroughly studied basins worldwide (Beyer and Bartow, 1987; Keller, 1987, and Beyer, 1988a, also see references below).

Many geologic studies of these basins have been published including Jennings and Troxel (1954), Nagle and Parker (1971), and Keller (1987) for the Ventura Basin. Studies of the San Joaquin Valley Basin include Hoots and others (1954), Hackel (1966), Foss and Blaisdell (1968), Bandy and Arnal (1969), Callaway (1971), Foss (1972), Harding (1976), MacPherson (1978), Zieglar and Spotts (1978), Ingersoll (1979), Dickinson and Seely (1979), Webb (1981), Graham and others (1982), and Williams and Graham (1982), Blueford (1984), Graham (1985, 1987), Graham and Williams (1985), Bartow (1987), and especially Beyer and Bartow (1987) for a complete review of previous work. Geologic studies of the Los Angeles Basin include: Driver (1948), Edwards (1951), Woodford and others (1954), Barbat (1958), Yerkes and others (1965), Brown (1968), Gardett (1971), Hill (1971), Harding (1973), Yeats (1973), Crowell (1974), Campbell and Yerkes (1976), Schwartz and Colburn

(1987), Wright (1987), Mayer (1987; 1991), Beyer (1988a), Blake (1991), Biddle (1991), Redin (1991), and Yeats and Beall (1991).

The southern California basins provide some of the most accurate equilibrium-burial temperatures worldwide, largely because of early exploration activities. For example, the Brea Olinda field, Los Angeles Basin, was discovered in 1880 (Biddle, 1991). From 1920 to 1950, numerous investigators aggressively pursued accurate determination of present-day equilibrium-burial temperatures in different areas, including the southern California basins, by closely monitoring production temperatures and determining long-term (as much as 3 years) shut-in temperatures. This resulted in numerous publications of equilibrium-burial temperatures in the southern California basins, including Carlson (1930a, b), Van Orstrand (1934), French (1940), Benfield (1947), and Moses (1961, 1962). Accurate equilibrium-burial temperatures also were later measured by John Castaño and coworkers (Castaño and Sparks, 1974; and Hood and Castaño; 1974) and by Wang and Munroe (1982). Consequently, we have knowledge of present-day equilibrium-burial temperatures, available in few other studies.

The current study involves a very large sample base composed of core samples from more than 70 wells in the Los Angeles, Ventura, and Southern San Joaquin Valley Basins (table 1), as well as cuttings-chips samples from the Apex-1 well, Los Angeles Basin, which was drilled with a water-base mud. Several wells from the northern San Joaquin Valley and Sacramento Valley Basins were also studied. This study's sample base spanned a wide temperature range, with maximum burial temperatures of 223°C. (Geothermal gradients for the different study areas are given in table 2.) Areas of uplift and erosion exist in all the basins studied; however, only samples from the basin synclinal areas at present-day maximal burial are reported here.

Early publications on the Los Angeles-Ventura (California), Douala (Cameroons, Africa), Paris (France), and Williston (North Dakota) Basins form the foundation for present-day petroleum geochemistry. However, 1974 to 1978 U.S. Geological Survey petroleum-geochemical research in the California basins resulted in data which fell outside of existing paradigm. Some of these data were presented in Walker (1982), Walker and others (1983), Price (1983, figs. 3,4) and Price and Barker (1985, fig. 4 and table 1), wherein different organic-matter (OM) types responded to the same burial conditions in dramatically different fashions. The California basins perhaps offer our best possibility to examine the thermal response of different OM types to the same burial conditions, because of the large burial-temperature range of the rocks there, the large sample base of cores, the wide range of OM types in contiguous samples, the well-known geologic history, and the accurately determined equilibrium-burial temperatures.

The Los Angeles-Ventura Basins are not the only examples of basins having data sets that strongly contradict established paradigm, constituted on the basis of original studies in the Los Angeles-Ventura, Douala, Williston, and Paris Basins. Investigations in the Williston Basin (Price and Le Fever, 1994) also demonstrate that the currently accepted model of oil expulsion and accumulation, a model formed on the basis of early studies in the Williston Basin, is dysfunctional in the very basin in which the model was derived.

In this study, the petroleum-geochemical analyses on the rocks of the California basins yielded complex results, for which interpretations were difficult. Much greater complexity would have been added to this study with any attempted oil to source-rock correlations. Moreover, sufficient rock-sample bases, regarding both maturity and basinal location, are not available for these basins to perform such a study.

This is a three part study. This first paper involves ROCK-EVAL and vitrinite reflectance (R_o) analyses. The second part (Price, 1999) concerns quantitative and qualitative results of the extracted bitumen and saturated hydrocarbons (HCS). The third part will involve biomarkers, aromatic HCS, aqueous-pyrolysis experiments, modeling studies, and whole-rock extraction as related to possible low-rank formation of commercial-oil deposits in these basins.

Stratigraphy, stratigraphic relationships, and depositional histories are not discussed in detail in these three studies. Bostick and others (1978) present detailed stratigraphy and burial histories for many of the areas of this study. Stratigraphy for all areas of this study is available in California Oil and Gas Fields (1973, 1974). Thick Pliocene to Pleistocene sections are present in the synclines of the Los Angeles, Ventura, and Southern San Joaquin Valley Basins. The oldest rocks we examine are upper mid Miocene in the Los Angeles-Ventura Basins and lower Miocene in the Southern San Joaquin Valley Basin. Thus, the burial histories of the rocks we studied from these three basins are very similar.

Samples and Methods

With the exception of the cuttings-chips samples from the Apex-1 wellbore, all samples were core (table 1). All wells were drilled with water-based muds. All core samples were cleaned by scrubbing them with a brush in warm water until all drilling mud was removed. The Apex-1 cuttings-chips samples (originally in packets of 30 or 60 ft (9.1 to 18.2 m) intervals) were cleaned in hot water, by an ultrasonic cleaner, to remove all drilling mud. The chips were then lightly rinsed with methanol to remove the water and dried in an oven at 50°C for five minutes.

Iron fragments from cuttings-chips samples were removed with a magnet, the chips were then sieved and microscopically picked (to 20 mesh) to dominant lithologies (black shales, brown shales, and dark or light silty shales or shaley silts, sandstones). Samples were then ground and sieved to 100 mesh for ROCK-EVAL analysis carried out at the U.S. Geological Survey from 1980 to 1994.

Many ROCK-EVAL analyses of sandstones and silty sandstones indicated oil staining which was also present in some siltstones. Four to five hundred milligrams of 100 mesh powder from many stained samples were solvent extracted for 3 to 7 days simultaneously together in small packets. These packets were made by folding over and stapling shut 5.5 mm diameter filter paper and were labeled with a soft lead pencil. The extracted samples were then reanalyzed by ROCK-EVAL. Reanalyzed oil-stained samples exhibited large decreases (125

Table 1. Wells, and well locations (including basins, fields, and areas) from which samples were obtained for this study. Latitude and longitude values for some wells are from Bostick and others (1978). Wilimington field wells are directionally-drilled wells from cluster sites of piers or offshore man-made islands.

LOS ANGELES BASIN
Santa Fe Springs Field
Union Oil "Bell" No. 62, lat 33°56'34" N., long 118°03'55" W.
Mobil (General Petroleum) "Santa Fe" No. 46A, lat 33°56'31" N., long 118°03'25" W.
Shell "GH & N" No. 15, lat 33°56'45" N., long 118°04'22" W.
ARCO (Richfield Oil Corporation), "Elliott" No. 2, lat 33°56'44" N., long 118°04'53" W.
Union Oil "Bell" No. 38, lat 33°56'39" N., long 118°04'00" W.
Mobil (General Petroleum) "Santa Fe" No. 243, lat 33°56'21" N., long 118°03'33" W.
Union Oil "Bell" No. 100, lat 33°56'36.8" N., long 118°03'54" W.
Union Oil "Bell" No. 107, lat 33°56'43.5" N., long 118°04'01.5" W.
Texaco Foix No.6, sec. 6, T. 3 S., R. 11 W.
Jordon No. 7, NW1/4 NW1/4 NW1/4 sec. 6, T. 3 S., R. 11 W.
Jordon No. 8, NW1/4 NW1/4 NW1/4 sec. 6, T. 3 S., R. 11 W.
Northwest Plunge Santa Fe Spring Field
Chevron (Standard Oil of California), "Houghton Comm. One" No. 1, lat 33°57'18" N., long 118°5'10.5" W., sec. 36, T. 2 S., R. 12 W.
Long Beach Field
Shell Stakemiller Rose No. 1, sec. 29, T. 4 S., R. 12 W.
Richfield Malcom Davis #8, SE sec. 19, T. 4 S., R. 12 W.
Shell Alamitos 48A, sec. 29, T. 4 S., R. 12 W.
Texaco Long Beach Airport-1, sec. 20, T. 4 S., R. 12 W.
Central Syncline
Chevron (Standard Oil Company of California), "Carlin Comm." No. 1, lat 33°54'19" N. long 118°13'07" W., NW1/4 NW1/4 sec. 14 T. 3 S., R. 13 W.
Western Gulf "Pacific Gas and Electric" No. 1, lat 30°57'11.9" N., long 118°14'34.4" W., NE1/4 SE1/4 sec. 33, T. 2 S., R. 13 W.
American Petrofina Central Core Hole-2, SW1/4 NE1/4 sec. 4, T. 3 S., R. 13 W.
Whittier Field
Standard Oil of California MW-101, sec. 26, T. 2 S., R. 11 W.
Standard Oil of California MW-62, NE1/4 NW1/4 sec. 26, T. 2 S., R. 11W.
Standard Oil of California MW-100, NE1/4 NE1/4 sec. 26, T. 2 S., R. 11W.
Huntington Beach Field
Standard Oil Calif. Lomita Land and Water Co., sec. 19, T. 5 S., R. 11 W.
Dominguez Field
Standard Oil Calif. Del Amo-1, sec. 8, T. 4 S., R. 13 W.
Shell (Dominguez-Oil), Reyes-1, sec. 33, T. 3 S., R. 13 W.
Shell (Dominguez-Oil), Reyes-27A, sec. 34, T. 3 S., R. 13 W.

Table 1—continued

Dominguez Field—continued			
Shell (Dominguez-Oil), Reyes-60, sec. 34, T. 3 S., R. 13 W.			
Shell (Dominguez-Oil), Reyes-97, sec. 33, T. 3 S., R. 13 W.			
Shell (Dominguez-Oil), Reyes-100, sec. 34, T. 3 S., R. 13 W.			
Shell (Dominguez-Oil), Reyes-109, sec. 34, T. 3 S., R. 13 W.			
Shell (Dominguez-Oil), Reyes-141, sec. 34, T. 3 S., R. 13 W.			
Shell (Dominguez-Oil), Reyes-147, sec. 33, T. 3 S., R. 13 W.			
Wilmington Field			
	WJ141	WD107	D308
	WD401	WD114	D102
	WC533	WD204	D605
	WD401	WC603	C403
Seal Beach Field and Evirons			
Texaco Bixby Ranch-1, sec. 36, T. 4 S., R. 12 W.			
Texaco Bixby Ranch-2 (NCT-1), sec. 36, T. 4 S., R. 12 W.			
Texaco Bryant Estate-1, SW Corner sec. 1, T. 5 S., R. 12 W.			
Continental Oil McGrath-18, sec. 10, T. 5 S., R. 12 W.			
Baldwin Hills Area			
Shell Baldwin Hills Community-1, sec. 9, T. 2 S., R. 14 W.			
Northeast Flank			
C.C.M.O. "Bandini" No. 1, lat 33˚59'16.5" N., long 118˚08'23.6" W., NW1/4 NE1/4 sec. 21, T. 2 S., R. 12 W.			
ARCO (Richfield Oil Corporation) "Vail" No. 1, lat 34˚00'16.5" N., long 118˚08'17" W., NE1/4 NE1/4 sec. 16, T. 2 S., R. 12 W.			
ARCO (Richfield Oil Corporation) "UP Unit" No. 1., lat 34˚00'09" N., long 118˚08'45.5" W., NE1/4 NW1/4 sec. 16, T. 2 S., R. 12 W.			
Anaheim Nose			
Mobil (General Petroleum Corporation), "Librown" No. 1, lat 33˚53'26" N., long 118˚01'44.5" W., sec. 21, T. 3 S., R. 11 W.			
General Petroleum La Mirada 46-1, sec. 16, T. 3 S., R. 11W.			
General Petroleum McNally-1, sec. 22, T. 3 S., R. 11 W.			
Standard Oil Calif. (Chevron), Pacific Community-1, sec. 26, T. 3 S., R. 11 W.			
VENTURA BASIN			
Ventura Avenue Field			
Getty Lloyd-183, Ventura Avenue Field, Ventura Basin, NW1/4 NW1/4 sec. 26, T. 3 N., R. 23 W.			
Shell Taylor 316, NE1/4 NE1/4 sec. 29, T. 3 N., R. 23 W.			
Shell Taylor 315, NW1/4 NW1/4 NW1/4 sec. 28, T. 3 N., R. 23 W.			
Shell Taylor 395.			
Central Syncline			
Standard Oil Calif. (Chevron) Limoneira-1, sec. 30, T. 3 N., R. 22 W.			
Chevron (Standard Oil Company of California) "Maxwell" No. 1, lat 34˚14'35"N., long 119˚15'06" W., sec. 23, T. 2 N., R. 23 W.			
Superior Oil Company "Limoneira" No. 1, lat 34˚16'07" N., long 119˚11'48" W., sec. 9, T. 2 N., R. 22 W.			

Table 1—continued

SOUTHERN SAN JOAQUIN VALLEY BASIN
Paloma Field
Ohio (Marathon) Oil KCLA 72-4, sec. 4, T. 32 S.,R. 26 E. (MDB)
Ohio Oil A-1, sec. 31, T. 31 S., R. 26 E. (MDB)
Ohio Oil KCLA 8, sec. 32, T. 31 S., R. 26 E. (MDB)
Ohio Oil KCLA 61-31, sec. 31, T. 31 S., R. 26 E. (MDB)
Ohio Oil KCL-F-71-10, sec. 10, T. 31 S., R. 26 E. (MDB)
Superior Anderson 56, sec. 35 T. 31 S., R. 26 E. (MDB)
KCL-74-3, sec. 35 T. 31S., R. 1, sec. 3, T. 32 S., R. 26 E. (MDB)
Coles Levee/Canal Fields
Shell Canal 21-14, sec. 14, T. 30 S., R. 25 E. (MDB)
Arco CLA 67-29, Coles Levee A, sec. 29, T. 30 S., R. 25 E. (MDB)
Southern Rim
Arco RSS 84-26, sec. 26, T. 11 N., R. 20 W.
Ohio Oil Mitchell Ranch-1, sec. 3, T. 32 S., R. 29 E. (MDB)
Tenneco-Superior Sand Hills 64X, sec. 34, T. 32 S., R. 28 E. (MDB)
MIDDLE SAN JOAQUIN VALLEY BASIN (JACALITOS FIELD)
Standard Oil of California 67-17E, Jacalitos Oil Field, sec. 17, T. 21 S., R. 15 E. (Fresno County), sec. 17, T. 21 S., R. 15 E. (MDB)
SACRAMENTO VALLEY BASIN (TRACY GAS FIELD)
Amerada Farmers Development Lands (FDL)-1, sec. 15 T. 2 S., R. 5 E. (MDB)

to 500 percent or more) in total organic carbon (TOC) and in the S_1 and S_2 pyrolysis peaks, either as normalized to TOC or in absolute concentrations (ppm by rock weight). However, these data are not presented here. Rocks with TOC values less than 0.5 percent are also largely excluded. Although some immature fine-grained rocks were oil-stained (discussed in Price, 1999), others had abnormally high indigenous-HC concentrations. Analyses of all such fine-grained rocks are included here.

Vitrinite reflectance (R_o) analyses were carried out by kerogen isolation by HCl-HF rock maceration, floating the kerogen in hydrogen bromide during centrifuging, water-rinsing, and freeze-drying the float kerogen. Microscopic analyses were largely performed from 1975 to 1984. All samples had at least 30 readings; almost all had 50–70 readings; some selected samples had up to 120 readings. Representative examples of the statistical distribution of the R_o histograms, and the number of readings per sample, are in Bostick and others (1978). Many R_o analyses of these same rocks published in Bostick and others, (1978) followed expected behavior regarding R_o increase with increasing burial temperature. However, other samples yielded abnormally low R_o values for their burial temperatures (discussed in Walker, 1982; Walker and others, 1983; and Price and Barker, 1985). Thus, these samples were sent to commercial (service) geochemical laboratories and to other investigators to verify the in-house measurements. Some samples had as many as 20 such separate measurements. Unlike previously reported "round-robin" petroleum-geochemical studies (Claypool and Magoon, 1985; Dembicki, 1984; and Isaacs and Rullkötter, 1993), in this case excellent interlaboratory agreement was consistently reported: anomalously low R_o values.

Results

Los Angeles Basin Central Syncline

The Apex-1, a 6,332.6 m wellbore, drilled in the central syncline of the Los Angeles Basin, is the deepest well in the basin. Rock lithologic characteristics of the Apex-1 wellbore bear on its petroleum geochemistry. In this well, from 1,067 m (the shallowest sample) to 3,350 m, gravel, sandstone, and silty sandstone constitute 70 to 95 percent of the material in the sample packets. From 1,067 m to 3,012 m, the only fine-grained rocks were silt; shale or shaley silt were absent. Shale was first encountered at 3,073 m. Conversely, deeper than 3,350 m, shale and shaley-silt constitute 50 to 80 percent of the sample packets. Similar lithologic changes versus depth were present in other areas of the Los Angeles (and Ventura) Basins and are due to the basins "sanding up" late in their history (upper-Miocene to

Table 2. Equations for geothermal gradients in the areas examined in this study. Temperatures are in °C and depths are in feet. Depths are given in feet and not meters, because all the original sample depths were in feet, thus allowing more direct comparison of other sample bases with that of this study and Price (1999). Log-header (nonequilibrium) temperatures were corrected by the formula in Price and others (1981).

Basin Field/Area	Equation for Geothermal Gradient	Reference	Source
Los Angeles Santa Fe Springs	˚C = 23.3˚ + 0.0107 x depth	Bostick and others (1978)	Shallow production temperatures and deep and shallow well shut-in temperatures.
Los Angeles Long Beach	˚C = 23.0˚ + 0.01066 x depth	French (1940)	Production emperatures. Surface temperature of 23.0˚C assumed.
Los Angeles Whittier	˚C = 21.7˚ + 0.01052 x depth	Van Orstrand (1934) and Carlson (1930a, b)	Shallow production temperatures.
Los Angeles Central Syncline	˚C = 23.3˚ + 0.008797 x depth (for 0-12,300 ft) ˚C = 131.5 + 0.0110 (depth-12,310 ft) (for >12,300 ft)	This study	Corrected nonequilibrium log-header temperatures.
Los Angeles Wilmington	˚C = 21.1 + .017002 x depth	Mayuga (1970)	Deep production temperatures.
Los Angeles, Anaheim Nose	˚C = 23.3 + 0.00086 x depth (for 0-6,000 ft) ˚C =74.9 + 0.0104 x (depth - 6,000 ft) (for >6,000')	Bostick and others (1978)	Deep well shut-in temperatures.
Los Angeles, Santa Fe Springs	˚C = 137 + 0.01222 x (depth -10,000 ft) (for 10,000 ft -15,000 ft)	Bostick and others (1978)	Corrected nonequilibrium temperatures.
Los Angeles, Los Angeles	˚C = 23.3 + 0.0102 x depth	Bostick and others (1978)	Deep well shut-in temperatures.
Los Angeles, Huntington Beach	˚C = 23.0 + 0.013479 x depth	Van Orstrand (1934)	Production temperatures. Surface temperature of 23.0˚C assumed.
Los Angeles, Dominguez	˚C = 23.0 + 0.010620 x depth	French (1940)	Production temperatures. Surface temperature of 23.0˚C assumed.
Los Angeles, Seal Beach	˚C = 23.0 + 0.011188 x depth	French (1940)	Production temperatures. Surface temperature of 23.0˚C assumed.
Los Angeles, Inglewood	˚C = 23.0 + 0.010318 x depth	Walker (1982)	Corrected nonequilibrium temperatures for Standard Oil Calif.-Packard 55 well. Surface temperature of 23.0˚C assumed.
Ventura, Central Syncline	˚C = 21.0 + 0.0071 x depth	Bostick and others (1978)	Deep well shut-in temperatures.
Ventura, Ventura Avenue	˚C = 21.1 + 0.008335 x depth	John Castaño, Shell Oil, oral commun., 1985	Six month shut-in temperatures from six separate deep wells.
Southern Sacramento Valley, Tracy	˚C = 22.2 + 0.00851 x depth	This study	Corrected nonequilibrium log-header temperatures
Northern San Joaquin Valley, Jacalitos	˚C = 22.4 + 0.01009 x depth	Van Orstrand (1934)	Shallow production temperatures
Southern San Joaquin Valley, Paloma	˚C = 22.0 + 0.009186 x depth	Hood and Castaño (1974)	Production and shut-in temperatures
Southern San Joaquin Valley, Coles Levee	˚C = 23.0 + 0.09658 x depth	Moses (1961)	
Southern San Joaquin Valley, Tejon Area	˚C = 20.1 + 0.007686 x depth	Castaño and Sparks (1974)	

Pliocene). The shallow coarse-grained rocks resulted from heavy erosion of crystalline rock from adjacent highland areas concurrently being uplifted. Upper Miocene rocks were still present at the bottom of the Apex-1 wellbore at 6,325 m.

One consequence of this "sanding up" in these basins is a strong decrease in rock organic richness with decreasing depth, from the increase in gravels and sands. This is apparent in figure 1, where TOC of the cleaned unpicked cuttings chips is plotted versus depth for random samples. Average TOC contents for rocks deeper than 3,350 m largely varies between 0.4 and 0.8 percent (fig. 1). The lower TOC values within this burial interval are from samples with higher sand contents, and higher TOC values are from samples with higher silty-shale and shale contents. Shallower than 3,350 m, average TOC contents dramatically decrease and remain low due to the high sand and gravel content of these rocks. Essentially the upper 3,350 m of the Los Angeles Basin central syncline is a sand and gravel pit. This has strong implications for meteoric water flow in the recent geologic past.

A second important lithologic characteristic of the Apex-1 wellbore is that rock samples, especially samples from deeper than about 3,500 m, often exhibited evidence of turbidite deposition. For example, sandstone, silt, or shale were swirled with each other in the same cutting chip (nonlinear depositional boundaries between different rock types in the same chip). In addition, grain size was poorly sorted in many chips. Poorly sorted silts were the most common fine-grained rocks in the wellbore, and shales contained occasional sand-size grains. However, well-sorted shales or sandstones also were present in the wellbore. Beyer (1988a), Redin (1991), and many other investigators have noted that turbidity currents played major roles in Los Angeles Basin sedimentation. Debris flows, fluidized-sediment flows, and grain flows also were significant (Redin, 1991). This infilling of the Los Angeles Basin central syncline by mass-transport sedimentation strongly affected rock OM characteristics (fig. 2).

The TOC content and the carbon-normalized (mg/g) ROCK-EVAL S_1 and S_2 (hydrogen index) peaks are plotted versus burial temperature and depth for rocks from the Apex-1 in figure 2. Only four samples have hydrogen index (HI) values above 225 (the maximum value being 294). Deeper than 5,650 m (200°C), a strong decrease of hydrogen index (HI) values occurs from intense HC generation. However, many of the figure 2 samples shallower than 5,250 m (and thus not affected by intense HC generation) also have low HI values (80 to 150), values characteristic of type IV OM. Many samples also exhibit HI values between 150 and 200 (type IV /III OM) and only a few samples have HI values over 200 (type III OM). The dominance of types IV and IV/III OM in these rocks precludes the possibility that they be considered as oil-source rocks. Additional ROCK-EVAL data (not shown here) collected from two other wellbores from 612 to 4,182.9 m in the Los Angeles Basin central syncline (Carlin Community-1, and Pacific Gas and Electric-1, table 1), also exhibit low TOC and low HI values, also indicating a lack of source rocks there.

Most past investigators have concluded that one of the most important reasons the Los Angeles Basin is so oil-rich, is that the basin has abnormally rich source rocks. However, there is almost no published data supporting this widespread assump-

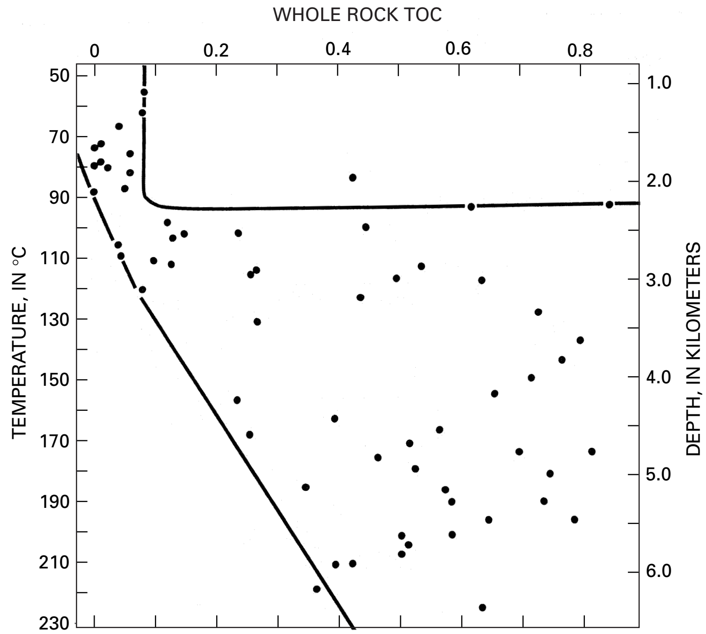

Figure 1. Plot of TOC (total organic carbon) versus burial temperature in °C and burial depth in kilometers for unpicked cleaned samples from random cuttings chips from the Apex-1 wellbore. Depth axis changes scale because of a dog-leg in the geothermal gradient.

tion, an assumption which the HI data of figure 2 suggest is not completely accurate. That at least 6,332.6 m of rocks in the Los Angeles Basin central syncline contain no hydrogen-rich OM is, to say the least, unexpected.

Our large ROCK-EVAL data base demonstrated that at different sites in the Los Angeles and Ventura Basins, the organic richness of the rocks there (as measured by TOC and HI values) increased dramatically with depth. In figure 2, TOC and HI values appear to be largely invariant with depth, contradicting this generally observed trend. However, the figure 2 data are from fine-grained rocks picked from the total sample. If TOC values of the total (unpicked) sample are considered (fig. 1), then rock organic richness at the Apex-1 site clearly does increase with depth, especially beyond 3,350 m. This general increase in rock organic richness with depth in these basins is caused by: (1) an increase in fine-grained rocks with depth; (2) possibly a general shift of depositional conditions for shallower rocks (resulting in lower HI values) compared to the depositional conditions for deeper rocks which resulted in higher HI values (350-800); (3) increasing hydrogenation of kerogen with increasing depth; and (4) lower sedimentation rates for deeper rocks compared to shallower rocks, resulting in less dilution of the OM deposited with the sediment. This last feature is thought to be an important overlooked depositional control of sediment organic richness (Caroline Isaacs, then U.S. Geological Survey, written commun., 1997).

As stated, one may argue that the HI data of figure 2 are largely depth-invariant to about 200°C, where HI values strongly decrease with depth from mainstage HC generation. However, as portrayed in figure 2, we interpret the data otherwise. From 1,000 m to 2,440 m, maximal HI values increase from 105 to 220. We attribute this increase both to kerogen hydrogenation and to changes in depositional conditions with

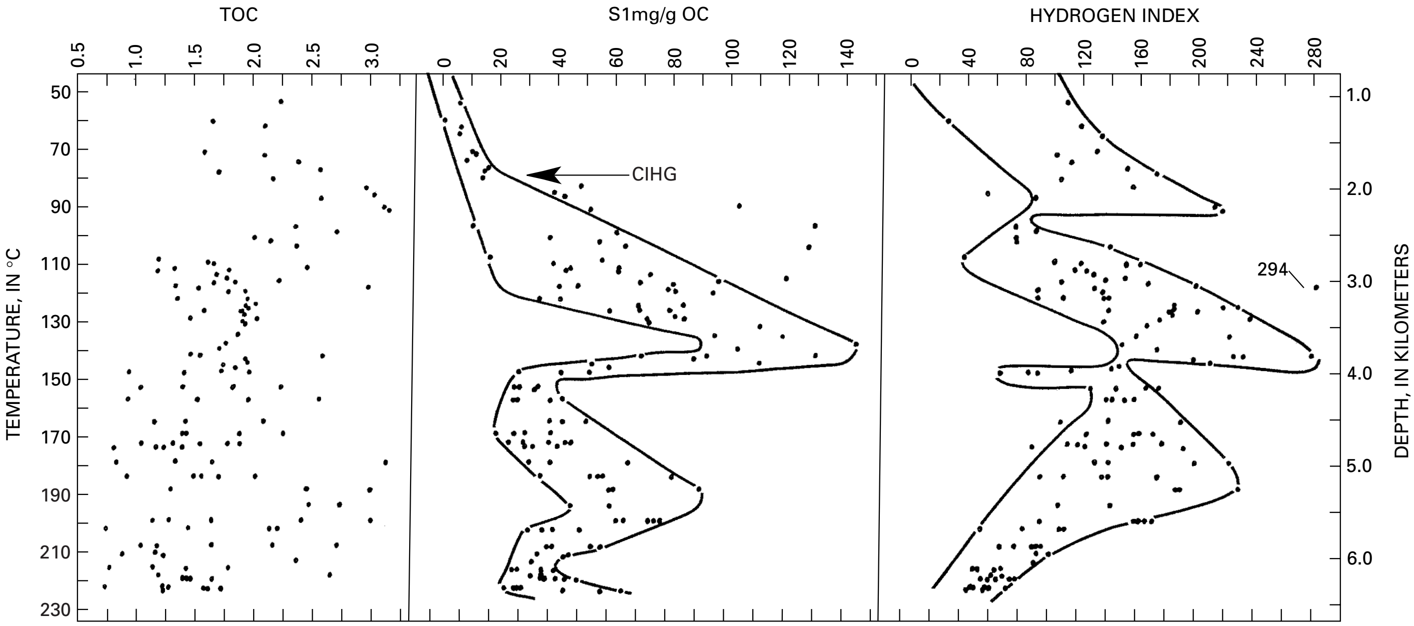

Figure 2. Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) S_1 and S_2 (HYDROGEN INDEX) ROCK-EVAL peaks versus burial temperature in °C and depth in kilometers for siltstones and shales from the Apex-1 wellbore, central syncline, Los Angeles Basin. Depth axis changes scale because of a dog-leg in the geothermal gradient (table 2). Trends defined by solid lines are discussed in text. The number 294 in the hydrogen index plot is an offscale high value. "CIHG" in the carbon-normalized S_1 plot is the commencement of intense HC generation by that measurement.

increasing depth. At 2,440 m, HI values begin decreasing to minimum values of about 70 (type IV OM) around 2,500 to 2,700 m. Hydrogen indices then increase with depth to maximal values of 230 at 4,054 m, with two outliers at 276 and 294. Hydrogen indices of 200–230 are still hydrogen-poor, type III OM; however; over a three-fold increase has occurred in maximal HI values from 2,700 m to 4,054 m. This significant increase is again attributed both to changes in depositional conditions and to kerogen hydrogenation with increasing depth . A significant decrease of maximum and minimum HI values from 142° to 165°C are not due only to HC generation, because maximal HI values increase from 140 at 165°C to 190 by 175°C. Thus, these changes in HI values over the temperature interval of 142° to 165°C are attributed partly to changing depositional conditions. Beyond 5,578 m (196°C), HI values strongly decrease to minimal values of 40 to 60 by 223°C (6,320.9 m), and we attribute the decrease to intense HC generation.

The ROCK-EVAL S_1 peak normalized to organic carbon (S_1 mg/g OC, fig. 2) is an indirect measure of the HC coefficient as would be determined from solvent extraction. The S_1 peak demonstrates significant increases from 1,070 m to 3,934.8 m, attributed here to both HC generation and to varying organic-geochemical characteristics from changing depositional conditions. Commencement of intense HC generation (CIHG, fig. 2) occurs at 85°C by the S_1 data of figure 2, in contrast to Phillipi's (1965) value of 120°C. Nevertheless, other data from this paper and from Price (1999) support the lower temperature value. However, the S_1 increase from 85° to 140°C is also related to two factors other than HC generation.

For example, the S_1 values of figure 2 maximize at 100 to 140 mg/g OC at 140°C. These are extreme values for OM with so little capacity for HC generation as demonstrated by the low HI values over this burial range (fig. 2). Moreover, production indices (fig. 3, PI) are abnormally high for these burial temperatures, ranging between 0.20 and 0.45. These production index (PI) values are characteristic of those of much deeper samples in figure 3. If such intense HC generation were occurring from 85° to 140°C, HI values should be concurrently decreasing. Instead, like the S_1 values, HI values strongly increase over this interval (fig. 2), exactly the opposite of expected behavior. This dual increase of S_1 and HI values for rocks between 80° and 140° C is more apparent in figure 4. The relationship between S_1 and HI is interpreted as evidence of varying depositional conditions controlling the organic richness of rocks, and thus partly controlling the increase in S_1 values, over this burial interval. In other words, the rocks are becoming more organic-rich with depth.

This increase in S_1 values from 80° to 140°C is also partly attributed to a characteristic of fine-grained rocks from the California oil basins discussed both below and in Price (1999). *Abnormally high carbon-normalized contents of immature indigenous HCS and bitumen are present in some rocks of these basins at ranks below mainstage HC generation.* The parameter(s) controlling this feature may have been operative when the rocks of the 80° to 150°C interval were deposited, apart from a general increase in organic richness with depth. The high HC concentrations in rocks over 85° to 140°C are neither from oil staining nor contamination during drilling. As noted above, the Apex-1 was drilled with a water-based mud and sandstones between 85° and 140°C have normal S_1 and S_2 values (fig. 5), precluding the possibility of contamination from staining or drilling.

Returning to figure 2, S_1 values strongly decrease between 140°and 150°C, correlating with the decreasing HI values over this interval. The correlation of decreasing S_1 values with

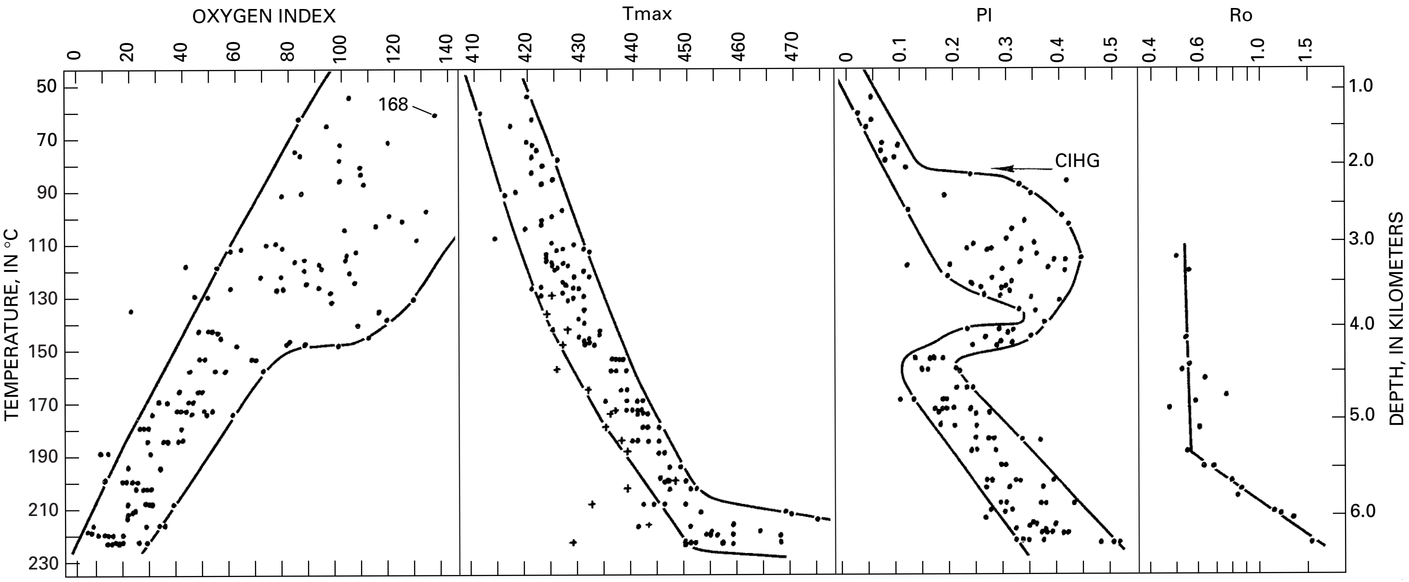

Figure 3. Plot of ROCK-EVAL oxygen index (S_3 mg/g OC), T_{max}, production index (PI) values; and R_o versus burial temperature in °C and burial depth in kilometers for siltstones and shales from the Apex-1 wellbore. Depth axis changes scale because of a dog-leg in the geothermal gradient (table 2). Trends defined by solid lines discussed in text. Crosses in the T_{max} plot are low-TOC siltstones. "CIHG" in the PI plot is the commencement of intense HC generation as indicated by that measurement. The number 168 in the oxygen-index plot refers to a sample point with an offscale value of 168.

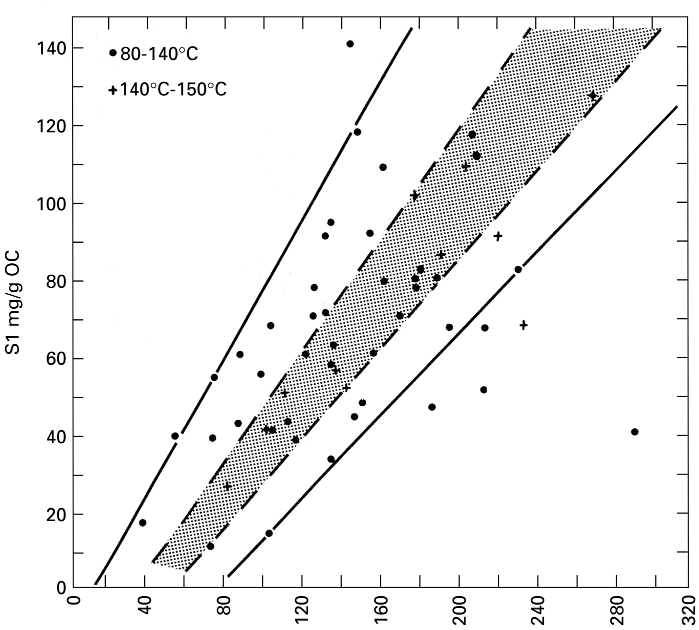

Figure 4. Cross plot of TOC-normalized ROCK-EVAL S_1 peak values (S_1 mg/g OC) versus hydrogen index for Apex-1 shales and silts with burial temperatures of 80° to 150°C. Samples from 80° to 139.9°C are shown by dots and are largely enclosed by the solid lines. Samples from 140.0° to 150.0°C are shown by crosses and are largely enclosed by the dashed lines and stippling.

decreasing HI values is also demonstrated in figure 4. This decrease is attributed to varying depositional conditions affecting OM characteristics, rather than to intense HC generation, which should result in increasing S_1 values versus decreasing HI values, exactly opposite the observed trends in figures 2 and 4.

From 150° to 195°C, S_1 values increase with depth (fig. 2), which we attribute to intense HC generation over this interval. ROCK-EVAL S_1 values decrease from 195° to 223°C at well bottom. Hydrogen index values also strongly decrease over this interval from continuing intense HC generation. The S_1 decrease is due to loss of generated HCS from the rocks and *is not due to HC thermal destruction.* This HC loss is from both HC expulsion and HC loss to the drilling mud in drilling operations (a topic discussed in Price, 1999). The loss of generated HCS may first commence at about 140°C in the Apex-1 wellbore, but intensifies with depth from increasing amounts of generated HC gases, especially above 195°C.

Katz (1983) demonstrated that the ROCK-EVAL oxygen index (mg S_3 peak/g OC) is not a valid measurement in low TOC rocks with elevated $CaCO_3$ concentrations, because of $CaCO_3$ thermal decrepitation. Katz (1983) also noted that the oxygen index is a valid parameter in rocks with moderate to high TOC values and low $CaCO_3$ concentrations. Both of Katz's (1983) observations are consistent with results of our studies. The fine-grained rocks of the California basins largely have moderate TOC contents (1 to 5 percent) and low $CaCO_3$ contents. Both the oxygen index and T_{max} data from the Apex-1 rocks broadly indicate that organic metamorphism proceeded in these rocks over all burial temperatures: In figure 3, oxygen indices consistently decrease over all burial temperatures to low values (7 to 30) at well bottom. The T_{max} values of most samples are rather tightly distributed in the swath defined in figure 3, increasing with depth to values (450°C and above) at well bottom to be expected from the high burial temperatures (>220°C) of these samples.

In the T_{max} plot of figure 3, at depths beyond about 3,700 m, light-colored silts (the crosses in the fig. 3 T_{max} plot) invariably had low T_{max} values, some abnormally so. These samples

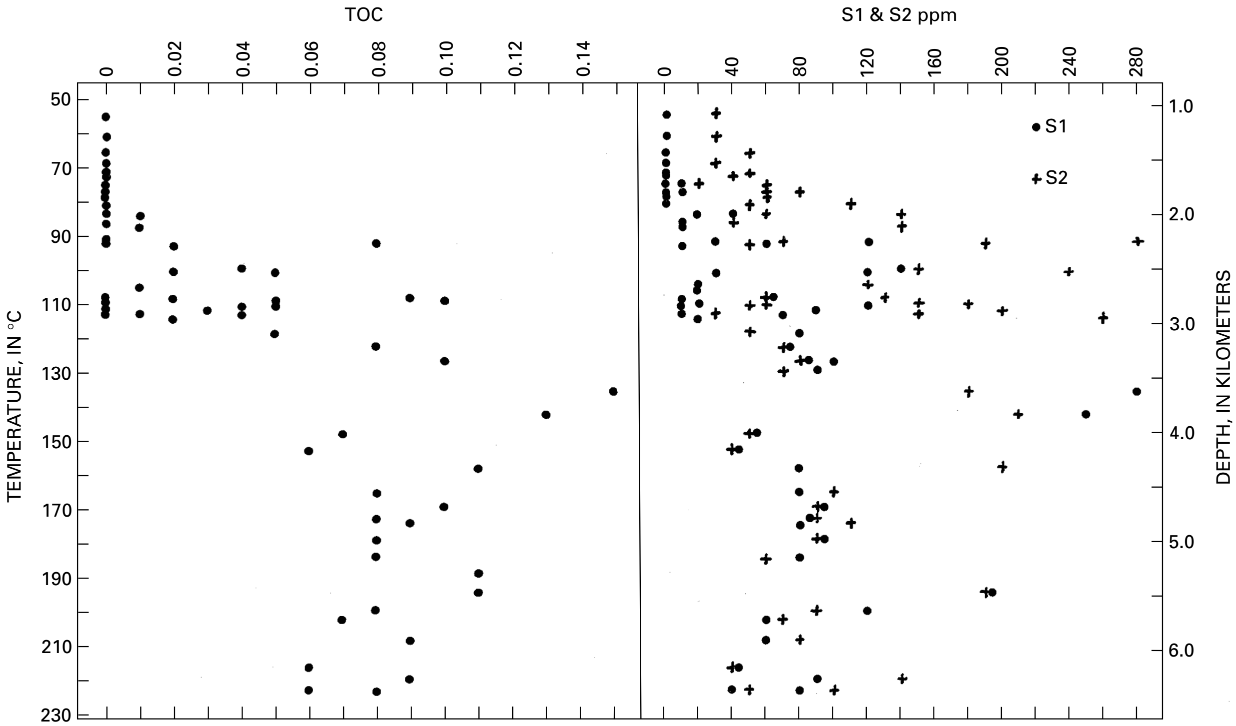

Figure 5. Plot of TOC and the ROCK-EVAL S_1 (dots) and S_2 (crosses) pyrolysis peaks (in ppm by rock weight) for sandstones from the Apex-1 wellbore versus burial temperature in °C and depth in kilometers. Depth axis changes scale because of a dog-leg in the geothermal gradient (table 2). Although there is an increase in TOC, S_1, and S_2 values deeper than about 2,000 m, the low values in these parameters at depth preclude the possibility of a general organic contamination of Apex-1 rocks.

had the lowest TOC values of the sample base (0.73 to 1.20 percent), but made up only a small percentage of the total sample base. The cause of the abnormally low T_{max} values in these silts is unknown, as is the cause of the abnormally high T_{max} values (464° to 475°C) of the six core samples at depth (silts and shales).

ROCK-EVAL oxygen indices and T_{max} values, both in this well and in general, were the best maturity indices of the study, usually indicating progressive organic metamorphism with increasing temperature, when other maturity indices failed to do so. For example, vitrinite reflectance (R_o) values for the Apex-1 (fig. 3) are nearly invariant from 110° to 188°C and provide no indication of the changes taking place in the OM of this well over this interval. From 188° to 223°C, R_o values increase tightly with depth. R_o suppression has been documented in hydrogen-rich OM in general (Price and Barker, 1985) and especially in the hydrogen-rich OM of the California basins (Walker, 1982; Walker and others, 1983; Price and Barker, 1985). However, the R_o plot of figure 3, and other R_o data of this study, demonstrate that R_o in the hydrogen-poor OM of the California basins, can also be significantly suppressed compared to expected values.

Production indices (fig. 3, PI) for Apex-1 rocks increase moderately from 50° to 81°C from the slightly increasing S_1 peak values over this interval (fig. 2). The large increase in production indices above 85°C, as discussed above, is attributed to both changing depositional conditions and to HC generation. The decrease in production indices over 140° to 150°C, as also discussed above, is attributed principally to variable depositional conditions. The significant increase in production indices from 150° to 223°C is attributed solely to mainstage HC generation.

Occasional Apex-1 cuttings chips below 4,000 m had discrete pieces of vitreous tar interbedded with the sediments, suggesting that oil macro seepage was active at the depositional site of such rocks. Oil shows were encountered in the Apex-1 from shallow depths to well bottom (Arco personnel, Bakersfield Exploration Office, oral commun., 1985). This fact was reflected by occasional pieces of tar on the surface of some cuttings chips or by discrete pieces of tar in varying amounts in the cuttings chips packets. All tar-bearing chips (external or internal) were excluded from ROCK-EVAL analysis. These oil shows would seem to contradict the low S_1 and TOC values of the sandstones in figure 5. However, when the samples shown in figure 5 were picked, all brown-stained (oil-bearing) sandstones, which were a small percentage of the total grains, were excluded from analysis.

Figure 6 shows porosity and percent residual-oil-saturation analyses from Core Laboratories for conventional core of a thick sandstone from 5,701.6 to 5,728.2 m in the Apex-1 and is a graphic example of the oil shows encountered at depth in the Apex-1. Porosities range from low (2.6 percent) to moderate (12.8 percent) values. Most sands contained no oil. However, the measurable to moderate residual-oil concentrations in some sands, at burial temperatures of 203°C, and higher, are unexpected by accepted paradigm concerning HC thermal stability. Table 3 presents porosity, permeability, and percent residual-oil saturation analyses from Core Laboratories for sandstones from sidewall core from between directionally drilled uncorrected vertical depths of 18,410 to 19,826 ft (corrected depths in meters of 5,483.4 m, 194.1°C, to 5,912.9 m, (209.7°C). These analyses augment the data shown in figure 6. The 5,890.0 m sample (208.9°C) with a porosity of 31.3 percent, a permeability of

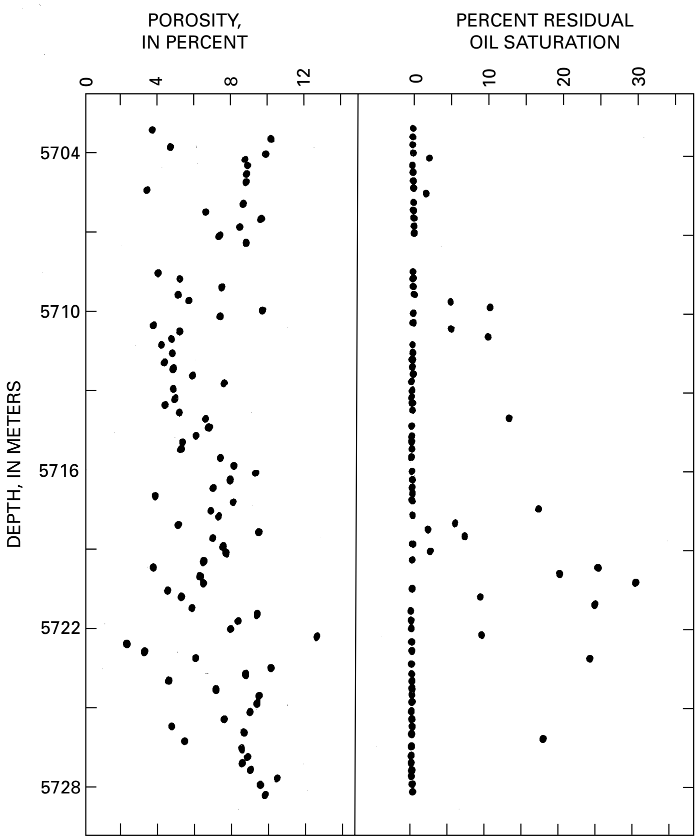

Figure 6. Plot of porosity in percent and percent residual-oil saturation versus depth in meters for a 26.6 m section of conventional core from a thick sandstone in the Apex-1 wellbore. Analyses by Core Laboratories.

1,375 millidarcies, and a residual-oil saturation of 41.6 percent is unexpected. The table 3 data also clearly demonstrate a greater thermal stability of oil than portrayed by current paradigm. The data of figure 6 and table 3 also dictate that the decrease of S_1 values from 195° to 223°C in figure 1 cannot possibly be from C_{15}+ thermal destruction.

Lastly, as discussed above, the Apex-1 data demonstrate that variable depositional conditions, even for this one (hydrogen-poor) OM type, can cause wide variance, versus depth, in different petroleum-geochemical parameters, including TOC (figs. 1, 2), the ROCK-EVAL S_1 peak (fig. 2), the production index (fig. 3), and the hydrogen-index (fig. 2). Indeed, the substantial variations of these latter three parameters versus depth, variations at times due solely to variable-depositional conditions, greatly obfuscate the degree of control that organic metamorphism actually has had on these parameters. This strong overprint by original depositional conditions on organic-geochemical characteristics, even within one OM type, was observed in other instances in this study.

Ventura Basin Central Syncline

ROCK-EVAL analyses of the Apex-1 fine-grained rocks provided a defined HC generation profile, albeit overlaid by OM characteristics inherited from depositional conditions. However, such defined generation profiles were not the case at all the sites studied. ROCK-EVAL and R_o analyses are presented in figure 7 for two deep wells in the Ventura Basin Central Syncline (“Santa Clara Trough” of Nagle and Parker, 1971), the Chevron Maxwell-1 (5,394 m) and the Superior Limoneira-1 (5,710 m), and for one shallow well, the Chevron Limoneira-1. The deepest data point from the Chevron Limoneira-1 is at 2,730 m. Both maximal TOC and HI values increase significantly beyond 4,270 m, demonstrating that the rocks become more organic-rich with depth. As stated, this trend was observed at other sites in the Los Angeles and Ventura Basins, including the Ventura Avenue Field (Ventura Basin) and along the entire southwestern shelf of the Los Angeles Basin from the Dominguez to the Huntington Beach Fields. Increases in organic richness with depth at these sites are assumed to be largely due to decreasing sedimentation rates with depth, an increase in the input of marine OM, continuously increasing kerogen hydrogenation, and subordinately to increasing percentages of fine-grained rocks (versus sandstones), all versus increasing depth.

Minimum and maximum values of the ROCK-EVAL S_1 peak normalized to TOC in figure 7 are invariant versus depth from 1,325 m to 4,225 m (131°C) where they begin to increase slightly. However, this deep increase is not from HC generation but is due instead to a shift to hydrogen-rich OM at depth. Note that the production index, especially maximal values, largely decrease slightly with depth, instead of increasing, as would be expected from HC generation. Moreover, neither the low production indices (0.05 to 0.07) nor the low carbon-normalized S_1 values of 18 to 37 for the three deepest samples at about 5,000 m are indicative of HC generation proceeding. However, T_{max} and R_o do increase with depth and the oxygen index decreases with depth (fig. 7). These three trends demonstrate that organic metamorphism is proceeding in these rocks, even though main-stage-HC generation has not commenced in figure 7 by 154°C. However, the R_o data do exhibit scatter, with a poor correlation coefficient ($r^2 = 0.474$). Moreover, R_o values of 0.40 to 0.43 percent at 150°C are significantly suppressed, and as with the R_o data from the Apex-1 rocks, R_o data in Santa Clara Trough rocks are not a valid measure of the actual organic-metamorphic ranks of the rocks.

The lack of HC generation in the deep, high-temperature rocks of the Santa Clara Trough is because all maturity indices, *including mainstage-HC generation*, are suppressed in rocks with hydrogen-rich OM, compared to rocks with hydrogen-poor (types IV and III) OM throughout the Los Angeles and Ventura Basins. For this reason, ROCK-EVAL analyses from rocks of these two basins were split into two categories and plotted separately versus burial temperature: (1) rocks with HI values <300, and (2) rocks with HI values >300.

Hydrogen-Poor OM Los Angeles Basin

The TOC values and the ROCK-EVAL S_1 and S_2 (HI) pyrolysis peak values normalized to TOC are plotted in figure 8, versus burial temperature in °C, for rocks with hydrogen-poor OM (HI values <300), for all wells analyzed in the Los Angeles Basin. These values are not plotted versus burial depth because of highly variable geothermal gradients throughout the Los Angeles Basin. The dots are samples with HI values <200 and

Table 3. Core analyses. Permeability (Perm.) in millidarcies (md); porosity (Por.) in percent; residual oil and water (in percent of porosity); and residual oil/water ratios, all for sidewall core of the Apex-1 wellbore. Uncorrected and corrected depth in feet are given, as well as corrected depth in meters, for the directionally drilled well.

Corrected Depth, Meters	Corrected Depth, Feet	Uncorrected Depth, Feet	Perm., md	Por. %	Residual Fluid		Oil/ Water
					Oil	Water	
5,483.4	17,990.1	18,410	486	19.0	8.9	54.7	0.16
5,492.5	18,020.1	18,440	74	24.5	5.7	66.1	0.09
5,493.7	18,024.0	18,444	103	16.9	0.0	52.7	---
5,500.1	18,045.1	18,465	392	23.4	5.1	78.6	0.06
5,501.6	18,050.0	18,470	42	24.6	5.3	82.1	0.06
5,522.4	18,118.0	18,538	69	22.9	7.0	55.5	0.13
5,527.2	18,134.0	18,554	19	12.9	26.4	54.3	0.49
5,527.8	18,136.0	18,556	24	15.4	21.4	48.7	0.44
5,530.9	18,146.0	18,566	316	25.0	0.0	83.2	---
5,535.2	18,160.0	18,580	183	20.6	0.0	54.4	---
5,536.4	18,163.9	18,584	73	19.7	3.6	66.0	0.05
5,554.0	18,221.8	18,642	936	32.6	40.2	56.3	0.71
5,568.6	18,269.7	18,690	374	21.6	10.2	44.9	0.23
5,588.0	18,333.5	18,754	1,184	15.2	7.9	59.9	0.13
5,588.6	18,335.5	18,756	457	26.7	5.2	67.8	0.07
5,591.4	18,344.5	18,765	241	26.4	17.8	58.7	0.30
5,592.3	18,347.4	18,768	758	32.4	6.8	54.3	0.13
5,606.3	18,393.4	18,814	529	33.9	19.8	69.3	0.29

the squares are samples with HI values of 200 to 300. Apex-1 data between 80° and 140°C were excluded from figure 8 to gauge commencement of intense HC generation versus burial temperature for hydrogen-poor OM at sites other than the Apex-1. Most of the data above 175°C in figure 8 is from the Apex-1.

The TOC values are invariant versus depth and range from 0.25 to 4.0 percent (fig. 8). Rocks with TOC values of 0.25 to 0.50 percent were largely light colored silts. Most rocks with TOC values of 0.5 percent or less have HI values of 200 or less. Maximum S_1 values increase noticeably at 105°C, which is taken as commencement of mainstage HC generation (CIHG in the S_1 plot of fig. 8). Minimum S_1 values increase slightly from 40° to 132°C and increase sharply thereafter. Maximum HI values increase acutely from 39° to about 90°C. Minimum HI values also increase acutely, but from 39° to about 142°C. Both these increases in HI values are attributed both to the increasing kerogen hydrogenation and to rocks with hydrogen-poor OM in the Los Angeles Basin generally becoming more organic-rich, both versus increasing depth. The sharp decrease in minimum and maximum HI values above 140°C is from intense HC generation at these elevated temperatures.

Oxygen indices decrease versus burial temperature for rocks with hydrogen-poor OM in the Los Angeles Basin (fig. 9). However, the range of values at low burial temperatures is large (about 90). At 125°C, the variation in oxygen indices begins decreasing to much more limited ranges above 200°C. ROCK-EVAL T_{max} increases with burial temperature (fig. 9). However, again scatter in the data is significant. Although the range of variation in T_{max} values decreases with increasing burial temperature, the range remains large at even high burial temperatures (about 12°C at 200°C burial temperature). Nonetheless, the oxygen index and T_{max} trends do demonstrate that organic metamorphism is proceeding in the rocks even at temperatures as low as 39° to 90°C. Maximum and minimum values of the production index are invariant from 40°C to 125° and 150°C respectively, where sharp increases take place. Thus, by production indices, mainstage HC generation commences in these rocks by 125° to 150°C. Vitrinite reflectance increases, with significant scatter, from minimum values of 0.3 percent at 40°C to 0.62 percent at 190°C, a suppressed R_o value at that temperature. The R_o data beyond 190°C are from the Apex-1.

Regarding the large variance in ROCK-EVAL T_{max} values discussed directly above, Caroline Isaacs reports (U.S. Geological Survey, written commun., 12/97) that in the Cooperative Monterey Organic Geochemistry Study (CMOGS, Isaacs and Rullkötter, 1993), a variance in T_{max} values of 5°–8°C was

Table 3.—continued

Corrected Depth, Meters	Corrected Depth, Feet	Uncorrected Depth, Feet	Perm., md	Por. %	Residual Fluid		Oil/ Water
					Oil	Water	
5,625.4	18,456.0	18,877	650	31.9	15.1	64.6	0.23
5,643.9	18,516.8	18,938	1,526	22.2	0.0	80.2	---
5,651.8	18,592.8	18,964	110	16.4	0.0	58.7	---
5,667.0	18,592.7	19,014	1,432	18.0	25.0	50.0	0.50
5,667.0	18,592.7	19,014	283	27.6	9.4	73.2	0.13
5,758.3	18,892.0	19,315	186	33.1	5.1	65.9	0.08
5,829.4	19,125.4	19,550	218	16.2	0.0	55.6	---
5,835.5	19,145.2	19,570	151	19.3	7.8	52.9	0.15
5,871.2	19,262.5	19,688	144	24.1	0.0	74.3	---
5,876.0	19,278.4	19,704	56	23.6	10.6	46.6	0.23
5,877.2	19,282.3	19,708	32	13.5	0.0	61.5	---
5,880.9	19,294.4	19,720	49	22.8	0.0	50.0	---
5,890.0	19,324.2	19,750	73	17.6	0.0	52.8	---
5,890.0	19,324.2	19,750	1,375	31.3	41.6	51.2	0.81
5,891.2	19,328.1	19,754	477	37.5	14.4	48.3	0.30
5,897.3	19,348.0	19,774	46	20.5	2.9	63.4	0.05
5,899.1	19,353.9	19,780	103	23.2	10.8	40.5	0.27
5,901.5	19,362.0	19,788	27	24.7	6.5	66.8	0.10
5,909.0	19,386.4	19,813	35	22.2	0.0	51.8	---
5,912.9	19,399.4	19,826	212	22.1	4.1	22.2	0.18

present for the same rock measured by the same laboratory, but at different time periods. For all laboratories measuring a given rock, the 95 percent confidence limit of T_{max} values was about 20°C (roughly +/-10°C). We have seen the same kind of poor ROCK-EVAL reproducibility in our laboratory, regardless of the steps taken in calibration, in the samples reported on here, as well as in other sample suites, for example Price and others (1984). These observations carry two implications we wish to comment on: (1) Within this study's rocks, T_{max} distributions versus rank may actually be quite tight, if T_{max} could be precisely measured. (2) Although ROCK-EVAL is a wonderful screening tool, it is a most imprecise instrument, an observation which calls into question the precision of ROCK-EVAL-based, computer-produced HC generation studies.

By figures 8 and 9, commencement of intense HC generation is vague, occurring at 105°C by the S_1 data (fig. 8) and somewhere between 125° and 150°C by the production index data (fig. 9). However, we believe that the S_1 data reflect reality regarding commencement of intense HC generation, and that the trend in the production index data from 40° to 120°C is an artifact from changing depositional conditions. From 40° to 105°C, S_1 values are essentially invariant and largely range from 15 to 30 mg/g, normal to slightly elevated values for immature rocks. However, over much of this same burial interval, HI values are low, largely 50 to 105 from 40° to 90°C. As a result, production indices for most samples between 40° and 105°C are unusually high, ranging from 0.025 to 0.150 (dashed lines, production index (PI) plot, fig. 9). By contrast, production indices for immature but more organic-rich rocks are commonly between 0.025 and 0.060. Thus, detection of commencement of intense HC generation by the production index in figure 9 is masked by two OM characteristics derived from deposition: (1) moderately high amounts of carbon-normalized HCS deposited in some of these rocks, and (2) low HI values in shallow rocks, HI values which increase with increase in depth. Thus, the significant increase in S_1 values at 105°C in figure 8 is taken as commencement of intense HC generation in Los Angeles Basin fine-grained rocks.

Hydrogen-Poor OM Ventura Basin

TOC and the ROCK-EVAL S_1 and S_2 (hydrogen index) pyrolysis peaks normalized to TOC are shown in figure 10 for rocks with hydrogen-poor OM (HI values <300) from the Ventura Basin, all versus burial temperature in °C. These values,

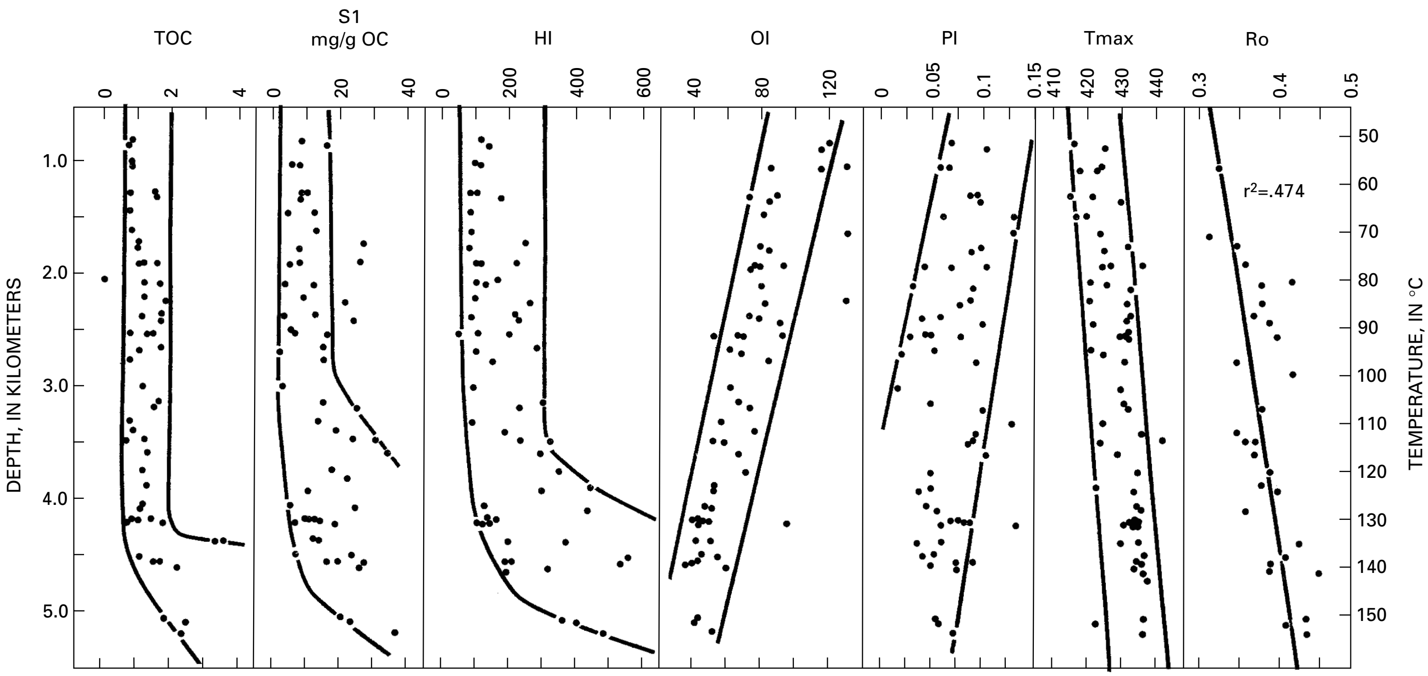

Figure 7. Plot of TOC (total organic carbon), TOC-normalized values (mg/g OC) of the ROCK-EVAL S_1, S_2 (HI, hydrogen index) and S_3 (OI, oxygen index) peaks; the ROCK-EVAL production index (PI) and T_{max}; and R_o, all versus burial temperature in °C, and depth in kilometers, for siltstones and shales from two deep wellbores from the Ventura Basin central syncline ("Santa Clara Trough"). Trends defined by solid lines are all explained in the text.

again, are not plotted versus depth because of variable geothermal gradients in the Ventura Basin. The dots are samples with HI values <200, and the squares are samples with HI values of 200 to 300. Both minimum and maximum TOC values increase gradually with depth. However, maximum TOC values increase more strongly over 95° to 105°C. Minimum HI values increase slightly from 50° to 130°C and then increase more strongly in the deepest samples. Maximum HI values increase dramatically from 50° to 105°C. As discussed above, these TOC and HI increases versus depth are attributed to organic richness increasing with depth, a characteristic feature throughout the Los Angeles and Ventura Basins.

Minimum values of the S_1 pyrolysis peak decrease slightly from 50° to 90°C and then increase slightly, but continuously, from 90° to 140°C (fig. 10). Maximum S_1 values increase strongly from 50° to 120°C, with three outliers. Beyond 120°C, S_1 values strongly decrease to low values (7–20) at the highest burial temperatures. The low S_1 values between 130° and 140°C preclude the commencement of mainstage-HC generation in these rocks. The increase in S_1 values between 50° and 120°C coincides with the strong increase in maximal HI values over much of this burial interval. Both increases are attributed to increasing organic richness versus depth.

The low S_1 values between 130° and 140°C strongly contrast with much higher S_1 values in both the Apex-1 wellbore (fig. 2) and in the Los Angeles Basin as a whole (fig. 8) at equivalent burial temperatures. Thus, HC generation appears to be suppressed in the Ventura Basin compared to the Los Angeles Basin. Phillipi (1965) also concluded that HC generation was suppressed in the Ventura Basin compared to Los Angeles Basin (see his figures 8a and 8d), due to the lower average geothermal gradient in the Ventura Basin (26.6°C/km) compared to Los Angeles (39.1°C/km). However, this does not explain why rocks at *equivalent burial temperatures* in the two basins have such disparate characteristics regarding commencement of HC generation, as demonstrated by Phillipi's (1965) figures 8a and 8d and by the data of this study (figs. 2, 8, and 10). Reasons for these differences are discussed below. For now, we conclude that mainstage HC generation has not begun in the Ventura Basin by 140°C (fig. 10).

With the exception of eight elevated values, oxygen indices in Ventura Basin rocks with hydrogen-poor OM tightly decrease versus increasing temperature (two solid lines, fig. 11). Even if the elevated oxygen indices are incorporated (dashed line, oxygen index (OI) plot, fig. 11), oxygen indices still uniformly decrease with temperature. Moreover, seven of the eight samples with elevated oxygen indices falling outside of the two solid lines have among the lowest TOC values of the figure 10 sample base (0.75 to 1.18 percent). These elevated oxygen indices may be due to a contribution of CO_2 from $CaCO_3$, a contribution which becomes evident in lower TOC rocks (Katz, 1983). ROCK-EVAL T_{max}, and R_o, regularly increase with burial (fig. 11). However, as in previous cases, T_{max} has an unacceptably large range of values (12°C). Although increasing R_o correlates moderately well with increasing burial temperature ($r^2 = 0.72$), R_o values of 0.42 to 0.44 percent at 130° to 144°C are significantly suppressed from values expected for hydrogen-poor OM at these burial temperatures. Thus, R_o does not yield a valid measurement of the true rank of these rocks. The oxygen-index, T_{max}, and R_o data, however, do demonstrate that organic metamorphism is ongoing over the entire temperature range of figure 11.

The production index (fig. 11) supports the pervious conclusion that mainstage-HC generation has not begun by 140°C in Ventura Basin rocks with hydrogen-poor OM. Excluding four points with values above 0.150, production indices broadly decrease with temperature, from 40° to 140°C. Three of the

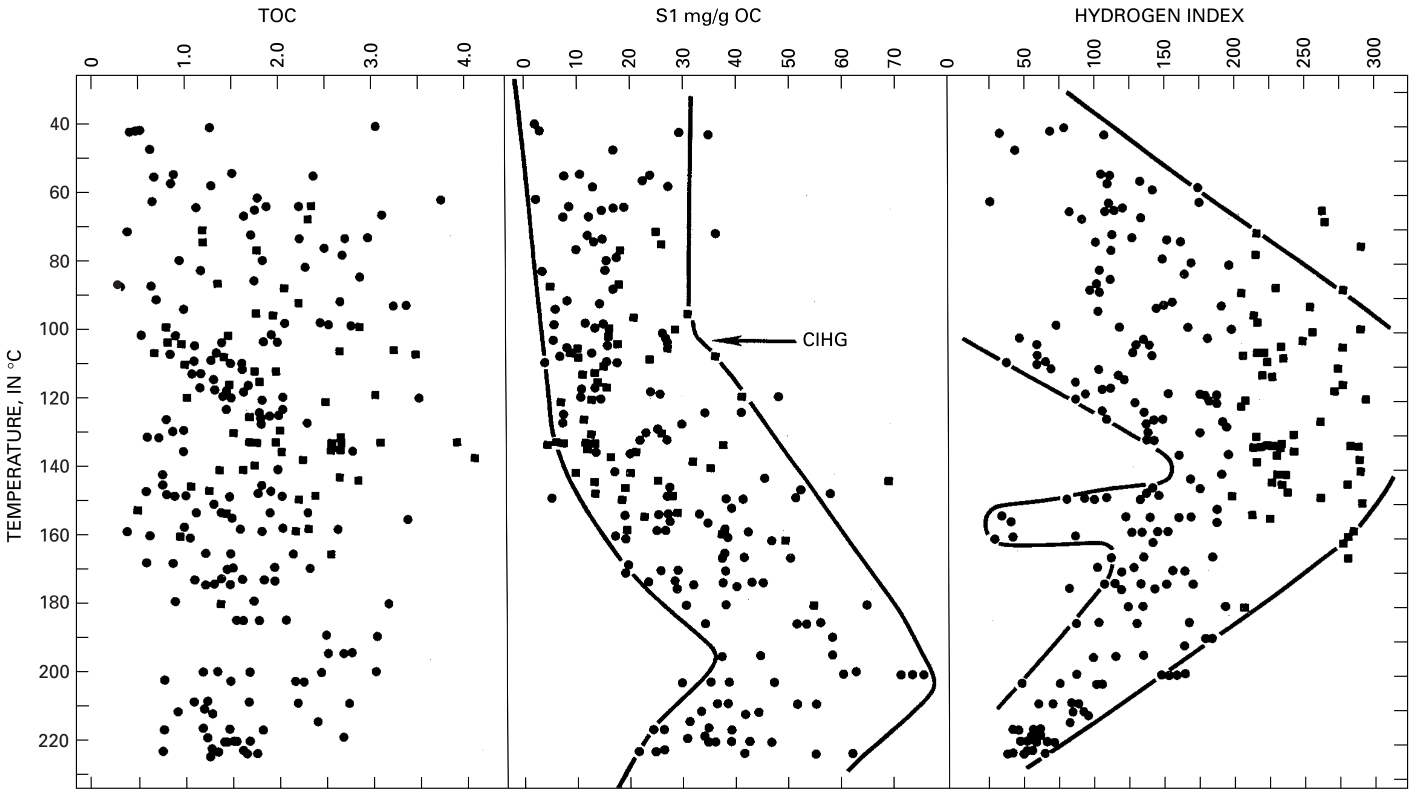

Figure 8. Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) S_1 and S_2 (HYDROGEN INDEX), ROCK-EVAL peaks, all versus burial temperature in °C for siltstones and shales with HI values <300 from the Los Angeles Basin. Trends defined by solid lines are discussed in text. Circles represent samples with HI values below 200, squares are samples with HI values of 200 to 300. "CIHG" in the carbon-normalized S_1 plot is commencement of intense HC generation by that measurement.

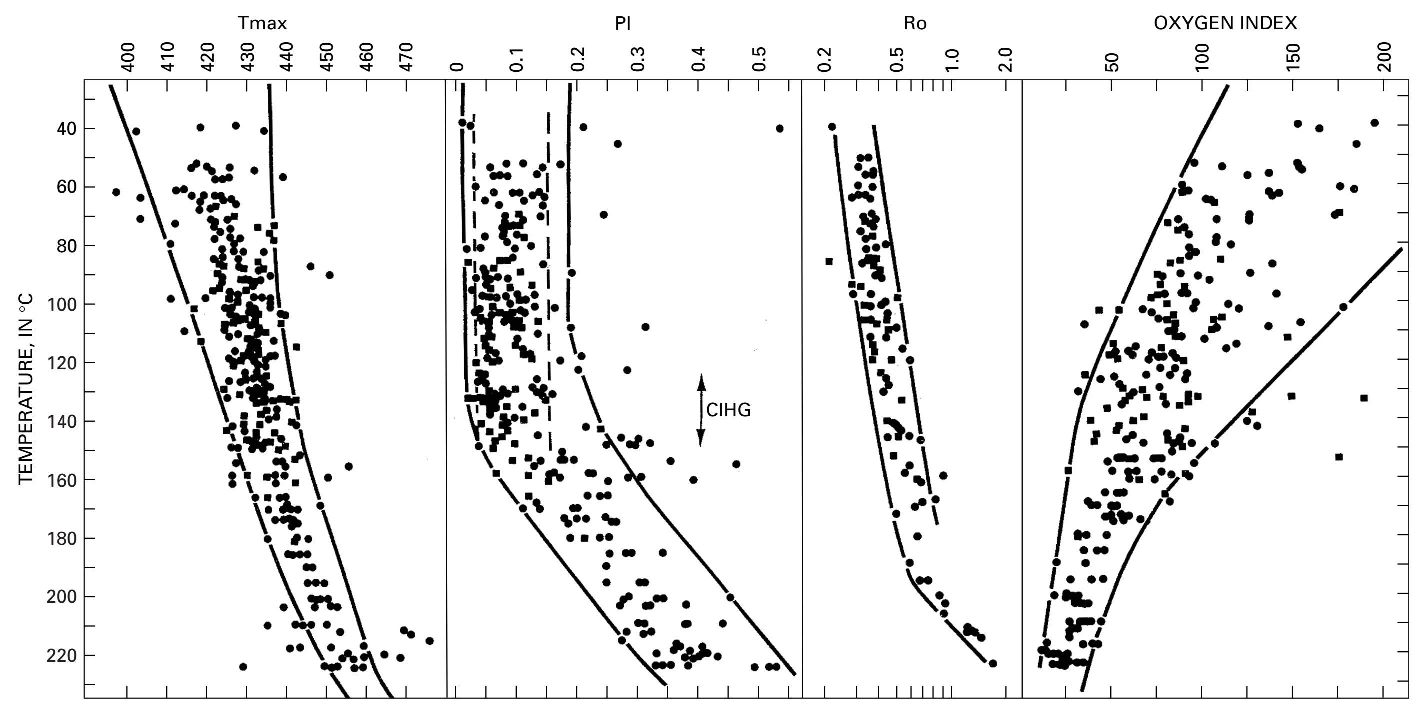

Figure 9. Plot of ROCK-EVAL T_{max} and production indices (PI), R_o, and the TOC-normalized value of the ROCK-EVAL S_3 peak (OXYGEN INDEX), all versus burial temperature in °C for siltstones and shales with HI values <300 from the Los Angeles Basin. Trends defined by solid lines are discussed in text as are dashed lines in the PI (production index) plot. Dots are samples with HI values below 200, squares are samples with HI values of 200 to 300. The vertical arrow and "CIHG" in the PI plot is the range of the commencement of intense HC generation by that measurement.

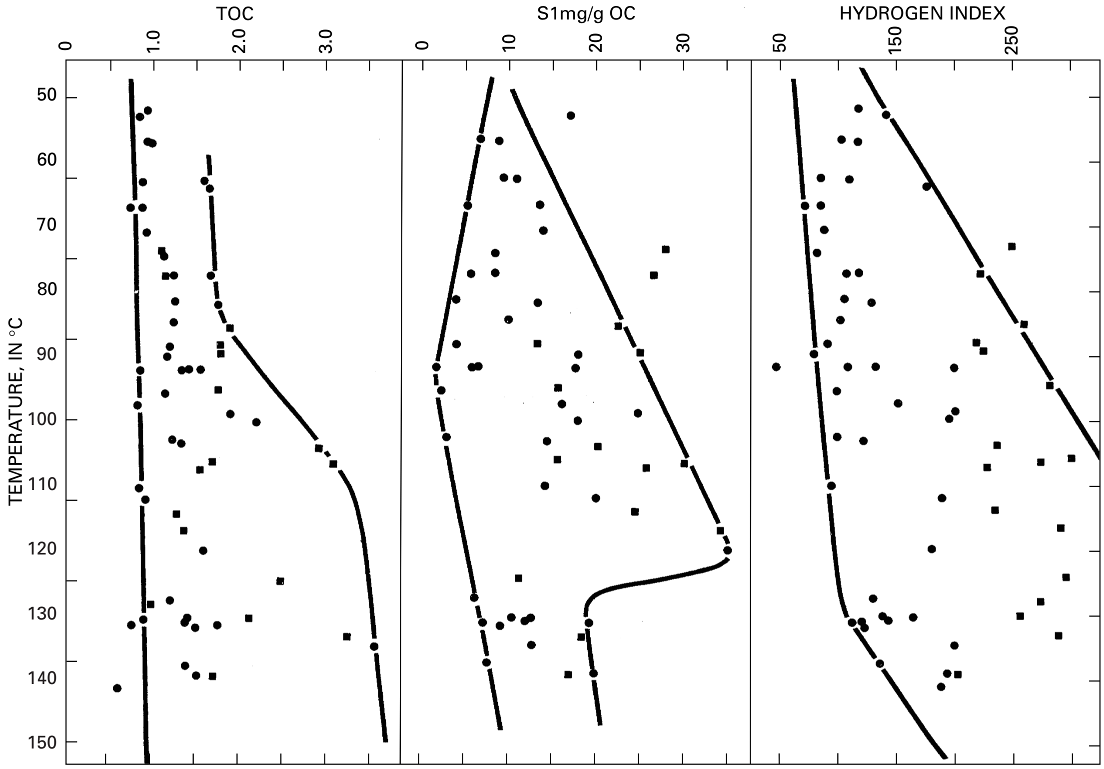

Figure 10. Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) S_1 and S_2 (HYDROGEN INDEX), ROCK-EVAL peaks versus burial temperature in °C for siltstones and shales with HI values <300 from the Ventura Basin. Trends defined by solid lines are discussed in the text. Dots are samples with HI values below 200, squares are samples with HI values of 200 to 300.

four points with elevated production indices had very low HI values (75–125), and the fourth point at 120°C was a 175 HI rock with the S_1 maximum in figure 10. Thus the four high production indices of figure 11 are attributed as analytical artifacts, with no relation to HC generation. Moreover, production indices of 0.05 to 0.08 between 130° and 140°C are not indicative of, and argue against, the commencement or occurrence of mainstage-HC generation.

Southern San Joaquin Valley

TOC contents and TOC-normalized ROCK-EVAL S_1 and S_2 (hydrogen index) peaks are shown in figure 12 for shale cores from six wells in the Paloma field, Southern San Joaquin Valley Basin (Maricopa-Tejon subbasin of Beyer and Bartow, 1987). The data from 1,232.6 m (59°C) to 3,666.0 m (132°C) are from three wells laterally within 1,980 m (6,500 ft) of one another. The data from 3,666.0 m (132°C) to 4,347.8 m (153°C) are from three more widely separated wells and the data from 4,347.8 m (153°C) to 6,498.8 m (218°C) are from the 6,547.4 m (21,482 ft) deep Ohio Oil KCL “A” 72–4 wellbore. Total organic carbon values fluctuate widely with depth (fig. 12). From 1,232.6 to 1,398.3 m, TOC increases dramatically (0.36 to 2.55 percent) followed by a decrease to low values (0.06 to 0.36 percent) from 1,511.7 to 2,389.2 m. From 2,759.7 to 4,062.5 m, TOC again dramatically increases, to a maximal value of 5.01 percent. Both minimal and maximal TOC values follow these trends, trends we attribute to variable depositional conditions at this site. From 4,062.4 to 6.493.8 m (all samples from the 72–4 wellbore), maximal TOC values decrease as portrayed by the solid curve; however, the seven samples defining this curve are only a small part of the sample population. Most samples from 4,062.4 to 6.493.8 m, actually range from 0.6 to 2.10 percent TOC and are largely invariant versus depth.

Minimal and maximal values of the TOC-normalized ROCK-EVAL S_1 peak increase gradually (with several outliers) to 170° and 140°C respectively (fig. 12). The gradual increase in maximal S_1 values from 60° to 140°C is ascribed principally to low-level HC generation. The significant increase in maximal S_1 values above 140°C is due to mainstage-HC generation. Between 180° and 217°C, S_1 values range from 15 to 214 mg/g. This very large range of S_1 values is attributed to: (1) more than a five-fold difference in original HI values (45 to 240 between 155° to 182°C, HI plot, fig. 12) with the originally higher HI rocks yielding significantly higher S_1 values; and (2) variable losses of generated HCS to expulsion and to the drilling mud. These last two parameters also account for the significant decline in maximal and minimal S_1 values from 203° to 218°C. The four elevated S_1 values between 128° and 141°C are attributed to higher than normal amounts of bitumen incorporated into the rocks at deposition, and not to HC generation.

The HI fluctuates widely from 1,232.6 m to 4,413.6 m (fig. 12), which is attributed to highly variable depositional conditions. From 1,232.6 to 2,130.8 m, with one exception (caused by that sample’s low TOC value, 0.09 percent), HI values strongly decrease from 341 to 20, and then increase from 2,130.8 to 3.973.5 m, with reversals, to a maximal value of 590. From

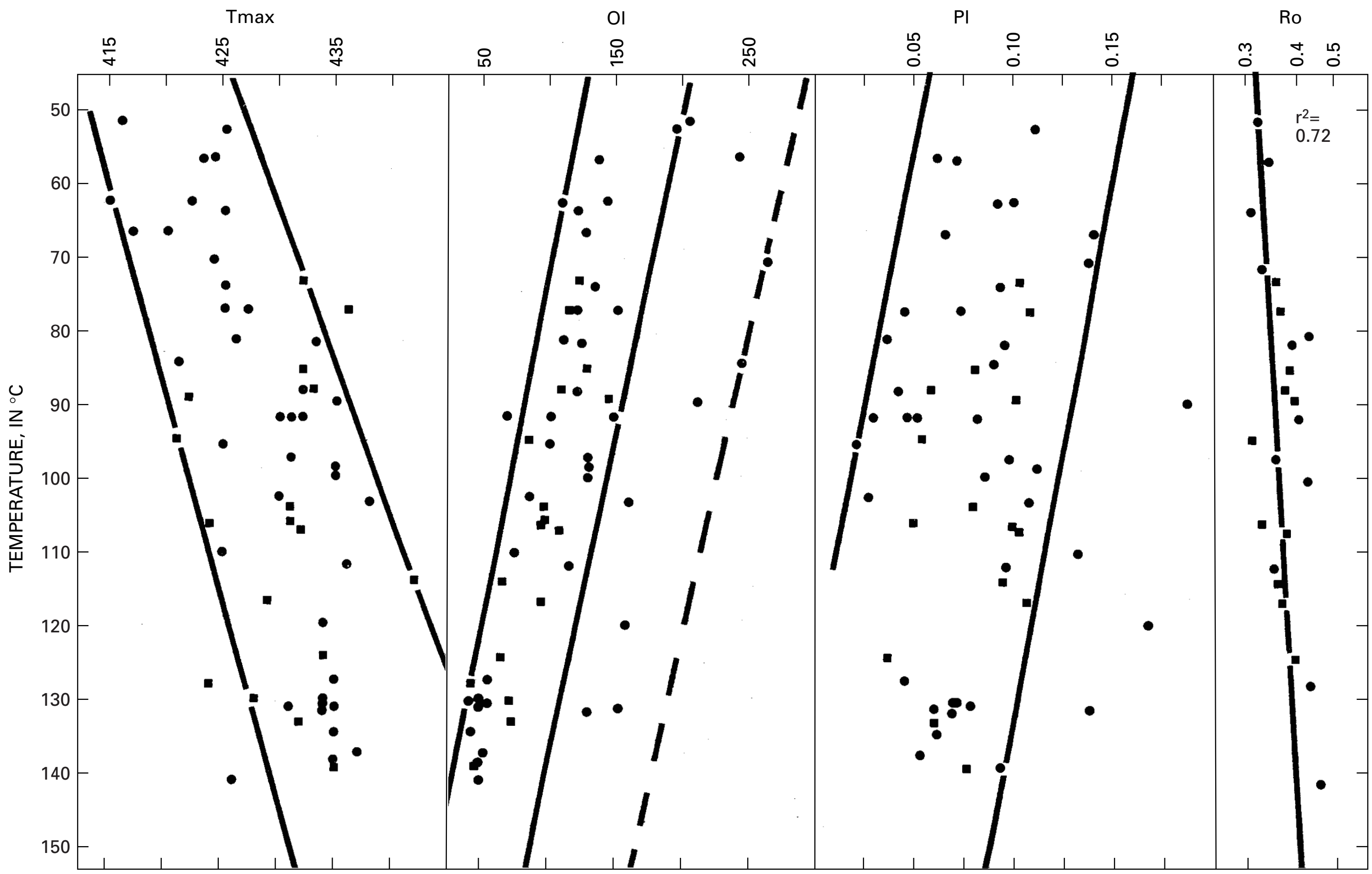

Figure 11. Plot of ROCK-EVAL T_{max}, the TOC normalized (milligrams per gram) S_3 peak (OI-oxygen index), and production indices (PI); and R_o, versus burial temperature in °C for siltstones and shales from the Ventura Basin with HI values <300. Trends defined by solid lines, and the dashed line in the OI plot, are discussed in text. Dots are samples with HI values below 200, squares are samples with HI values of 200 to 300.

3,973.5 to 4,376.7 m, HI values again decrease to a minimum of 82. From 4,376.7 m to 5,181.8 m, HI values are invariant with depth and range widely from 43 to 211 (fig. 12, dashed lines). Beyond 5,181.8 m, both maximal and minimal HI values decrease with depth, as portrayed by the solid lines. Moreover, the range of HI values significantly decreases over this depth. Both these features are due to mainstage-HC generation taking place, documented by the increase in both S_1 values (fig. 12) and production indices (fig. 13) over this interval.

As is evident from the HI values of figure 12, the rocks at Paloma deeper than 4,376.7 m have a mixture of types III and IV OM. Considering their respective HI values, rocks shallower than 4,376.7 m were deposited under variable conditions. Low-TOC, low-HI rocks were deposited from 1,511.7 to 2,389.2 m. In contrast to the rocks between 1,511.7 to 2,389.2 m with S_2 values of 50–520 ppm (by rock weight, not shown), Paloma rocks between 3,190.5 to 4,182.0 m are a more impressive source section, with elevated TOC and HI values and S_2 values of 4,380 to 27,380 ppm (not shown). The top of the upper to middle Miocene Monterey Formation in the KCL "A" 72–4 wellbore was at 2,654.4 m, where both TOC and HI values demonstrate dramatic increases (fig. 12). The TOC and HI values maximize in figure 12 over 3,804.6 to 4,182.0 m, which is the lower-middle portion of the upper Miocene Antelope member of the Monterey Formation. However, from 4,238.0 to 5,596.8 m (the base of the Monterey Formation) HI values are modest (primarily 45 to 165, with some values as high as 240, fig. 12). Thus, a large part of the Monterey Formation at Paloma appears to be not especially organic rich.

One might attribute the strong decrease in HI values from 3,973.5 to 4,376.7 m to intense HC generation in the type II OM, rather than to a shift in depositional facies. However, this is not the case. Over this depth interval, neither S_1 values (fig. 12) nor production indices (fig. 13) proportionately increase, given that this proposed decrease in the HI values (values of 300 to 600 decreasing to 50 to 150) is from HC generation. Moreover, optical analyses of isolated kerogens between 4,376.7 to 6,493.8 m showed them to be composed of the same kerogen type, with either no, or only small, amounts of algal kerogen.

ROCK-EVAL oxygen indices at Paloma strongly decreased from 1,232.6 to about 3,900 m (fig. 13). Elevated oxygen indices (174 to 633) of three shallow samples are attributed to low (0.06 to 0.23) TOC values and thermal decrepitation of calcite in the samples (Katz, 1983). Samples from 1,852.8 to 2,389.2 m in figure 13 also have low TOC values (0.19 to 0.36 percent). However, these low TOC values do not appear to significantly affect the elevated (87 to 136) oxygen indices of these samples. From 3,916.5 to 5,263.8 m, maximum and minimum oxygen indices are invariant. The Paloma field was the only area of this study where, unaccountably, oxygen indices did not uniformly decrease with depth over the entire sample interval. From 5,263.8 m to well bottom, oxygen indices generally decrease

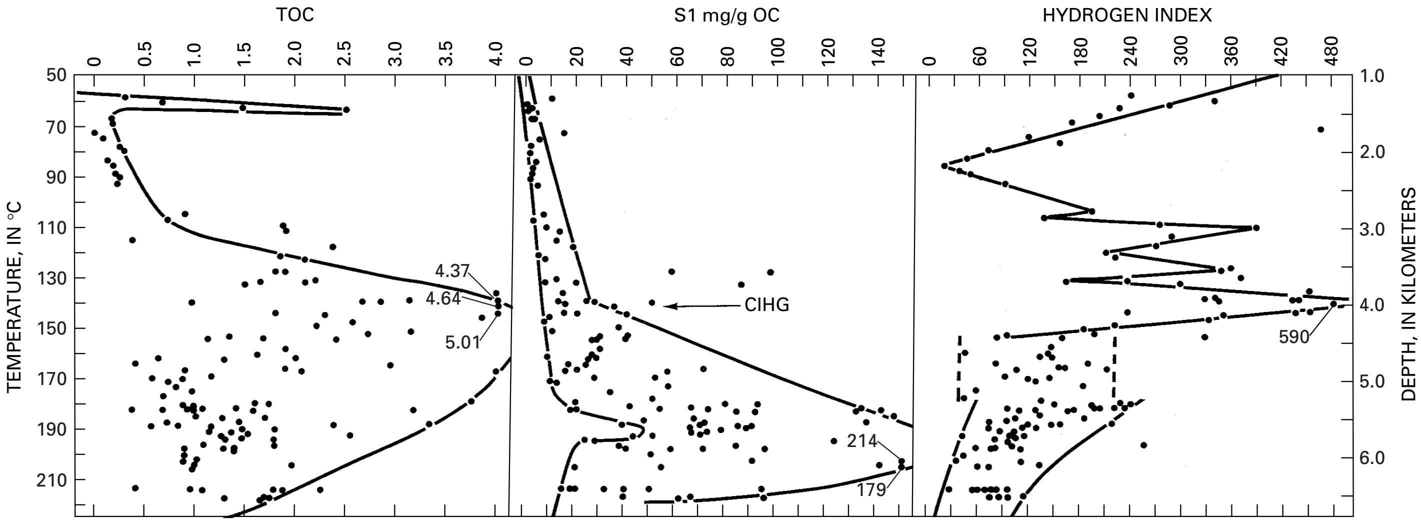

Figure 12. Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) S_1 and S_2 (HYDROGEN INDEX), ROCK-EVAL peaks versus burial temperature in °C and depth in kilometers for siltstones and shales from six wellbores in the Paloma field, Southern San Joaquin Valley Basin. Trends defined by solid and dashed lines are discussed in text. Numbers to the right of each plot are values for the respective samples which fell off the scale. "CIHG" in the carbon-normalized S_1 plot is the commencement of intense HC generation by that measurement.

with depth, with two exceptions at about 5,300 m and less so at 6,070 m, where maximum oxygen indices unaccountably increase.

Maximum and minimum production indices (fig. 13) increase slightly from 1,232.6 m to about 3,750 m, where they dramatically increase from the commencement of intense HC generation. After maximizing at 205°C, production indices decrease from 205° to 217°C due to significant losses of generated HCS from either expulsion or loss to the drilling mud, corresponding to similar decreases in the S_1 peak (fig. 12). Samples with high production indices outside the defined trend from 85° to 90°C are due to abnormally low HI values over this interval (fig. 12). Samples between 127° to 133°C with high production indices outside the defined trend (fig. 13) are from high values of the S_1 peak, in turn attributed to high amounts of HCS incorporated into the rocks at deposition.

ROCK-EVAL T_{max} values are moderate (427° to 435°C) to highly elevated (455° to 563°C) from 1,232.6 to 2,265.5 m (fig. 13), not reflecting the true immature rank of these samples. Of the seven shallow samples with highly elevated T_{max} values, six are due to the low TOC and/or low HI values of the samples. From 2,760 to 3,700 m, T_{max} values are both reasonable for the burial temperatures and regularly increase with burial temperature. From 3,704.4 m, maximal and minimal T_{max} values are invariant to 4,740.3 m and to 5,078.9 m respectively, mirroring similar behavior of the oxygen indices over this interval (fig. 13). With further increase in depth, T_{max} values uniformly increase (fig. 13). However, beyond 5,078.9 m, the range of T_{max} is unacceptably large. For example, from 5,181.8 to 5,437.3 m (stippled band), T_{max} varies from 428° to 455°C, or from pre-HC generation to post mature. Even discounting extreme low and high values, the range of T_{max} in these deeper samples is 18°C for the same OM type throughout this section, certainly an unacceptable level of precision for any analytical tool.

The Paloma R_o data from this study (crosses, solid line, fig. 13) agree moderately well with previously published data (dots, dashed line, Hood and Castaño, 1974). In this study, five samples shallower than 2,760 m macerated for kerogen did not yield sufficient vitrinite for analysis. Moreover, the recovered vitrinite from two samples shallower than 3,100 m, had unrealistically high R_o values for their rank. Thus only samples deeper than 3,230 m yielded realistic R_o values. Both data sets have good correlation coefficients ($r^2 = 0.930$ this study; $r^2 = 0.957$, Hood and Castaño, 1974). However, both data sets yield unrealistically low R_o values at surface intercept (22°C): 0.135 percent for this study, 0.078 percent for Hood and Castaño (1974), versus expected values of 0.25–0.29 percent. Assuming intense HC generation to commence at Paloma at 150°C from the production index plot (fig. 13), yields the expected R_o value of 0.60 percent.

The Paloma samples provide a well-defined HC-generation profile for hydrogen-poor OM, commencing at 150°C and largely complete by 220°C. However, like the Apex-1 wellbore where a thick sample sequence was also available, organic metamorphic trends at Paloma are strongly overlaid by OM characteristics inherited from deposition. In this case, a stratigraphic section with hydrogen-rich OM lies between 3,508.7 m (127.7°C) and 4,238.0 m (148.0°C), the burial temperature range where we might expect commencement of mainstage generation in the type III/IV OM. Thus it could be suggested that mainstage generation in hydrogen-poor OM would be observed below 150°C at Paloma, if this OM type were present in the section. Two points argue against this hypothesis. First, in this section of rocks with hydrogen-rich OM, a sample is present at 4,075.6 m (144.8°C) with type III OM (HI = 238, fig. 12). This sample has a TOC-normalized S_1 value of 21.7 and a production index of 0.084, values not characteristic of intense HC generation. Thus, even the type III OM at these burial temperatures has not commenced intense HC generation. Second, beyond 150°C, S_1 values (fig. 12) and production indices (fig. 13) dramatically increase. However, the values of these two indices just beyond 150°C are not that much greater than the background values of type III/IV OM at temperatures as low as 80°C. Both considerations dictate that HC generation could not

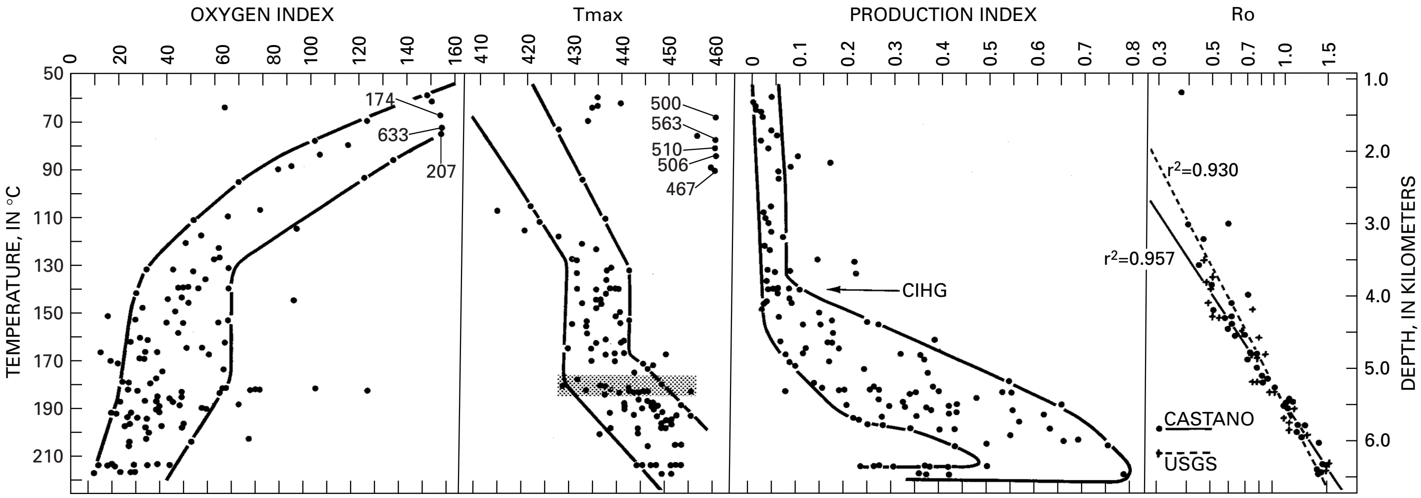

Figure 13. Plot of R_o and ROCK-EVAL oxygen-indices, T_{max}, and production indices, versus burial temperature in °C and depth in kilometers for siltstones and shales from six wellbores in the Paloma field, Southern San Joaquin Valley Basin. Trends defined by solid lines are discussed in the text, as is the stippled band in the T_{max} plot. Numbers at the top-right of the T_{max} and oxygen indices plots are values for the respective samples which are off the scale. Crosses and solid line in the R_o plot are U.S. Geological Survey data, dots and dashed line are R_o data from Hood and Castaño (1974). Correlation coefficients versus depth (r^2) are shown for both data sets. "CIHG" in the production index plot is the commencement of intense HC generation by that plot.

have started significantly before 150°C for the type III/IV (or II) OM at Paloma.

Hydrogen-Rich OM Los Angeles-Ventura Basins

The TOC contents and S_1, S_2 (HI, hydrogen index), and S_3 (OI, oxygen index) TOC-normalized ROCK-EVAL peaks for all samples with hydrogen-rich OM (HI>300) for the Los Angeles and Ventura Basins are shown in figure 14. Again, the data are plotted versus burial temperature, and not burial depth, because of variable geothermal gradients in these basins. The data are subdivided into two populations in figure 14 (and 15): samples with HI values of 300 to 400 (dots) and samples with HI>400 (squares). Total organic carbon values are invariant with depth and range from 1 to 7 percent. Minimum carbon-normalized S_1 values increase slightly from 60° to 200°C (4 mg/g to 8 mg/g), whereas maximal S_1 values increase significantly from 60° to a maximum of 60 to 70 at about 115°C. However, beyond 115°C, maximal S_1 peak values strongly decrease to values of 20 to 30 mg/g around 200°C. This deeper decrease is unexpected. These, and other data we discuss, suggest that mainstage-HC generation is not occurring in these rocks with hydrogen-rich OM at temperatures of 150° to 200°C. Thus, the general increase in S_1 values from 60° to 115°C cannot be from intense mainstage HC generation. Instead we attribute this shallow increase in S_1 values either to low-level HC generation occurring over 60° to 115°C and/or possibly to changing depositional conditions (increasing organic richness) in the rocks with depth.

As discussed in Price (1999), strong qualitative changes occur in the bitumen and saturated HCS from rocks with hydrogen-rich OM over burial temperatures of 50° to 120° C, demonstrating that a low-level HC generation is occurring in these rocks. However, this low-level HC generation does not usually result in significant quantitative changes, such as the increase in S_1 peak values from 60° to 115°C in figure 14. Note that maximal HI values, like the S_1 peak, strongly increase from 60° to 115°C (fig. 14). This is another example of the general increase in organic richness of rocks with depth in the Los Angeles and Ventura Basins and would suggest that the increase in S_1 values (fig. 14) is due more to increasing organic richness with depth, than to low-level HC generation.

Minimum oxygen indices moderately decrease from 60°C to about 140°C (fig. 14), whereas maximal oxygen indices are invariant over this interval. From 140° to 200°C, maximal oxygen indices significantly decrease. This general decrease suggests that organic metamorphism is occurring in these rocks over these burial temperatures of 50° to 200°C, even though intense HC generation has not yet commenced. This conclusion is supported by the fact that T_{max} increases with depth over the entire sample set (fig. 15). However, as in previous sample sets, the range of T_{max} values (about 18°C at any given burial temperature) is unacceptably large. Minimum production indices (fig. 15) are invariant over the entire sample set. Production indices, in general, are invariant to 150°C; however, maximum production indices increase slightly with depth to about 160°C and then strongly decrease with depth to 200°C. The low production indices (0.01 to 0.07) from 160° to 200°C are further evidence, along with the low S_1 values and high HI values in this interval, that significant HC generation is not occurring in these deeper rocks.

Vitrinite reflectance values of this sample set are invariant with depth, ranging from 0.20 to 0.48 percent and are highly suppressed (Price and Barker, 1985) at high burial temperatures. Moreover, at any given burial temperature in figure 15, samples with higher HI values (the squares) usually have lower R_o values than do the lower HI samples (the dots).

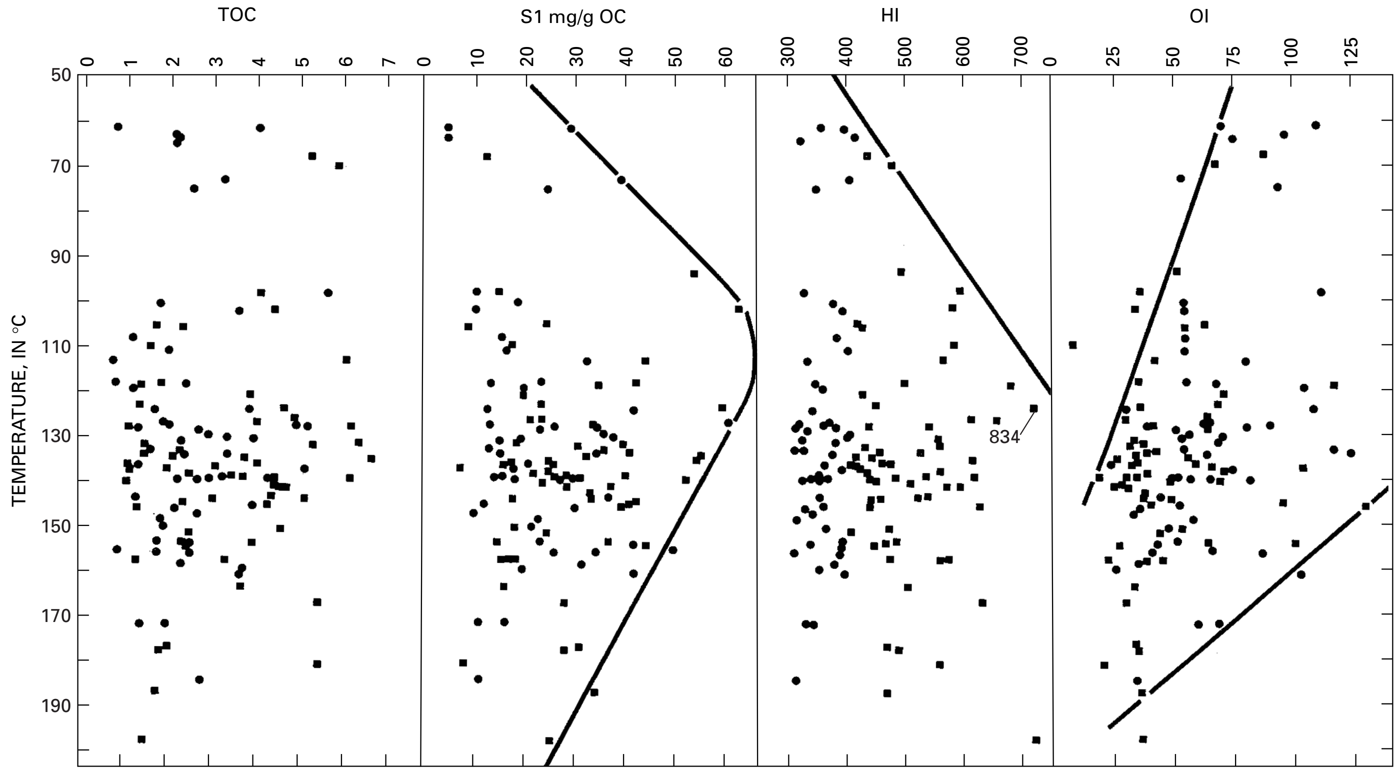

Figure 14. Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) S_1, S_2 (HI-hydrogen index), and S_3 (OI-oxygen index) ROCK-EVAL peaks versus burial temperature in °C for siltstones and shales with hydrogen indices of 300 and greater from the Los Angeles and Ventura Basins. Trends defined by solid lines are discussed in text. Dots are samples with HI values of 300 to 400, squares are samples with HI values of 400 or above.

ROCK-EVAL and R_o data for rocks from the Wilmington field, Los Angeles Basin are given in figure 16. Shales with high S_1 values (70 to 184 mg/g OC) over 620 to 1,250 m are delineated by crosses. Solvent extraction demonstrates that at least some of these samples are stained by migrated oil from reservoirs interbedded with the shales, probably via cap-rock leakage. Although this topic is discussed in Price (1999), we note that the intense faulting and fracturing in the Wilmington anticline (Mayuga, 1970) would greatly facilitate such cap-rock leakage. Thus, vertical migration of reservoired oil is probably the principal cause of the shallow elevated S_1 values and production indices shown by crosses in figure 16. However, elevated amounts of HCS in these immature shales, a moderately common occurrence in the shales of California basins, could also be contributing to these values. In any case, analyses in Price (1999) demonstrate that the high concentrations of these shallow HCS are not from HC generation.

The TOC values in figure 16 are depth invariant. The S_1 values for unstained samples (the dots) increase slightly from 600 to 1,800 m, an increase is attributed to an increase in organic richness over this depth interval, from original depositional conditions. This increase in organic richness is also reflected by an increase in HI values over part of this interval. Low-level HC generation over this interval may also be partially contributing to these increasing S_1 values. A persistent decrease in S_1 values from 60 to 25 over 1,800 to 3,150 m is unexpected and demonstrates that intense HC generation is not responsible for the shallower increase in S_1 values. This conclusion is supported by the slight, but persistent, decrease in production indices in the unstained samples over the entire burial interval. Moreover, from 150° to 198°C, production indices are low (0.013 to 0.081) as are S_1 values (7–33). The HI values are high (400–700) and are depth invariant. These data, from a single depositional site in the Los Angeles Basin, demonstrate that HC generation has not commenced in these rocks with hydrogen-rich OM at temperatures as high as 198°C.

ROCK-EVAL T_{max} increases, with scatter, from 400° to 410°C at 620 m to 430° to 440°C at depth, demonstrating that some form of organic metamorphism is occurring in these samples with increasing burial temperature. This metamorphism is also reflected by the significant decrease in oxygen indices, from 80 to 100 at 620 m to about 30 by 1,680 m. Vitrinite reflectance data at Wilmington exhibit scatter and are highly suppressed at moderate to elevated burial temperatures. In fact, R_o values of 0.21 to 0.29 percent from 181° to 198°C demonstrate that R_o suppression in some hydrogen-rich OM can be quite severe. Moreover, as discussed above, the R_o data of figure 16 result from readings by numerous service companies, and investigators both within and outside of the U.S. Geological Survey.

The data of figures 14 to 16, and other analyses in Price (1999), demonstrate that not only R_o, but almost all aspects of organic metamorphism, including mainstage HC generation, are suppressed in some hydrogen-rich OM, even at highly elevated burial temperatures. We believe that such wholesale suppression of intense HC generation is not uncommon, which has significant ramifications for petroleum-geochemical exploration models.

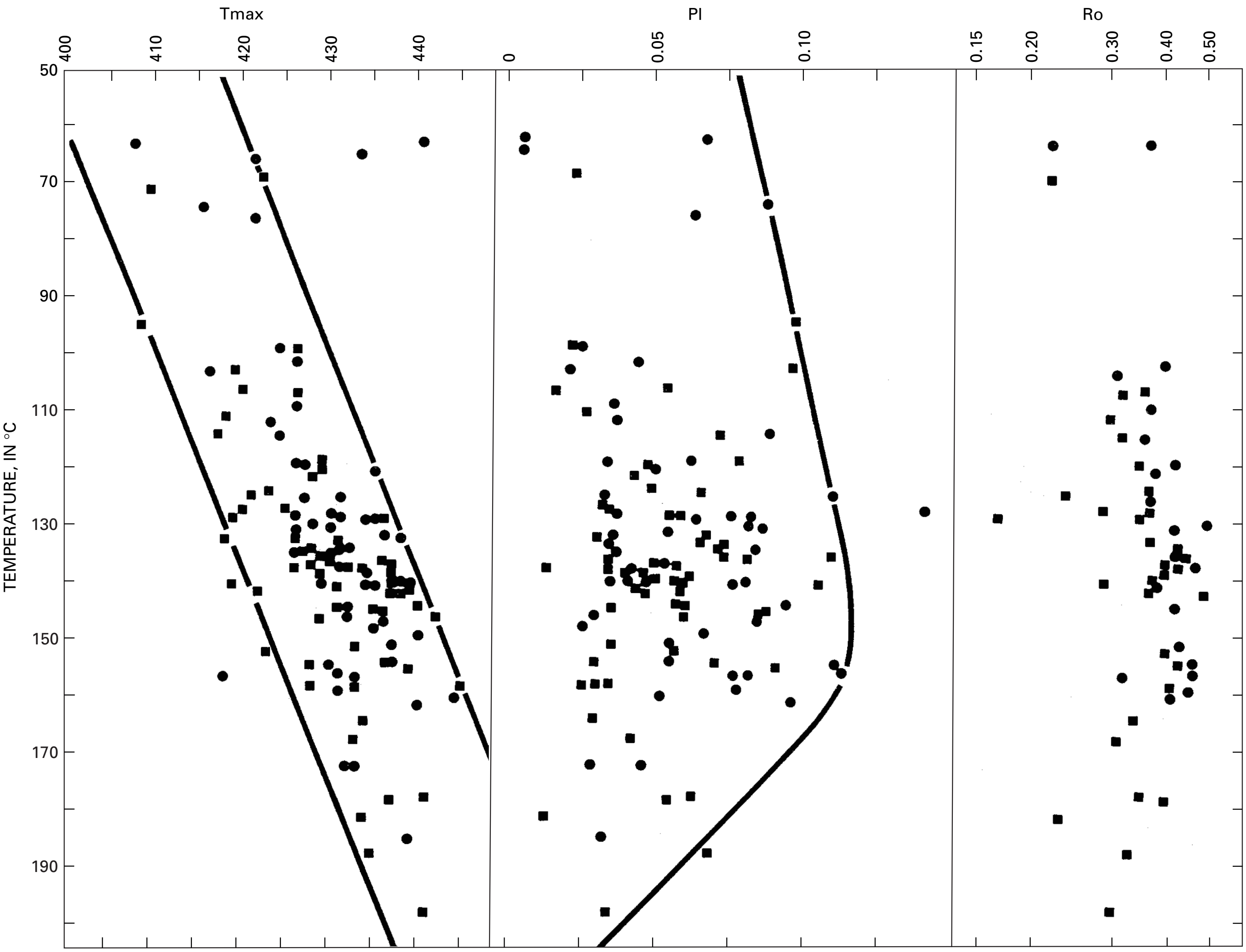

Figure 15. Plot of R_o and ROCK-EVAL T_{max} and production index (PI) values, versus burial temperature in °C for siltstones and shales with hydrogen-indices of 300 and greater from the Los Angeles and Ventura Basins. Trends defined by solid lines are discussed in text. Dots are samples with HI values of 300 to 400, squares are samples with HI values of 400 or above.

Northern San Joaquin-Southern Sacramento Valley Basins

Figure 17 presents R_o and ROCK-EVAL data for shale core from the Standard Oil of California 67–17E wellbore, one of the deeper wells in the Jacalitos oil field, Northern San Joaquin Valley Basin. These data help illustrate that as one proceeds north from the Southern San Joaquin Valley to the Sacramento Valley Basin, organic richness in the fine-grained rocks continuously decreases in any given stratigraphic interval. Rocks between 914 m to 1,200 m in figure 17 belong to the middle and lower Miocene Temblor Formation and have low to moderate TOC values (0.33 to 1.00 percent) and, excepting one sample, low to moderate HI values (78 to 230). The one exception (HI = 433) also has a high TOC-normalized S_1 peak (65 mg/g) and a low TOC value (0.40 percent). The high HI and S_1 peak values are most likely analytical artifacts from the low TOC value. The equivalent to the Temblor Formation in the Paloma 72–4 well (fig. 12) was the middle and lower Miocene Carneros Formation (5,621.5 m to 5,835.1 m). In the Paloma well, TOC values ranged from 0.9 to 2.7 percent, and probably were higher before mainstage HC generation, contrasting with the lower TOC values (0.33–1.00 percent) of the Temblor Formation in the Jacalitos well. Three samples between 1,200 to 1,400 m in figure 17 have elevated TOC values (2.35 to 5.27 percent) and moderate HI values (260 to 304). These are reasonable organic richnesses. However, these three rocks are from the Oligocene to upper Eocene Kreyenhagen Formation which is much more organic-rich further south in the Great Valley (Milam, 1985).

Beyer and Bartow (1987) noted that the thick section of marine Neogene rocks in the Southern San Joaquin Valley contrasts with a thin entirely nonmarine section of equivalent age rocks in the north of the basin. This difference in depositional conditions explains the decrease in organic richness in the Neogene rocks northward. Eocene and Upper Cretaceous rocks are deeper than about 1,400 m in figure 17, and TOC and HI val-

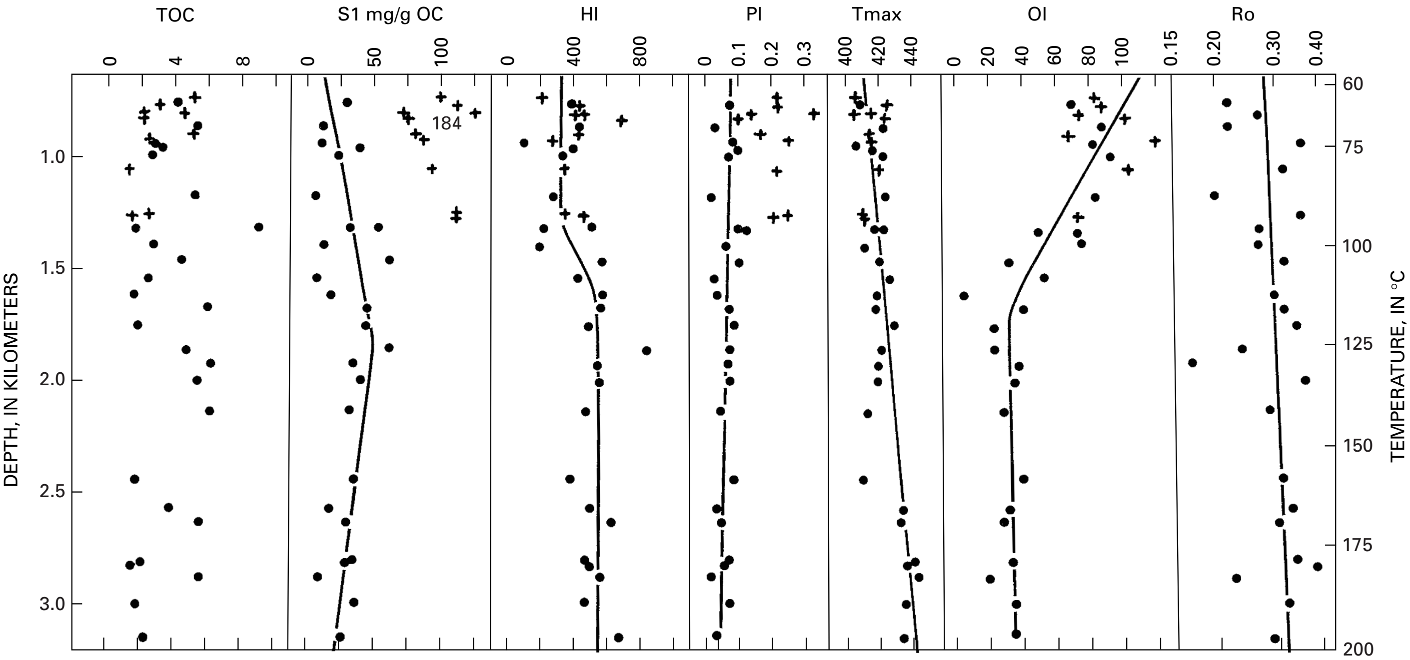

Figure 16. Plot of TOC (total organic carbon); the TOC-normalized (milligrams per gram, mg/g OC) S_1, S_2 (HI-hydrogen index), S_3 (OI-oxygen index) ROCK-EVAL peaks; the ROCK-EVAL production index (PI) and T_{max}; and R_o, all versus burial temperature in °C and depth in kilometers for shales from various wells in the Wilmington field, Los Angeles Basin. Trends defined by solid lines are discussed in text. Crosses are immature (pre-HC generation) samples with large amounts of indigenous or stained HCS. The sample with 184 to the far right of the S_1 plot is the S_1 value of that sample, which fell off scale of the S_1 plot.

ues both decrease (compared to values from the shallower Kreyenhagen Formation rocks) ranging from 0.56 to 2.00 percent and 72.2 to 118, respectively.

Production index (PI), T_{max}, oxygen indices (OI), and R_o values are scattered and (or) exhibit unexpected trends in figure 17. Oxygen indices are probably heavily influenced by changes in organic facies with depth. Also, the reduced TOC values of some samples, may allow a significant contribution from decomposition of $CaCO_3$ to the S_3 peak (Katz, 1983). Trends in the oxygen indices are not likely due to organic metamorphism. The significant scatter in production indices largely occurs in the low to moderate TOC and low HI rocks which can have elevated production indices for immature ranks because of their low HI values. The shallow trend of T_{max} values decreasing with depth correlates with, and is due to, HI values increasing with depth over the same interval. We have found that often, immature rocks with low HI values have higher T_{max} values than rocks with higher HI values at equivalent ranks. The R_o data are scattered, and the solid line is our interpretation of the most probable correct trend. The T_{max} and R_o data suggest that maturities are too low in the deepest rocks of figure 17 for significant levels of HC generation to have occurred.

ROCK-EVAL and R_o data are presented in figure 18 for shale core from the Amerada Hess FDL-1 well, Tracy Gas Field, southernmost Sacramento Valley Basin. This well, drilled in 1935, has historical significance, for it is the first commercial gas well of the Sacramento Valley Basin and opened that gas province. Beyer (1988b) provides a through overview of the Sacramento Valley Basin as well as references on previous work in the basin. Samples from 350 to 1,000 m (fig. 18) are from post-Eocene undifferentiated nonmarine strata and have very low TOC values (0.08 to 0.20 percent). The moderate S_1 peak and high HI values of these rocks are analytical artifacts from the low TOC values. Upper Cretaceous rocks deeper than 1,000 m have much higher TOC values compared to the shallower rocks. The S_1 values of Upper Cretaceous rocks are very low (around 6 mg/g) at 1,000 m and decrease slightly with depth to even lower values of 2 to 3 mg/g at 3,000 m. This mirrors similar decreases in both TOC (values of 2 to 3 percent at 1,100 m, to 1.2 to 1.5 percent by 3,000 m) and HI values (about 100 at 1,000 m, to 40 to 50 at depth). Although TOC values of these Upper Cretaceous rocks are moderate to elevated, HI values are very low (41 to 111, type IV OM), except for one sample at 217. Moreover, S_1 peak values are low (1.6 to 7.8 mg/g, except for one sample at 13.1 mg/g). These are very organic-poor rocks with essentially "dead" carbon.

In the shallower rocks from the FDL-1 well, oxygen indices are very high (316 to 700, except for one sample at 160, fig. 18) and are due to the very low TOC values of these rocks. Oxygen indices regularly decrease in the Upper Cretaceous rocks from values around 100 to 125 at 1,000 m to around 60 at well bottom. Vitrinite reflectance increases regularly with, and correlates moderately well ($r^2 = 0.80$) to, depth. These decreasing oxygen indices and increasing R_o values both demonstrate that organic metamorphism is proceeding with burial. Production indices are low (primarily between 0.025 to 0.050) and are largely invariant versus depth, as are T_{max} values. The FDL-1 T_{max} and R_o data, like the Jacalitos T_{max} and R_o data, demonstrate inadequate maturities for significant levels of HC generation in the deepest samples.

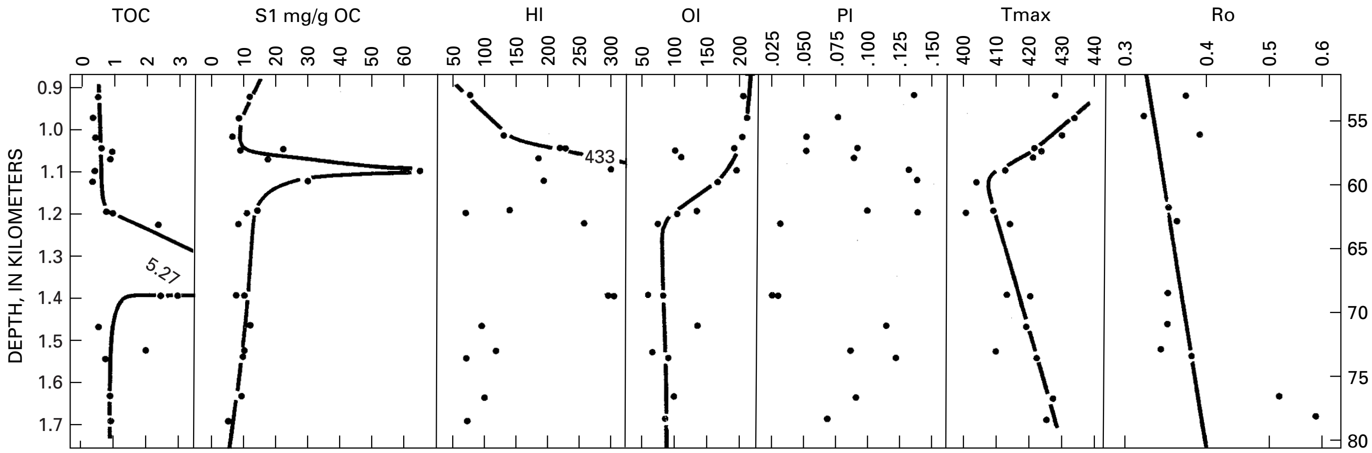

Figure 17. Plot of TOC (total organic carbon); the TOC-normalized (milligrams per gram, mg/g OC) S_1, S_2 (HI, hydrogen index), and S_3 (OI-oxygen index), ROCK-EVAL peaks; the ROCK-EVAL production index (PI) and T_{max}; and R_0 versus burial temperature in °C and depth in kilometers for shales from the Standard of California 67-17E wellbore, Jacalitos field, Central San Joaquin Valley Basin. Solid lines defining trends are explained in text. Numbers in the TOC (5.27), and HI (433) plots are values for samples which fell offscale. Stratigraphy, from California Oil and Gas Fields (1973), is as follows: bottom of the lower and middle Miocene Temblor Formation and top of the middle and upper Eocene and lower Oligiocene Kreyenhagen Formation about 1,204 m; top of the lower to middle Eocene Avenal Formation, about 1,432 m; top of the Upper Cretaceous Moreno Formation, about 1,600 m.

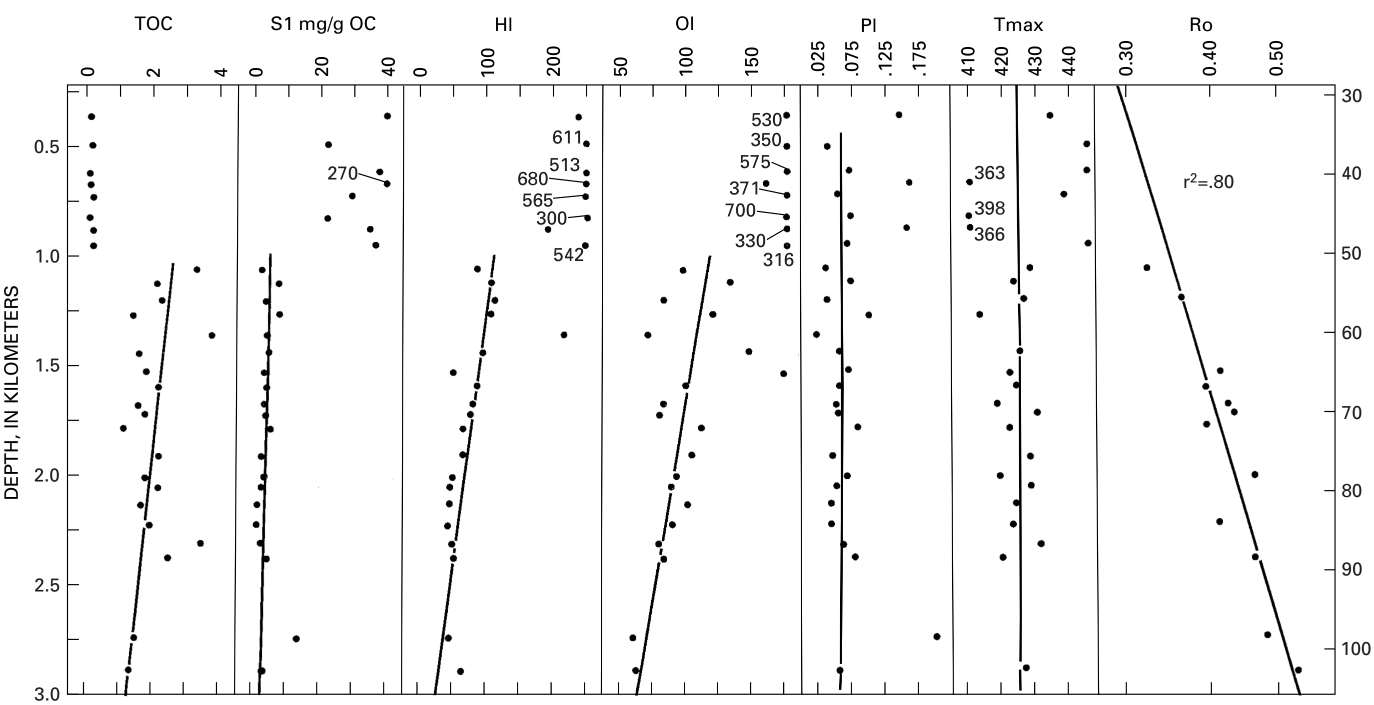

Figure 18. Plot of TOC (total organic carbon); the TOC-normalized (milligrams per gram, mg/g OC) S_1, S_2 (HI, hydrogen index), and S_3 (OI, oxygen index) ROCK-EVAL peaks; the ROCK-EVAL production index (PI) and T_{max}; and R_0 versus burial temperature in °C and depth in kilometers for shales from the Amerada Hess FDL-1 wellbore, Tracy gas field, Sacramento Valley Basin. Solid lines defining trends are discussed in text. Any numbers on the right-hand side of the above plots are values which fell off the scale for the respective sample. Stratigraphy, from California Division of Oil and Gas Fields (1973), is as follows: bottom of the post-Eocene undifferentiated nonmarine strata and top of the Upper Cretaceous Panoche Formation, about 1,036 m.

Beyer (1988b, p. 30) had noted that the Mesozoic marine rocks of the Sacramento Valley Basin ".....generally contain type III kerogen and less than 1 percent total organic carbon...". However, previously published petroleum-geochemical analyses of Sacramento Basin rocks are limited to Jenden and Kaplan (1989), who provided TOC analyses from rocks of five wells along a north-south strike of the length of the Sacramento Valley Basin (as deep as about 3,350 m (11,000 ft)). Their Mesozoic rock samples had TOC values primarily around 1 percent with some values as high as 2 percent. Tertiary rocks generally had values substantially below 1 percent, although, several had values between 1 and 2 percent. Jenden and Kaplan (1989) presented microscopic kerogen analyses which demonstrated a dominance of higher plant (woody) OM and intertinite, and an absence of algal OM in these rocks. Their kerogen analyses thus agree with the low HI values of these age rocks in figure 18. The significant decreases in rock organic richness, at least of rocks penetrated by the drill, northward in the Great Valley of California, is reflected by the transition from a rich oil province in the southern San Joaquin Valley Basin to a mediocre (regarding discovered reserves) dry-gas province in the Sacramento Valley Basin.

Discussion

HC Generation Potential from the ROCK-EVAL Hydrogen Index

Baskin (1993, 1997, in press) noted that previous studies (Katz and Elrod, 1983; Grabowski, 1984; Crossey and others, 1986; Katz and Pheifer, 1986; Burwood and others, 1988; Scott and Hussain, 1988) have demonstrated that ROCK-EVAL HI values often do not correlate well with kerogen elemental hydrogen to carbon (H/C) ratios. On the other hand, ROCK-EVAL HI values have been classically portrayed as correlating very well with kerogen H/C ratios (Tissot and Welte, 1984, their figure V.1.11; p. 511). The reasons for this lack of correlation between H/C and HI have been discussed by various investigators (including Horsfield and Douglas, 1980; Peters, 1986; and Larter, 1988), and largely have been attributed to erroneous ROCK-EVAL analyses. However, the details of these discussions will not be reviewed here.

This lack of correlation appears to be pronounced in suites of extremely immature source rocks from both the Santa Maria and Ventura Basins (Baskin 1993; in press) and also from the offshore California Borderland basins (Katz and Elrod, 1983). Figure 19 from Katz and Royle (1993) demonstrates this point. Kerogen elemental H/C ratios are invariant versus a large range of ROCK-EVAL HI values (100 to 750). Moreover, Baskin (in press) presents similar plots (figs. 3, 7, 8, and 9; also see fig. 3 in Baskin, 1997). It could thus be argued that the data and conclusions of this paper are invalid, because, on the basis of figure 19, the ROCK-EVAL HI would appear to be an inappropriate measurement of HC generation potential, at least for California Miocene source rocks.

In this light, a random suite of samples from this study was assembled and subjected to elemental kerogen and ROCK-

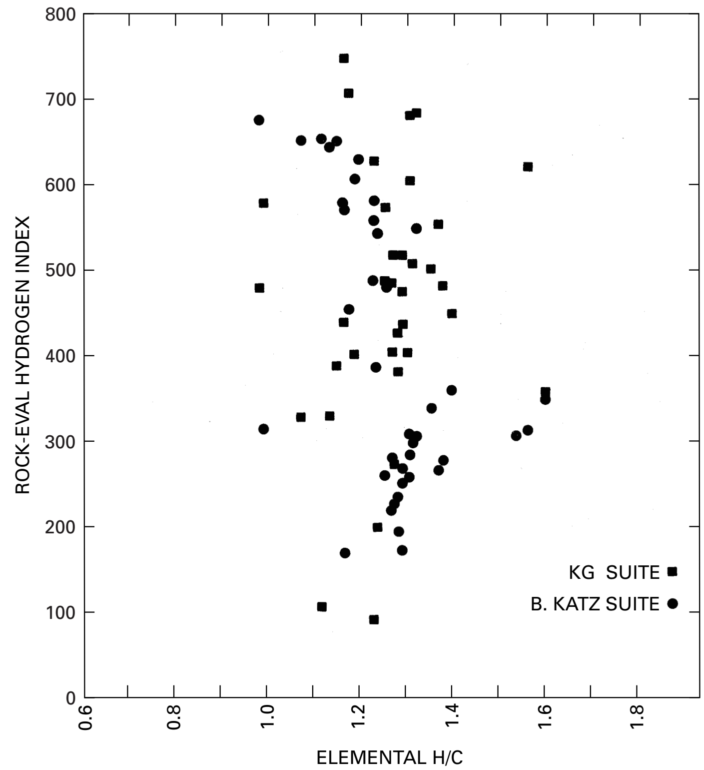

Figure 19. ROCK-EVAL hydrogen index plotted versus kerogen elemental hydrogen to carbon (H/C) ratios for the "KG" suite of the Cooperative Monterey Organic Geochemistry Study (CMOGS, Isaacs and Rullkötter, 1993) and for a supplemental sample suite collected by Barry Katz. All data collected by Barry Katz.

EVAL analyses. Three criteria had to be met in this sample suite. First, the samples had to be immature, not having entered the HC-generation stage. The lack of HC generation was principally determined by either low production indices (generally 0.07 or less) or by low values of the carbon-normalized S_1 peak (20–50). However, some samples either had very low starting HI values (and hence higher production indices) or had abnormally high concentrations of indigenous (pre HC-generation) bitumen. In fact, some samples were purposefully chosen for this latter characteristic. In such cases, the rank of these samples was set by numerous other samples, at nearly the same depth as the sample in question, from the same wellbore. The second criterion was that as wide a range of HI values as possible be chosen for this sample suite (based on previously existing ROCK-EVAL analyses). The third criterion was that the isolated kerogen had to be available from kerogen macerations performed from 1974 to 1977 for the Bostick and others (1978) study. Thus the samples chosen for ROCK-EVAL versus H/C analysis in this study were truly random, determined principally by kerogen macerations carried out more than 20 years ago. Note that some of the samples with high HI values (≥400) could be deeply buried and at burial temperatures substantially above 100°C (table 4).

Once the sample suite was selected, newer, replicate, ROCK-EVAL analyses were performed on the rocks to optimize analytical reproducibility. This was because the older ROCK-EVAL analyses had been performed over a 16 year time period. The elemental kerogen analyses were carried out concurrently with the newer ROCK-EVAL analyses.

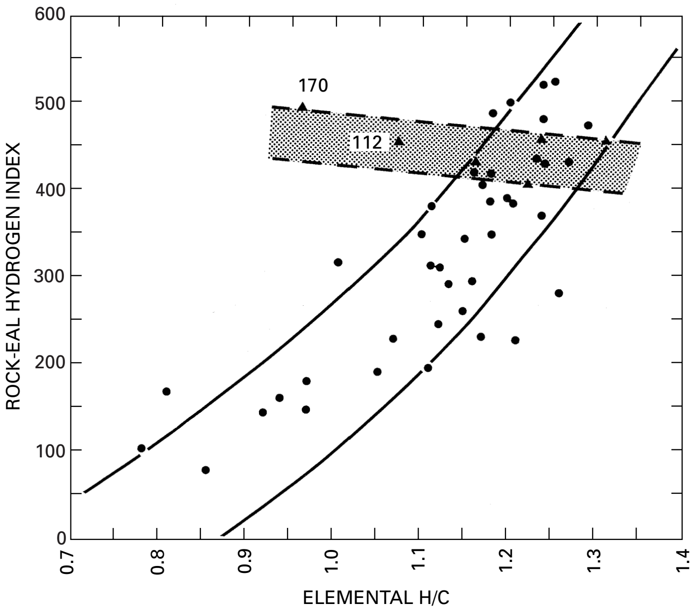

Figure 20. Plot of kerogen elemental H/C (hydrogen/carbon) ratios versus the ROCK-EVAL hydrogen index for the samples of table 4. Triangles are samples with high contents of pre-HC-generation indigenous bitumen. Two of these samples ("170", "112") had much lower HI values (170 and 112) after solvent extraction. Stippled pattern and solid lines are explained in the text.

The results of these analyses are plotted in figure 20 where there is a reasonable agreement between increasing ROCK-EVAL HI values and kerogen elemental H/C ratios, as delineated by the two solid lines. Thus for the samples of this study, ROCK-EVAL HI is taken as a representative measurement of hydrogen richness, and thus the HC generation potential. This agreement between the ROCK-EVAL HI and kerogen elemental H/C ratios was also supported by "spot check" visual-kerogen analyses, which demonstrated all suspected hydrogen-poor OM (types III/IV OM by ROCK-EVAL HI to be structured ("terrestrial") kerogen and all hydrogen-rich OM to be amorphous kerogen.

The triangles in figure 20 represent samples with large amounts of extractable bitumen (samples with asterisks, table 4). As delineated by the dashed lines and stippled pattern, these samples plot in a trend almost perpendicular to the trend of the main body of samples (the dots), and despite a wide range of H/C ratios (0.83 to 1.26), are invariant versus HI. However, this stippled trend is opposite to the invariant trend in figure 19, and as reported by Baskin (1993; in press), where elemental H/C is invariant versus large ranges of HI. Thus, based on the limited sample base of figure 20 (6 samples), large concentrations of indigenous bitumen appear to obfuscate expected HI versus H/C trends. However, high indigenous bitumen concentrations do not appear to explain the spurious trend of figure 19.

Although we have no explanation for the trend of figure 19, this trend may be linked to the fact that the rank of the figure 19 samples ranges from extremely low to low, whereas the rank of the figure 20 samples is substantially higher. Elemental kerogen H/C ratios demonstrate excellent correlation with ROCK-EVAL hydrogen indices for Lower Mississippian-Upper Devonian Bakken shale sample suites, where the Bakken shales are immature and have wide ranges in hydrogen-richness (L. C. Price, unpub. data). For example, HI values can range from 75 to 850 in 12.2 m (40 ft) of section. However, these suites of Bakken shales, although decidedly immature, have been exposed to significantly higher burial temperatures than the immature Miocene shales of the California petroleum basins, which yield such poor kerogen H/C to ROCK-EVAL HI correlations (fig. 19). Thus, it would appear that at least some source rocks must be exposed to minimal burial temperatures of perhaps 70° to 80°C before the ROCK-EVAL HI becomes a valid measure of kerogen hydrogen richness.

As stated, the kerogens of figure 20 were macerated from 1974 to 1977. A split of each core sample was taken years later and powdered for ROCK-EVAL analysis. This explains some of the variance in figure 20, because some degree of facies variance exists even within one core sample. A split, for ROCK-EVAL, of the powdered rock used for kerogen maceration would have decreased the scatter in figure 20. However, such splits were not available. Lastly, we agree with Baskin's (1993, 1997, in press) principal conclusions: ROCK-EVAL is a fast, inexpensive screening tool which allows large numbers of samples to be analyzed. However, kerogen elemental H/C ratios provide the most accurate estimate of kerogen (and thus source-rock) richness, although this analysis is much more expensive and time consuming. When possible, ROCK-EVAL HI values should be calibrated against kerogen H/C ratios, such as in figure 20.

Two of the figure 20 triangles have numbers (112 and 170) beside them. These numbers are HI values for solvent-extracted splits of the two samples (all HI values in figure 20 are from unextracted rocks). Thus, most of the HI value from the two unextracted samples under discussion are clearly from the higher-molecular-weight portion of the high bitumen concentrations (the effect of Clementz, 1979). Solvent extraction of the two samples resulted in reduced HI values. However, such solvent extraction removes the asphaltenes, which are small pieces of kerogen. Moreover, many unpublished analyses by L. Price, and related to the effect described by Price and Clayton (1992), demonstrate that the asphaltenes in source rocks are intimately associated with kerogen and not distributed throughout the mineral matrix of source rocks. Some investigators recommend running ROCK-EVAL and elemental H/C analyses only on rocks which have been solvent-extracted to determine generation potential. However, such extractions remove the asphaltenes from the kerogen, which in many California shales constitute a significant part of the shale's HC-generation potential. We may conclude from this discussion that unresolved problems clearly remain concerning the proper analytical steps for characterization of source-rock HC-generation potential.

Type III/IV OM Kinetic Differences between Different Basins

The apparent differences in reaction kinetics between the type III/IV OM of the Los Angeles, Ventura, and Southern San Joaquin Valley Basins warrant discussion. By the S_1 data of the Los Angeles Basin Apex-1 well (fig. 2), mainstage HC generation commences by 85° to 90°C (CIHG, Commencement of Intense Hydrocarbon Generation), which is supported by the production indices for the Apex-1 (fig. 3, CIHG). Solvent-

Table 4. ROCK-EVAL and kerogen elemental analyses for randomly selected samples from the Los Angeles and Ventura Basins, California. Wells and field or basin areas, and basin, are shown for each sample, as are depth in feet and burial temperature in °C. Depth is given in feet and not meters because the original sample depths were in feet. HI is the ROCK-EVAL hydrogen index; H/C is the kerogen atomic elemental hydrogen to carbon ratio; S_1 mg/g OC is the ROCK-EVAL S_1 pyrolysis peak normalized to total organic carbon (TOC); PI is the ROCK-EVAL production index (S_1/S_1+S_2); and %S is weight percent sulfur in the kerogen. Kerogen carbon and hydrogen contents were determined at the USGS laboratories. Kerogen sulfur and iron contents were determined by Huffman Laboratories, Golden, Colorado. Iron was assumed to be pyrite and pyritic sulfur was subtracted from total sulfur. Samples with asterisks over the depth values had high concentration of indigenous pre-HC-generation bitumen.

Well	Depth in feet	Temp. °C	HI	H/C	S_1 mg/g OC	PI	%S
Wilmington Field, Los Angeles Basin							
WD401	2411	62.1	350	1.18	20.2	0.054	
WJ141	2569*	64.8	456	1.31	121	0.210	
WD401	2764	68.1	372	1.24	4.47	0.012	
WD107	3017	72.4	104	0.78	4.62	0.042	
WC533	3083	73.5	228	1.21	10.2	0.043	
WD107	3414*	79.1	460	1.23	100	0.179	
WD114	3828	86.2	312	1.12	4.11	0.013	
WD204	4116*	91.1	410	1.22	79.9	0.163	
WC603	4294	94.1	230	1.07	18.4	0.074	
WC603	4531	98.1	195	1.11	10.7	0.052	
WC603	5019	106.4	298	1.16	4.31	0.014	
WC603	5261	110.5	433	1.24	92.3	0.176	
D308	5455	113.8	433	1.27	36.7	0.078	4.90
D102	6071	124.3	476	1.29	46.9	0.090	4.66
D605	8607	167.4	484	1.24	26.0	0.051	13.77
C403	9412	181.1	492	1.18	5.41	0.011	
C403	10,387	197.7	390	1.18	12.1	0.030	
Long Beach Field, Los Angeles Basin							
Shell Alamitos-48A	8061-8071	109.0	80	0.86	2.59	0.031	
Richfield Malcom Davis	9985	129.4	345	1.15	24.9	0.067	
Richfield Malcom Davis	10,065	130.3	389	1.20	40.0	0.093	
Richfield Malcom Davis	10,210	131.8	526	1.25	14.6	0.027	4.63
Shell S. Rose-1	10,583	135.8	524	1.24	41.2	0.073	3.58
Shell S. Rose-1	10,931-10,941	139.6	503	1.20	33.4	0.062	2.33

extraction analyses of Los Angeles Basin rocks with type III/IV OM (Price, 1999) also suggest that mainstage HC generation begins at 100°C there. By the maximum carbon-normalized S_1 values for all Los Angeles Basin rocks with type III/IV OM (fig. 8), mainstage HC generation begins by 105°C, although maximum carbon-normalized values of production indices (fig. 9) suggest 125° to 150°C for this event. Thus, these different data sets suggest that mainstage HC generation commences somewhere from 85° to 130°C, most likely around 100° C, for type III/IV OM in the Los Angeles Basin.

In contrast, commencement of intense HC generation in type III/IV OM is not observed in the Ventura Basin by 140°C (figs. 10, 11), and only by 145°C at Paloma (Southern San

Table 4.—continued

Well	Depth in feet	Temp. °C	HI	H/C	S_1 mg/g OC	PI	%S
Anaheim Nose, Los Angeles Basin							
Mobil Librown-1	8826-8834	104.3	148	0.97	13.5	0.084	
Mobil Librown-1	9018-9030	106.3	180	0.97	8.6	0.046	
Santa Fe Springs Field, Los Angeles Basin							
Mobil Santa Fe-243	9494-9502	124.9	320	1.02	9.68	0.029	
Union Bell-107	12,570	157.8	422	1.16	13.9	0.032	1.65
Bandini Field, Los Angeles Basin							
C.C.M.O. Bandini-1	10,070-10,090	126.1	193	1.05	28.6	0.129	
Ventura Avenue Field, Ventura Basin							
Lloyd-183	12,705-12,720	127.0	436	1.23	18.7	0.041	10.28
Lloyd-183	13,067-13,097*	130.1	433	1.16	82.1	0.160	5.58
Lloyd-183	13,843-13,867	136.6	421	1.18	23.9	0.054	
Lloyd-183	14,546-14,564	144.2	393	1.20	25.4	0.061	3.84
Lloyd-183	15,064-15,074	146.7	291	1.13	24.9	0.079	
Ventura Basin Central Syncline							
Chevron Maxwell-1	4343-4352*	51.9	454	1.07	77.4	0.146	
Chevron Maxwell-1	6058-6068*	64.0	495	0.96	54.5	0.099	
Chevron Maxwell-1	8568-8580	81.9	147	0.92	4.19	0.028	
Chevron Maxwell-1	9997-10,014	92.0	170	0.81	9.09	0.051	
Chevron Maxwell-1	10,394-10,402	94.8	263	1.15	10.1	0.037	
Chevron Maxwell-1	10,763-10,774	97.5	163	0.94	7.35	0.043	
Superior Limoneira-1	13,080-13,098	113.9	232	1.17	14.2	0.058	
Superior Limoneira-1	13,988	120.3	288	1.26	7.95	0.027	
Chevron Maxwell-1	15,100-15,112	128.3	247	1.12	12.6	0.049	<0.50
Chevron Maxwell-1	16,493-16,503	138.1	315	1.11	12.1	0.037	1.02
Chevron Maxwell-1	16,694-16,697	141.4	405	1.17	23.8	0.056	<0.50
Superior Limoneira-1	18,428-18,438	151.9	351	1.10	22.8	0.061	
Superior Limoneira-1	18,711-18,721	153.9	383	1.11	26.8	0.066	2.14

Joaquin Valley Basin; figs. 12, 13). Differences of 45°C for the onset of intense HC generation are significant. We envision only four possible explanations why HC generation begins at such lower temperatures in the Los Angeles Basin. First, the analyses performed are not reflecting reality. This is unlikely because these are standard widely used petroleum-geochemical analyses of a very large sample base. Second, kinetic differences may exist between the type III/IV OM in the three basins. This also appears unlikely because qualitative characteristics of the extracted bitumen (Price, 1999) suggest the same starting OM in the three basins. Third, rocks now at 85° to 100°C (and deeper) in the Los Angeles Basin incorporated unusually high concentrations of HCS at deposition compared to shallower rocks. Such a HC concentration increase with depth would give the appearance of commencement of intense HC generation. This normally would be an unlikely explanation. However, significant increases in organic richness occur in the Los Angeles (and Ventura) Basins with depth. Moreover, as discussed in Price (1999), many examples exist throughout the California oil basins of fine-grained immature rocks with abnormally high concentrations of indigenous immature HCS. A fourth explanation, and one that we prefer, is that some parts of the Los Angeles Basin have been hotter and have cooled significantly in the recent geologic past. Other considerations support this hypothesis.

Numerous investigators have maintained that the Los Angeles Basin is currently at maximal burial temperatures, including McCulloh and others (1978), Bostick and others (1978), Price and Barker (1985), Naeser and others (1987), and Beyer (1988a). However, this is not a known fact, because one of the weakest areas in petroleum geochemistry is still accurate determination of paleoburial temperatures. In our opinion, no consistently dependable tool exists to achieve this end. The R_o data of this study certainly illustrate this point. In fact, correct determination of even present-day burial temperatures has been a serious problem in many past petroleum-geochemical studies, because log-header drilling temperatures, rather than corrected-equilibrium temperatures, were often used in these studies (Price, 1983). Only in the last five to seven years has this latter problem become more widely recognized and steps taken to correct it. In reality, we have no valid way to determine if present-day Los Angeles Basin burial temperatures are maximal. Geologic inferences simply do not answer the question.

If such a cooling occurred, it had to occur in the very recent geologic past. This is because the most intense structuring in the basin occurred from the early Pliocene to Recent (Biddle, 1991), the probable time of emplacement of most of the oil fields. Moreover, high-ground water flow is the only possible cause of such a recent cooling. The present arid climate of the Los Angeles Basin and environs cannot support significant ground-water flow. However, during the last glaciations, 10,000 to 70,000 years ago, *much larger* ground-water flow occurred. These ground-water flows were aided by (1) the ring of mountains (which serve as a watershed) surrounding the Los Angeles Basin, some peaks of which are over 3,000 m, and (2) by the very high sand and gravel content of the shallower Los Angeles Basin rocks (fig. 1, and accompanying discussion), rocks which are highly transmissible fluid conduits for high ground-water flow.

Evidence of past elevated meteoric water flow is rampant in the reservoired oils of the Los Angeles Basin, many of which are highly degraded (Bruce Bromley, Unocal, oral commun., 6/94); and Jeffrey and others, 1991). An example of oil biodegradation is also given in Price (1999). Such extensive biodegradation could not occur under present climatic conditions, especially given the short emplacement times of the oils. These degraded oils could only have resulted from much greater ground water flows in the recent geologic past. One other convincing line of evidence supports such ground water flow. The Los Angeles Basin is the smallest basin in the world with major reserves (3,367 km^2, 1,300 mi^2; Price, 1994). Yet, as demonstrated by table 2, and as previously noted by Bostick and others (1978), much different geothermal gradients exist in different basin areas. Given the basin's very small area, it is very difficult to explain how such different temperature gradients exist there.

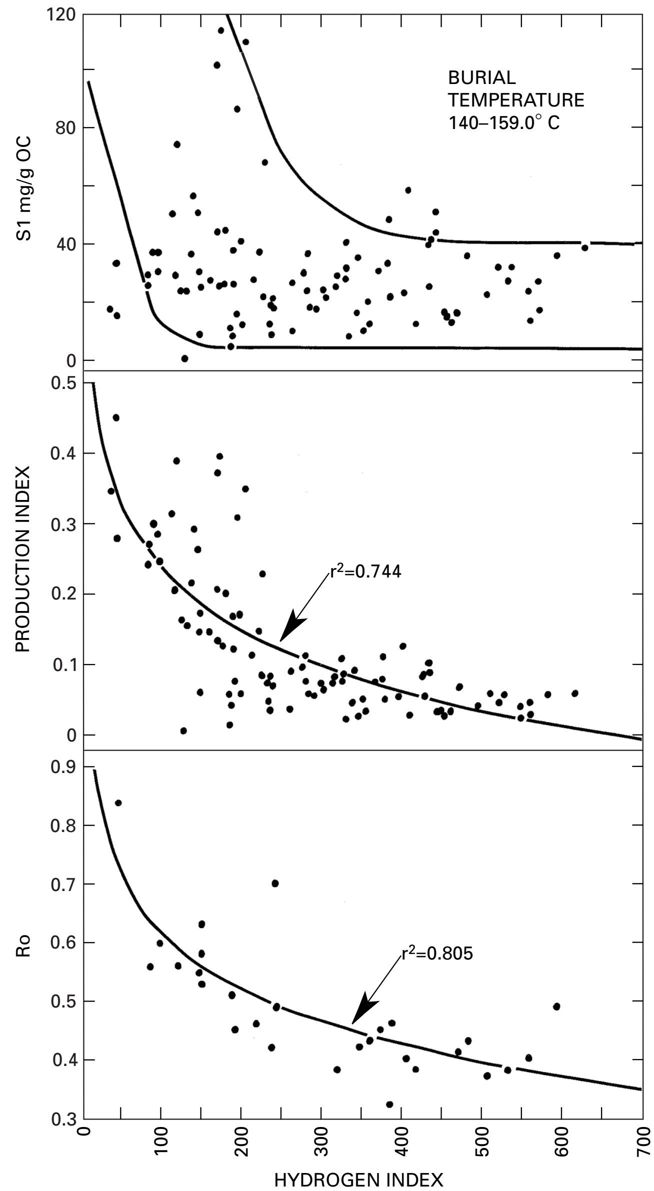

Figure 21. Plot of R_o, and the ROCK-EVAL production index and S_1 peak normalized to organic carbon (mg/g OC), all versus the ROCK-EVAL hydrogen index for rocks from the California petroleum basins at equilibrium-burial temperatures of 140° to 159.9°C. Samples are from the Ventura central syncline and the 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 area; the Apex-1 and the Long Beach Airport-1 wellbores; from various wells in the Anaheim nose and northeast flank areas of the Los Angeles Basin; and from wells in the Paloma field, Southern San Joaquin Valley Basin. All samples are core, except for the Apex-1 samples (cuttings chips). The curved line in the R_o plot results from logarithmic regression analysis of the data and has a correlation coefficient of r^2= 0.805 to the data. The curved line in the production index plot results from logarithmic regression analysis of the data and has a correlation coefficient of r^2 = 0.744 to the data. The lines in the S_1 pyrolysis-peak plot define the principal sample population.

However, enhanced meteoric water flows would have been channeled into basinal areas which could best transmit fluids and thus would preferentially cool relative to other areas. Therefore, the variable gradients provide strong evidence to us of large ground-water flow in the basin in the recent geologic past.

Kinetic Differences between Hydrogen-Rich and Hydrogen-poor OM

Data from this study, (Price, 1999), and other investigators, demonstrate the strong suppression of organic metamorphism in hydrogen-rich OM compared to type III/IV OM for the same burial histories and conditions in these basins. For example, R_o, ROCK-EVAL S_1 pyrolysis peak values (normalized to TOC, mg/g OC), and production indices are all plotted versus ROCK-EVAL HI in figure 21 for all samples of this study buried between 140° to 159.9°C. This temperature interval normally would be high enough to initiate mainstage HC generation, which would be reflected by significant increases in production indices and S_1 peak values. In figure 21, as HI increases, the three indices of organic metamorphism progressively decrease. Samples with HI values of less than 200 are demonstrably in mainstage HC generation; samples with HI values greater than 250 clearly are not. Equivalent plots were made for samples between 160° to 179.9°C (not shown) and 180° to 199.9°C (fig. 22), with the same results, as evident in figure 22. Moreover, T_{max} also decreased with increase in HI values for these same samples, when plotted over these three burial temperature intervals.

Other investigators have also noted a strong suppression of different aspects of organic metamorphism in the hydrogen-rich OM of these basins. For example, Walker (1982) and Walker and others (1983) found very strong R_o suppression in the "nodular shale" of the Los Angeles Basin, a phosphatic organic-rich (high TOC and HI values) source rock at the base of the upper Miocene Modelo Formation occurring on the northwest shelf of the Los Angeles Basin. R_o data, versus burial temperatures, from Walker (1982) are given in figure 23. The observed R_o values are highly suppressed for their burial temperatures, compared to the values expected for the burial conditions of these rocks.

One may argue that the cooling proposed to have occurred in the Los Angeles Basin (discussed above) renders meaningless any conclusions regarding differential reaction kinetics between hydrogen-rich and types III/IV OM. However, this is not the case, because commencement of intense HC generation has not yet occurred in rocks with hydrogen-rich OM at 198°C at Wilmington. Even if significant cooling has occurred at Wilmington, 198°C is still far too high for commencement of intense generation by accepted models. Moreover, no evidence of significant cooling exists in the Ventura or Southern San Joaquin Valley Basin central synclines. However, intense HC generation commences in the Paloma field rocks with type III/IV OM by 145°C, yet this event has not occurred by 150°C in the Ventura Avenue field rocks with hydrogen-rich OM. Many of the present-day Los Angeles Basin equilibrium-burial temperatures are most probably not maximal, and thus this temperature data base is somewhat flawed. However, even within the temperature limitations of this data base, one may only conclude that large differences exist in the reaction kinetics between the hydrogen-rich and type III/IV OM of this data base.

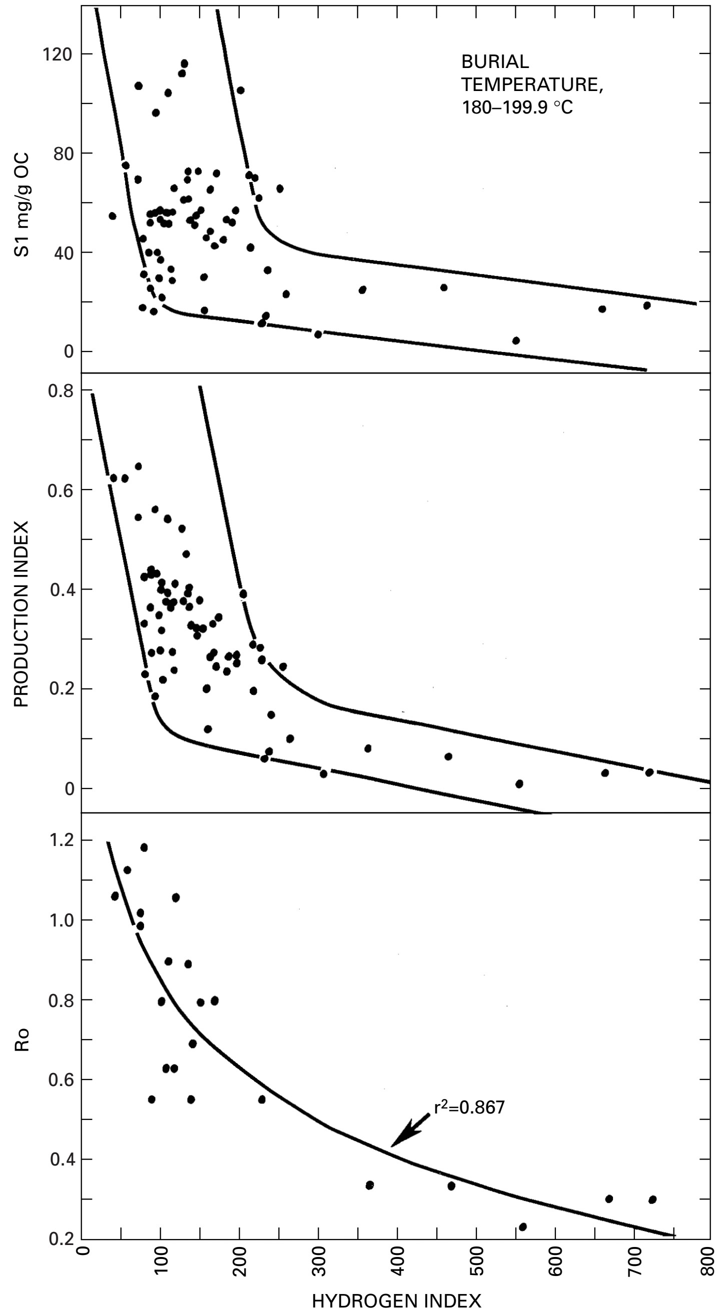

Figure 22. Plot of R_o, and the ROCK-EVAL production index, and S_1 peak normalized to organic carbon (mg/g OC), all versus the ROCK-EVAL hydrogen index for rocks from the California petroleum basins at equilibrium-burial temperatures of 180° to 199.9°C. Samples are from the Wilmington field, the northwest plunge of the Santa Fe Springs field (Houghton Community-1), and the Apex-1 in the Los Angeles Basin; and the KCLA 72-4 wellbore, Paloma Field, Southern San Joaquin Valley Basin. The curved line in the Ro plot results from logarithmic regression analysis of the data and has a correlation coefficient of $r^2 = 0.867$ to the data. The lines in the S_1 pyrolysis peak and production index plots define the principal trends of the data.

Jarvie and Lundell (in press), based on kinetic considerations from open-system pyrolysis of two suites of immature

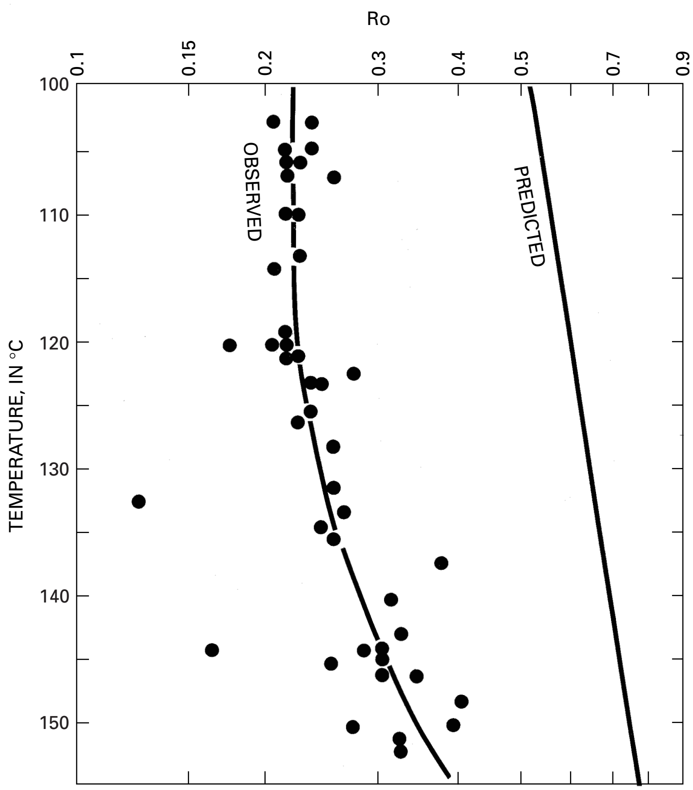

Figure 23. Plot of observed R_o data versus burial temperature in °C from the nodular shale (northwest shelf of the Los Angeles basin) versus expected R_o values given the burial histories of the rocks. Data from Walker (1982).

Monterey Formation source rocks, concluded that kerogen atomic oxygen to carbon (O/C) ratios were a dominant control of the timing (burial temperatures) for commencement of intense HC generation from these kerogens. Kerogens having higher O/C ratios and lower H/C ratios generated earlier than kerogens having lower O/C ratios and higher H/C ratios. Thus, open-system laboratory experiments seem to confirm the data of this study from the natural system: type III/IV OM (high-oxygen-content OM) enters intense HC generation before more hydrogen-rich oxygen-poor OM.

Differences between the different OM types (hydrogen-rich versus hydrogen-poor) have been discussed with examples provided, by Price (1991, p. 532–534). Price (1991) attributed these differences in OM reactivity to different bond strengths in the different OM types. Tissot and Welte (1984, p. 151–154) discuss the chemical bonds in the different OM types of sediments. As one passes from hydrogen-rich OM to type III (or IV) OM, the oxygen in the OM goes from ester bonds to exclusively carboxylic acid bonds (in type III OM). Esters have much greater bond strengths than carboxylic acids. Thus, more hydrogen-rich (ester-rich) OM requires higher ranks to react than hydrogen-poor OM.

Jarvie and Lundell (in press) also noted that a modest variation in kerogen sulfur to carbon (S/C) ratios among these high-sulfur kerogens had no effect on the timing of HC generation. This observation is contrary to the widely held opinion that high-sulfur kerogens enter mainstage HC generation at lower burial temperatures ("earlier") than low-sulfur kerogens (Orr, 1986; Baskin and Peters, 1992). Jarvie and Lundell (in press) recommended reexamination of the widely held belief concerning early HC generation from sulfur-rich kerogens. Data from our study supports Jarvie and Lundell's (in press) position on this matter. Fourteen of the hydrogen-rich kerogens of table 4 were randomly selected for sulfur analysis with the intent of demonstrating that the hydrogen-rich OM of the Los Angeles and Ventura Basins was largely sulfur-poor OM. Kerogens from twelve of the samples had low to moderate sulfur concentrations, from 0.50 to 5.86 weight percent sulfur (table 4). Two samples, D605 (8,607 ft) and Lloyd-183 (12,705–12,720 ft), had high sulfur concentrations (13.77 and 10.28 weight percent of the kerogen, respectively).

The ROCK-EVAL S_1 carbon-normalized peak and production indices for these two samples (26.0 mg/g OC and 0.051 (T_{max} = 426°C) for D605, and 18.7 mg/g OC and 0.041 (T_{max} = 425°C) for Lloyd-183) demonstrate that neither rock has begun HC generation. This in spite of the high burial temperatures of these two samples (Lloyd-183: 127°C, D-605: 167°C). Clearly, some sulfur-rich kerogens from early to early mid Miocene shales in the California basins do not appear to commence premature HC generation, contrary to accepted paradigm. Also, sulfur-rich kerogens clearly exist in some parts of the Los Angeles and Ventura Basins. However, a far greater sample base than two samples is needed for definitive insight on the matter.

Conclusions

1. In the Los Angeles and Ventura Basins, rock organic richness significantly increases with depth from increases in : TOC, kerogen hydrogen content, the percentage of fine-grained versus coarse-grained rocks, and most probably from other unrecognized controls.
2. Los Angeles Basin shales are perceived to be dominated by hydrogen-rich amorphous OM. In reality, large rock volumes contain only types III/IV OM, including the upper 6,000 m of parts of the Los Angeles Basin central syncline, the shallowest 3,000 m of which is essentially a sand and gravel pit.
3. ROCK-EVAL HI values are a representative measurement of the HC generation potential for the rocks of this study, as demonstrated by a cross plot of ROCK-EVAL HI and kerogen elemental hydrogen to carbon ratios. Visual kerogen analyses corroborate this finding.
4. In type III/IV OM, by ROCK-EVAL data, mainstage HC generation begins at present-day (cooled) burial temperatures of about 100°C in the Los Angeles Basin, at 145°C in the Southern San Joaquin Valley Basin, and somewhere above 140°C in the Ventura Basin. In Los Angeles and the Southern San Joaquin Valley, HC generation is largely complete in type III/IV OM by 220°C.
5. The lower temperatures for commencement of mainstage HC generation in the Los Angeles Basin are attributed principally to cooling of parts of that basin from previous maximal burial temperatures due to elevated meteoric water flows during the last glaciations. These water flows would have also resulted in degradation of much of the reservoired

oil in that basin and created the variable geothermal gradients observed throughout the basin.

6. All aspects of organic metamorphism, including mainstage HC generation, are strongly suppressed in the hydrogen-rich OM of these basins compared to the type III/IV OM there. For example, HC generation has not commenced in the hydrogen-rich OM of these basins by 200°C. Moreover, decreasing values of maturity indices, such as the carbon-normalized S_1 ROCK-EVAL peak, production indices, T_{max}, and $R_{o,}$ all correlate well with increasing HI values for given burial temperature ranges. This suppression is attributed to stronger bonds in hydrogen-rich OM compared to type III/IV OM, and has pronounced relevance to petroleum-geochemical exploration models.
7. Increasing T_{max} and decreasing oxygen indices both reflect ongoing organic metamorphism in the hydrogen-rich OM of the basins at all burial temperatures, a metamorphism not revealed by some other maturity indices of this study. However, for all OM types, the ranges of T_{max} and oxygen indices at any given burial temperature are unacceptably large, due to the lack of precision of the ROCK-EVAL instrument.
8. Pronounced OM characteristics inherited from deposition, overprint, and confuse, the interpretation of OM characteristics from HC generation in the rocks of these basins.
9. Immature shales with all OM types in the California basins can have high values of carbon-normalized immature indigenous HCS and bitumen, including rocks with type IV OM.
10. Coarse-grained rocks in and adjacent to oil fields in the California basins almost invariably have high concentrations of HCS and bitumen, apparently from oil staining.
11. Organic richness in fine-grained rocks significantly decreases northwards from the Southern San Joaquin Valley Basin towards the Northern San Joaquin and Sacramento Valley Basins.
12. Wide ranges observed in ROCK-EVAL S_1 peak values at any burial temperature after commencement of mainstage generation in type III/IV OM are hypothesized as due to significantly different original HI values (for example, 50 versus 250) and to loss of generated HCS to expulsion, or to the drilling mud during drilling operations.
13. We have no widely applicable tool for dependable and accurate estimation of paleoburial temperatures, which remains the greatest weakness in petroleum geochemistry.
14. The hypothesis that sulfur-rich OM generates HCS at substantially lower burial temperatures than sulfur-poor OM is not supported by two samples in this study. However, more analyses are needed to support this finding.

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