# Organic Metamorphism in the California Petroleum Basins:

## Chapter B—Insights from Extractable Bitumen and Saturated Hydrocarbons

*By* Leigh C. Price

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## Abstract

Seventy-five shales from the Los Angeles, Ventura, and Southern San Joaquin Valley Basins were extracted and analyzed. Samples were chosen on the basis of ROCK-EVAL analyses of a much larger sample base. The samples ranged in burial temperatures from 40° to 220°C, and contained hydrogen-poor to hydrogen-rich organic matter (OM), based on OM visual typing and a correlation of elemental kerogen hydrogen to carbon ratios with ROCK-EVAL hydrogen indices.

By extractable bitumen measurements, rocks with hydrogen-poor OM in the Los Angeles Basin began mainstage hydrocarbon (HC) generation by 90°C. The HC concentrations maximized by 165°C, and beyond 165°C, HC and bitumen concentrations and ROCK-EVAL hydrogen indices all began decreasing to low values reached by 220°C, where HC generation was largely complete. Rocks with hydrogen-poor OM in the Southern San Joaquin Valley Basin commenced mainstage HC generation at 135°C and HC concentrations maximized by 180°C. Above 180°C, HC and bitumen concentrations and ROCK-EVAL hydrogen indices all decreased to low values reached by 214°C, again the process of HC generation being largely complete. In both cases, bell-shaped HC-generation curves were present versus depth (burial temperature). Mainstage HC generation had not yet begun in Ventura Basin rocks with hydrogen-poor OM by 140°C. The apparent lower temperature for initiation of mainstage generation in the Los Angeles Basin is attributed to very recent cooling in that basin from meteoric-water flow. Thus, HC generation there most probably occurred at higher burial temperatures.

In contrast, mainstage HC generation, and all aspects of organic metamorphism, were strongly suppressed in rocks with hydrogen-rich OM at temperatures as high as 198°C. For example, shales from the Wilmington field (Los Angeles Basin) from 180° to 198°C retained ROCK-EVAL hydrogen indices of 550-700 and had saturated-HC coefficients of only 4-15 mg/g organic carbon. The rocks with hydrogen-rich OM were subjected to the same burial conditions as the rocks with hydrogen-poor OM. We attribute this suppression of organic metamorphism in this study primarily to much stronger bonds in the hydrogen-rich OM compared to the bonds in hydrogen-poor OM. Trends in bitumen compositions (qualitative characteristics) versus burial temperature were also very different for rocks with hydrogen-poor OM compared to that in rocks with hydrogen-rich OM. This observation demonstrated that the two OM types also had significantly different reaction pathways, in addition to different reaction kinetics. Strong exploration implications arise from these observations.

Above 40°C, but before mainstage HC generation, a low-temperature (pre-mainstage) HC generation occurred in all rocks, and all OM types, studied. This low-temperature generation resulted in significant qualitative changes in the bitumen and HCS (hydrocarbons) from rocks of all OM types, especially in rocks with hydrogen-rich OM, from 40° to 70°C. This, and previous studies, document that very high carbon-normalized concentrations of indigenous bitumen and HCS occur in late Neogene immature rocks of any OM type in all southern California basins. This characteristic is attributed to the low-temperature generation occurring in both sulfur-poor and sulfur-rich kerogens, which originally had unusually high concentrations of weak (15-40 Kcal/mole) bonds. These observations and considerations have marked relevance to exploration regarding the possible formation of commercial oil deposits at immature ranks in these basins. Other significant geochemical observations also result from this study.

## Introduction

Price and others (1999) listed the reasons for the overall study. Samples were chosen for Soxhlet extraction from trends observed in, or hypotheses made from, the data of Price and others (1999). These samples provide a unique opportunity to study the effects of organic matter (OM) variation on hydrocarbon (HC) generation for several reasons: First, hydrogen-rich (types I and II) OM and hydrogen-poor (types III and IV) OM were intermittently deposited with each other in different areas of the southern California petroleum basins. In fact, many examples exist (based on ROCK-EVAL analyses, Price and others, 1999) where different OM types occur in rocks several meters apart in the same wellbore. Second, all OM types have been exposed to high burial temperatures (180° to 219°C) in the basins studied, which should result in high organic maturities. Thirdly, as discussed in Price and others (1999), the present-day burial temperatures in the synclines of two of the three basins studied are believed to be maximal and are some of the most accurate

equilibrium temperatures available worldwide. *Thus, organic maturities can be directly related to maximum burial temperature.* As in Price and others (1999), data are plotted here versus (equilibrium) burial temperatures and not depth because geothermal gradients vary both between basins and between different sites in the same basin. Lastly, sediment age ranges from upper Miocene to Pliocene (roughly 2 to 8 million years) and thus the influence of geologic time (if any, Price, 1983) is minimized in these samples.

This is the second paper of a three-part study. The first paper (Price and others, 1999) discussed vitrinite reflectance ($R_o$) and ROCK-EVAL analyses, and related those analyses to OM type. The third part of the study will examine biomarkers, aromatic HCS, the results of aqueous-pyrolysis experiments, modeling studies, whole-rock extraction (Price and Clayton, 1992), $\delta^{13}C$ measurements of bitumen and macerated kerogens, and kerogen visual analyses.

Plots, versus burial temperature, of milligrams of extractable $C_{15}$+ bitumen or HCS, both normalized to grams of total organic carbon (the bitumen and HC coefficients), wherein all samples were put on one plot, had no definable trends. Thus, the sample base was broken into three subgroups. Samples from the Los Angeles and Ventura Basins were put into two groups: (1) samples with ROCK-EVAL hydrogen indices less than 300 (all but 4 of 28 samples studied herein had hydrogen indices less than 240), in other words, types III or IV OM; and (2) samples with hydrogen indices greater than 380, or more hydrogen-rich OM (one sample with an HI of 306 (TOC = 5.18) was put in this class). The Southern San Joaquin Valley Basin samples made up the third class, and 13 of these 16 samples had types III or IV OM. Organic-matter type identification was determined by the relationship between kerogen elemental hydrogen to carbon ratios and the ROCK-EVAL hydrogen-index established in Price and others (1999).

## Samples and Methods

All samples were core except for two cuttings chips samples from the Apex-1 wellbore. See Price and others (1999) for a description of cleaning methods. All cleaned rocks were ground and sieved to 100 mesh and Soxhlet extracted in dichloromethane for 72 hours. The dichloromethane and bitumen were reduced in volume by passive evaporation (Price and Wenger, 1992), retaining all $C_8$+ compounds. (All solvent evaporation was by passive evaporation.) After transferring the extract to a 50 mL volumetric flask, a 5 mL aliquot was taken for bitumen determination. The dichloromethane was passively evaporated to 1 mL, and 3 aliquots of 5 mL of hexane were added, with intervening passive evaporation to 1 mL, to deasphaltene the bitumen. After the last evaporation, the asphaltenes were filtered and weighed, and the remaining bitumen passively evaporated to 0.5 to 1.0 mL for silica-gel-alumina column chromatography to separate the bitumen into saturated and aromatic HCS and resins. Saturated HCS were eluted with 10 mL of hexane, aromatic HCS with 25 mL of benzene, and resins with 7 mL of 1:1 benzene-methanol. The saturated and aromatic HCS were transferred to 10 mL volumetric flasks and 5 mL of each were taken for $C_8$+ gas chromatography, and the other 5 mL were used

for $C_{13}$+ weights (obtained by letting the 5 mL aliquot in tared vials stand for 12-18 hours after losing their last solvent).

Samples are identified by feet and not meters in this paper because sample depths were originally in feet and conversion to meters would cause loss of the prime identifier. Extraction data are presented in table 1.

## Results

### Los Angeles/Ventura Hydrogen-Poor OM: Extractable Bitumen-Amounts and Characteristics

#### Introduction

Although the Los Angeles and Ventura Basins are separate, they are geographically close with very similar depositional and geologic histories. The rocks and extracted bitumen from the two basins were qualitatively indistinguishable from one another and the starting OM in the two basins also appears identical. Because of these reasons, and the more limited number of samples from the Ventura Basin, samples from both basins were plotted together.

#### HC Generation

Milligrams of $C_{15}$+ bitumen (triangles) and $C_{15}$+ HCS (dots), both normalized to total organic carbon (TOC), are plotted versus burial temperature for rocks with types III and IV OM from the Los Angeles and Ventura Basins in figure 1. The numbers at each bitumen coefficient sample point are ROCK-EVAL hydrogen indices (left number) and TOC contents (right number). Two bell-shaped curves have been fitted to the data, the solid line is the HC coefficient and the dashed line is the bitumen coefficient. Sixteen of the 27 HC coefficients lie on or near the inferred (solid-line) curve for those samples as do 16 of the 27 bitumen coefficients for their inferred (dashed) curve. Bell-shaped HC or bitumen coefficient (generation) curves are not always present, where expected, for sample bases that have sufficient maturity ranges (discussed below). However, when present, these curves invariably have significant scatter, as in figure 1. In fact, the inferred bell-shaped generation profile of figure 1 is not at all well defined, and it could be argued that a HC-generation profile is not necessarily even present in figure 1. However, the inferred profile of figure 1 is partly based both on well-defined generation profiles from the very large ROCK-EVAL data base for the Los Angeles Basin in Price and others (1999, figs. 1, 3, 8, 9) and the lack of detectable HC generation in samples from the Ventura Basin in the data base of Price and others (1999). In fact, one purpose of figure 1 is to examine the causes resulting in the scatter of data points throughout, and thus the lack of definition in, HC-generation profiles ("bell-shaped curves"), including those of figure 1.

Both the inferred HC and bitumen coefficient curves begin noticeable increases over 90° to 100°C, rather than the 120°C reported by Phillipi (1965). Moreover, the figure 1 data agree with the much larger ROCK-EVAL sample base of Price and

**Table 1.** Soxhlet-extraction data for core samples of shales from selected southern California basins. Original sample depths are given in feet. TOC is total organic carbon content in percent of rock weight. PPM is parts per million (dry rock weight) of the respective species. MG/G OC is milligrams (of the respective species) per gram of organic carbon (for example, the bitumen coefficient). SATS are saturated HCS, AROS are aromatic HCS, NSO are resins, ASP are asphaltenes, and TOTAL BIT, is total bitumen. Tmax and HI are the ROCK-EVAL $T_{max}$ and hydrogen index, respectively. BURIAL TEMP. °C is the burial temperature in °C. All wells in the Wilmington field and the Apex-1 wellbore were directionally drilled and depths in table 1 are true burial depths and not driller depths. Wilmington field wells are cluster wells drilled from piers or islands as named in table 1. In the Los Angeles Basin: Apex-1 is the American Petrofina Central Corehole (all Apex-1 samples are core except for two cuttings chips samples, labeled as cuttings). Dominguez field well names are as shown. La Mirada 46-1 is the General Petroleum La Mirada 46-1 in the Anaheim Nose area. LL&W-1 is the Standard Oil of California (SOCAL) Lomita Land and Water Company-1 (slightly northwest of the most northwest extension of the Huntington Beach Field). McGrath-18 is the Continental McGrath-18 (Seal Beach field). G.P. Santa Fe-243 is the General Petroleum Santa Fe Springs-243 (Santa Fe Springs field). Del Amo-1 is the SOCAL Del Amo-1 southwest of the Dominguez field and northeast of the Torrance-Wilmington field). Bryant Estate-1 is the Texaco Bryant Estate-1 (just northeast of the Seal Beach field). Bald. Hills Comm.-1 is the Shell Baldwin Hills Community-1 (Baldwin Hills area). Alamitos 48-A is the Shell Alamitos 48-A (southeast end of Long Beach field). L.B. Airport-1 is the Texaco Long Beach Airport-1 (just northeast of the central Long Beach field). Houghton Comm.-1 is the SOCAL Houghton Community-1 (northwest plunge of the Santa Fe Springs field). In the Ventura Basin: Taylor 315 is the Shell Taylor 315 and Lloyd-185 is the Getty Oil Co. Lloyd-185 (both wells are in the Ventura Avenue field). SOCAL Lim.-1 is the SOCAL Limoneira-1 and Sup. Lim.-1 is the Superior Oil Co. Limoneira-1 (both Santa Clara Trough area). In the Southern San Joaquin Valley Basin, Paloma field: Ohio Oil A-1 is as named; Ohio Oil KCLA-8 is as named; KCL-F-71-10 is the Ohio Oil KCL-F-71-10; Anderson 56-35 is the Superior Oil Anderson 56-35; and the KCL A 72-4 is the Ohio Oil KCL A 72-4. One sample is not from the Paloma field, the Shell 21-14 which is the Shell Canal 21-14 from the Canal field, 12.9 km (8 mi) north of the Paloma field. The Ventura Basin outcrop sample is explained in the text.

| WELL | DEPTH | TOC | PPM SATS | AROS | NSO | ASP | TOTAL BIT. | MG/G OC SATS | AROS | NSO | ASP | TOTAL BIT. | Tmax | HI | BURIAL TEMP. °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WD401 | 2,411 | 3.99 | 466 | 323 | 543 | 183 | 1,515 | 11.7 | 8.1 | 13.6 | 4.6 | 38.0 | 407 | 382 | 62.1 |
| WD401 | 2,764 | 5.16 | 2,590 | 1,230 | 1,690 | 460 | 5,970 | 50.2 | 23.8 | 32.7 | 8.9 | 116 | 422 | 425 | 68.1 |
| WD107 | 3,017 | 2.60 | 3,122 | 3,346 | 2,460 | 736 | 9,664 | 120 | 129 | 95 | 28 | 372 | 411 | 372 | 72.4 |
| WC533 | 3,083 | 3.20 | 245 | 107 | 184 | 43 | 579 | 7.7 | 3.3 | 5.8 | 1.3 | 18.1 | 415 | 391 | 73.5 |
| WD114 | 3,828 | 5.18 | 745 | 275 | 989 | 261 | 2,270 | 14.4 | 5.31 | 19.1 | 5.04 | 43.8 | 423 | 291 | 86.2 |
| WD204 | 4,286 | 8.93 | 887 | 582 | 655 | 418 | 2,542 | 9.9 | 6.5 | 7.3 | 4.7 | 28.5 | 412 | 500 | 94.0 |
| WC603 | 4,292-4,296 | 1.65 | 600 | 310 | 425 | 105 | 1,440 | 36.4 | 18.8 | 25.8 | 6.4 | 87.3 | 422 | 215 | 94.1 |
| WC603 | 4,521-4,540 | 2.70 | 670 | 280 | 525 | 215 | 1,690 | 24.8 | 10.4 | 19.4 | 8.0 | 62.6 | 410 | 198 | 98.1 |
| WC603 | 5,019 | 2.29 | 885 | 565 | 504 | 426 | 2,380 | 38.6 | 24.7 | 22.0 | 18.6 | 104 | 426 | 416 | 106.4 |
| WC603 | 5,261 | 1.76 | 2,428 | 1,361 | 1,441 | 466 | 5,696 | 138 | 77.3 | 81.9 | 26.5 | 324 | 418 | 577 | 110.5 |
| D308 | 5,455 | 5.98 | 1,165 | 1,030 | 1,398 | 972 | 4,820 | 19.5 | 17.2 | 23.4 | 16.3 | 80.6 | 417 | 560 | 113.8 |
| D102 | 6,071 | 4.59 | 1,845 | 1,160 | 2,195 | 1,039 | 6,631 | 40.2 | 25.3 | 47.8 | 22.6 | 144 | 421 | 834 | 124.3 |
| D102 | 6,296 | 6.12 | 1,870 | 1,440 | 1,655 | 1,165 | 6,130 | 30.6 | 23.5 | 27.0 | 19.0 | 100 | 419 | 535 | 128.3 |
| D308 | 6,541 | 5.27 | 2,185 | 2,425 | 3,049 | 2,821 | 10,480 | 41.4 | 46.0 | 57.9 | 53.5 | 111 | 418 | 551 | 132.3 |
| D605 | 8,408 | 3.66 | 610 | 500 | 717 | 983 | 2,810 | 16.7 | 13.7 | 19.6 | 26.8 | 76.9 | 434 | 500 | 164.0 |
| D605 | 8,607 | 5.40 | 530 | 509 | 605 | 1,105 | 2,749 | 9.8 | 9.4 | 11.2 | 20.5 | 50.9 | 433 | 630 | 167.4 |
| C403 | 9,412 | 5.40 | 214 | 976 | 910 | 1,035 | 3,135 | 4.0 | 18.1 | 16.9 | 19.2 | 58.1 | 434 | 556 | 181.8 |
| C403 | 10,387 | 2.13 | 324 | 427 | 582 | 493 | 1,826 | 15.2 | 20.0 | 27.3 | 23.1 | 85.7 | 441 | 700 | 197.7 |

Organic Metamorphism in the California Petroleum Basins

**APEX-1 WELLBORE**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Cuttings) | 16,337-16,641 | 1.93 | 1,135 | 559 | 424 | 238 | 2,385 | 58.8 | 29.0 | 22.0 | 12.3 | 122 | 438 | 116 | 176.2 |
| | 16,974 | 1.25 | 952 | 528 | 338 | 276 | 2,094 | 76.1 | 42.2 | 27.0 | 22.1 | 168 | 439 | 219 | 183.2 |
| (Cuttings) | 18,255-18,451 | 1.20 | 587 | 295 | 320 | 261 | 1,463 | 48.9 | 24.6 | 26.7 | 21.8 | 122 | 435 | 174 | 198.3 |
| | 19,510-19,513 | 1.02 | 580 | 240 | 129 | 141 | 1,090 | 56.9 | 23.5 | 12.6 | 13.8 | 107 | 469 | 87.0 | 210.9 |
| | 19,590-19,592 | 1.06 | 790 | 220 | 186 | 104 | 1,300 | 74.5 | 20.8 | 17.6 | 9.81 | 123 | 470 | 96.7 | 211.8 |
| | 19,970-19,973 | 0.87 | 630 | 239 | 225 | 91 | 1,185 | 72.4 | 27.5 | 25.9 | 10.5 | 136 | 454 | 95.4 | 216.0 |
| | 20,219-20,222 | 2.10 | 833 | 612 | 456 | 221 | 2,122 | 39.7 | 29.1 | 21.7 | 10.5 | 101 | 458 | 84.4 | 218.7 |
| | 20,660-20,750 | 1.28 | 688 | 223 | 289 | 172 | 1,372 | 53.8 | 17.4 | 22.6 | 13.4 | 107 | 446 | 50 | 223.0 |

**DOMINGUEZ FIELD**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Union Reyes-1 | 1,515 | 2.93 | 128 | 149 | 303 | 159 | 739 | 4.4 | 5.1 | 10.3 | 5.4 | 25.2 | 426 | 76.8 | 39.1 |
| Union Reyes-1 | 2,830-2,833 | 1.36 | 229 | 124 | 307 | 120 | 780 | 16.8 | 9.1 | 22.6 | 8.8 | 57.4 | 419 | 107 | 58.1 |
| Shell-Reyes-27A | 3,725 | 1.43 | 805 | 372 | 446 | 55 | 1,177 | 56.3 | 26.0 | 31.2 | 3.85 | 117 | 424 | 197 | 65.2 (62.6-67.7) |
| Shell-Reyes-27A | 4,013-4,024 | 1.50 | 154 | 85 | 171 | 17 | 427 | 10.3 | 5.7 | 11.4 | 1.1 | 28.5 | 426 | 90.7 | 65.7 |
| Shell-Reyes-97 | 7,805-7,809 | 3.41 | 361 | 397 | 557 | 175 | 1,490 | 10.6 | 11.6 | 16.3 | 5.1 | 43.7 | 426 | 207 | 105.9 |

**MISCELLANEOUS WELLS**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La Mirada 46-1 | 7,732-7,735 | 0.88 | 91 | 50 | 141 | 132 | 414 | 10.3 | 5.7 | 16.0 | 15.0 | 47.0 | 427 | 98 | 92.9 |
| La Mirada 46-1 | 11,992 | 3.04 | 280 | 710 | 1,065 | 735 | 2,790 | 9.2 | 23.4 | 35.0 | 24.2 | 91.8 | 426 | 406 | 137.2 |
| La Mirada 46-1 | 11,988 | 2.18 | 547 | 678 | 1,126 | 603 | 2,954 | 25.1 | 31.1 | 51.7 | 27.7 | 136 | 429 | 217 | 137.2 |
| LL&W-1 | 10,250-10,254 | 3.63 | 1,439 | 1,597 | 2,159 | 1,658 | 6,853 | 39.6 | 44.0 | 59.5 | 45.7 | 189 | 440 | 388 | 161.2 |
| LL&W-1 | 10,235-10,558 | 3.54 | 1,442 | 1,275 | 1,230 | 514 | 4,461 | 40.7 | 36.0 | 34.8 | 14.5 | 126 | 427 | 404 | 163.2 |
| McGrath-18 | 6,045-7,901 | 4.53 | 744 | 567 | 691 | 255 | 2,257 | 16.4 | 12.5 | 15.2 | 5.6 | 49.8 | 418 | 388 | 103.4 (95.0-111.7) |
| G.P. Santa Fe-243 | 8,504-8,524 | 1.98 | 450 | 345 | 433 | 142 | 1,370 | 22.7 | 17.4 | 21.9 | 7.2 | 69.2 | 432 | 277 | 114.3 |
| G.P. Santa Fe-243 | 9,485-9,502 | 1.43 | 495 | 330 | 382 | 225 | 1,420 | 34.6 | 23.1 | 26.7 | 15.7 | 99.3 | 429 | 262 | 124.9 |
| Del Amo-1 | 10,155-10,157 | 3.31 | 624 | 526 | 758 | 767 | 2,675 | 18.9 | 15.9 | 22.9 | 23.2 | 80.9 | 426 | 390 | 130.9 |
| Bryant Estate-1 | 11,443-11,452 | 4.54 | 1,046 | 1,171 | 1,094 | 1,132 | 4,444 | 23.0 | 25.8 | 24.1 | 24.9 | 97.9 | 435 | 467 | 151.0 |
| Bald. Hills Comm.-1 | 12,406 | 1.22 | 991 | 524 | 701 | 367 | 2,583 | 81.2 | 43.0 | 57.5 | 30.1 | 212 | 443 | 189 | 151.0 |
| Alamitos 48-A | 12,655-12,664 | 1.27 | 141 | 407 | 498 | 472 | 1,518 | 11.1 | 32.0 | 39.2 | 37.2 | 120 | 428 | 557 | 158.0 |
| L.B. Airport-1 | 12,747 | 1.74 | 580 | 667 | 581 | 415 | 2,243 | 33.3 | 38.3 | 33.4 | 23.9 | 129 | 450 | 87.4 | 158.9 |
| Houghton Comm.-1 | 12,875-12,890 | 1.38 | 486 | 431 | 338 | 194 | 1,449 | 35.2 | 31.2 | 24.5 | 14.1 | 105 | 430 | 192 | 172.2 |

**VENTURA BASIN**

Ventura Avenue Field

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Taylor 315 | 11,855 | 1.56 | 1,146 | 461 | 694 | 354 | 2,655 | 73.5 | 29.6 | 44.5 | 22.7 | 170 | 434 | 176 | 119.9 |
| Lloyd 185 | 12,705-12,715 | 4.03 | 432 | 643 | 1,135 | 444 | 2,654 | 10.7 | 16.0 | 28.2 | 11.0 | 65.9 | 420 | 652 | 127.0 |
| Lloyd 185 | 14,546-14,564 | 3.01 | 624 | 802 | 1,172 | 360 | 2,958 | 20.7 | 26.6 | 38.9 | 12.0 | 98.3 | 431 | 517 | 144.2 |
| Lloyd 185 | 14,990-15,074 | 3.12 | 1,065 | 665 | 689 | 225 | 2,644 | 34.1 | 21.3 | 22.1 | 7.21 | 84.7 | 426 | 441 | 146.6 |

**Table 1**—continued

**SANTA CLARA TROUGH**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Social Lim.-] | 5,074 | 0.88 | 215 | 249 | 302 | 477 | 1,243 | 24.4 | 28.3 | 34.3 | 54.2 | 141 | 423 | 112 | 57 |
| Sup. Lim.-1 | 9,989-10,005 | 1.35 | 145 | 85 | 183 | 85 | 448 | 10.7 | 6.3 | 13.6 | 2.6 | 33.2 | 430 | 128 | 98.1 |
| Sup. Lim.-1 | 13,080-13,098 | 1.26 | 432 | 240 | 340 | 96 | 1,108 | 34.9 | 19.0 | 27.0 | 7.6 | 87.9 | 442 | 232 | 113.9 |
| Sup. Lim.-1 | 14,526-14,537 | 2.41 | 492 | 358 | 479 | 92 | 1,428 | 20.4 | 14.8 | 19.9 | 3.8 | 59.2 | 434 | 293 | 124.2 |
| Sup. Lim.-1 | 16,626-16,635 | 1.70 | 258 | 154 | 306 | 94 | 812 | 15.2 | 9.1 | 18.0 | 4.9 | 47.8 | 435 | 200 | 139.1 |

**SOUTHERN SAN JOAQUIN VALLEY BASIN (PALOMA FIELD)**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ohio Oil A-1 | 4,574-4,583 | 2.10 | 153 | 67 | 224 | 41 | 485 | 7.3 | 3.2 | 10.7 | 2.0 | 23.1 | 4.33 | 399 | 64.1 |
| Ohio Oil A-1 | 5,554-5,557 | 0.09 | 99 | 42 | 82 | 1 | 224 | 110 | 46.7 | 91.1 | 1.1 | 249 | 427* | 467 | 73.0 |
| Ohio Oil A-1 | 6,750 | 0.19 | 76 | 36 | 90 | 8 | 210 | 40.0 | 18.9 | 47.4 | 4.2 | 111 | 443* | 47.4 | 84.0 |
| Ohio Oil A-1 | 7,424-7,446 | 0.32 | 77 | 30 | 84 | 5 | 196 | 24.1 | 9.4 | 26.3 | 1.6 | 61.3 | 438* | 53.1 | 90.3 |
| Shell 21-14 | 8,608 | 1.67 | 406 | 392 | 596 | 218 | 1,612 | 24.3 | 23.5 | 35.7 | 13.1 | 96.5 | 430 | 257 | 101.1 |
| Ohio Oil KCLA-8 | 10,824-10,830 | 1.90 | 292 | 299 | 359 | 117 | 997 | 15.4 | 15.7 | 18.9 | 6.2 | 52.5 | 437 | 212 | 121.5 |
| KCL-F-71-10 | 12,028 | 2.16 | 220 | 454 | 402 | 181 | 1,257 | 10.2 | 21.0 | 18.6 | 8.4 | 58.2 | 437 | 164 | 132.5 |
| KCL-F-71-10 | 12,480-12,486 | 4.03 | 366 | 969 | 843 | 553 | 2,731 | 9.1 | 24.0 | 20.9 | 13.7 | 67.8 | 437 | 452 | 136.7 |
| Ander. 56-35 | 13,037 | 4.64 | 1,440 | 1,383 | 1,607 | 514 | 4,944 | 31.0 | 29.8 | 34.6 | 11.1 | 107 | 437 | 590 | 141.8 |
| Ander. 56-35 | 13,905 | 2.26 | 3,167 | 1,990 | 2,585 | 765 | 8,507 | 140 | 88.1 | 114 | 33.8 | 376 | 440 | 222 | 149.7 |
| KCL-A 72-4 | 15,293-15,302 | 1.36 | 833 | 478 | 485 | 205 | 2,001 | 61.3 | 35.1 | 35.7 | 15.1 | 147 | 435 | 146 | 162.5 |
| KCL-A 72-4 | 17,160 | 2.97 | 1,157 | 539 | 559 | 364 | 2,619 | 39.0 | 18.1 | 18.8 | 12.3 | 88.2 | 448 | 94 | 179.6 |
| KCL-A 72-4 | 17,269-17,272 | 1.66 | 2,326 | 517 | 696 | 245 | 3,784 | 140 | 31.1 | 41.9 | 14.8 | 228 | 441 | 227 | 180 |
| KCL-A 72-4 | 18,286-18,297 | 1.22 | 1,394 | 389 | 390 | 83 | 2,256 | 114 | 31.9 | 32.0 | 6.8 | 185 | 445 | 112 | 190.0 |
| KCL-A 72-4 | 20,003 | 1.33 | 1,606 | 431 | 288 | 24 | 2,349 | 121 | 32.4 | 21.6 | 1.82 | 177 | 452 | 157 | 205.7 |
| KCL-A 72-4 | 20,922-20,925 | 1.14 | 925 | 387 | 372 | 100 | 1,734 | 81.1 | 29.6 | 32.6 | 8.8 | 152 | 452* | 95.6 | 214.2 |
| KCL-A 72-4 | 20,930 | 2.02 | 323 | 108 | 90 | 29 | 550 | 16.0 | 5.3 | 4.5 | 1.4 | 27.2 | 444 | 39.6 | 214.3 |
| KCL-A 72-4 | 20,933 | 2.21 | 1,480 | 343 | 238 | 75 | 2,136 | 66.9 | 15.5 | 10.8 | 3.41 | 96.6 | 445 | 35.3 | 214.3 |

**VENTURA BASIN**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Outcrop | 29.46 | 244 | 552 | 1,312 | 3,565 | 5,673 | 0.83 | 1.87 | 4.45 | 12.1 | 16.6 | 387 | 430 | 40-50? |

others (1999), which also showed intense HC generation beginning by 90° to 100°C for hydrogen-poor OM in the Los Angeles Basin. Part of the disagreement between the two studies is from Phillipi's (1965) incorrect assumption of uniform geothermal gradients throughout the Los Angeles Basin. Notwithstanding, the data of figure 1 illustrate that HC generation appears well underway by 120°C, with bitumen concentrations maximizing at about 155°C, and HC concentrations maximizing at about 165°C. Both curves then exhibit continuous decreases with increasing temperature to the highest temperatures examined (about 220°C).

Samples at 200°C and greater have low hydrogen indices, with the deepest sample at 219°C having a hydrogen index of only 50. Samples at 220°C are approaching burnout for hydrogen-poor OM, or a loss of all HC generation potential (Price, 1989). *This is not equivalent to $C_{15}$+ HC thermal destruction.*

It appears from figure 1 that mainstage-HC generation commences in Ventura Basin rocks with hydrogen-poor OM by 90° to 100°C. However, other considerations suggest that this is not the case. First, ROCK-EVAL analysis of a much larger sample base of Ventura Basin rocks (Price and others, 1999, figs. 7, 10, 11) demonstrates that mainstage-HC generation has not begun there by 140°C. Secondly, the high bitumen and HC coefficients for the Ventura Basin 176/1.56 sample at 120°C (fig. 1), and probably to some extent the moderate values of the Ventura Basin 232/1.36 sample at 114°C (fig. 1), are an unusual characteristic of some immature shales in all the southern California petroleum basins: abnormally high carbon-normalized concentrations of immature bitumen and HCS (discussed below). Thus, we do not interpret the elevated coefficients in these two samples as due to HC generation. Lastly, two deeper Ventura Basin samples (282/2.41 (124°C); and 200/1.70 (139°C); fig. 1) have lower coefficients than the trend of the curves, the 200/1.70 sample significantly so. These low values are attributed to mainstage-HC generation not having begun in these rocks.

### Loss of Generated HCS

The bitumen and HC concentration decreases at temperatures above 155° to 165°C, respectively in figure 1, are usually attributed to $C_{15}$+ HC thermal destruction (Tissot and Welte, 1984). However, data below demonstrate that this cannot be the case. We attribute these decreases to both HC expulsion and to loss of generated HCS to the drilling mud. These two controls may also result in some of the higher temperature (≥140° C) discordant sample points of figure 1.

The data point labeled "HC" at 172°C in figure 1 is core from the Houghton Community-1 wellbore. This, and other, samples of this study were submitted to both whole-rock extraction (Price and Clayton, 1992) and conventional powdered-rock extraction. Whole-rock extraction detects an oil phase fractionated from the whole-rock bitumen, which is poised for expulsion in cracks and parting laminae of the rock, when such bitumen is present. Unpublished research by L. C. Price, subsequent to the Price and Clayton (1992) study, demonstrates that this fractionation of bitumen to an oil-like phase depends largely on both organic richness and increasing maturity. Differences exist between the whole-rock and powdered-rock extracts for the
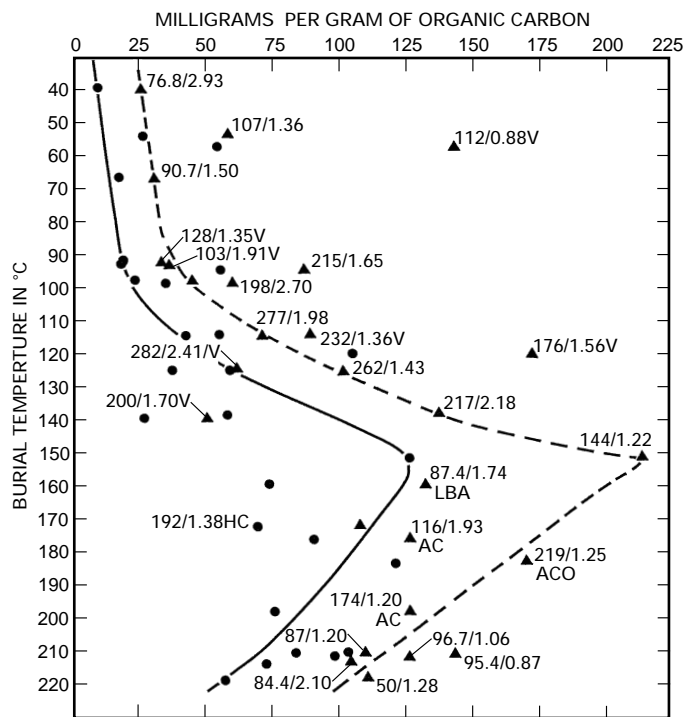


**Figure 1.** Plot of the HC coefficient (mg $C_{15}$+ saturated plus aromatic HCS/g OC; dots, solid line) and the bitumen coefficient (mg bitumen/g OC; triangles, dashed line) versus present-day burial temperature in °C for shales with hydrogen-poor OM from the Los Angeles and Ventura Basins. Thus, there are two data points for each sample. Ventura Basin samples are labeled by "V", all others are Los Angeles Basin. The left-hand number of each sample pair (eg. - 76.8/2.93) is the ROCK-EVAL hydrogen index (76.8); the right-hand number is the TOC (2.93). One unlabeled sample at 98°C (just below "103/1.91V") has values of 207/2.41. LBA is Long Beach Airport-1; HC is Houghton Community-1; AC is Apex-1 cuttings chips; and ACO is Apex-1 core.

Houghton sample (fig. 2). Note the reduced amounts of isoprenoid HCS (especially pristane and phytane) and the higher concentrations of n-paraffins in the whole-rock extract. Elevated percentages of saturated HCS (SATS) and reduced percentages of asphaltenes (ASP) and resins (NSO) are also present in the whole-rock extract compared to the powdered-rock extract (fig. 2).

Thus, whole-rock extraction demonstrates, as expected, that a more oil-like phase, compared to the extract from the powdered rock, has been fractionated from the Houghton-1 bitumen and exists in cracks and parting laminae ready for expulsion. Considering the sample's burial temperature (172°C), it is also probable that some expulsion of oil has already occurred from this rock, partially accounting for the abnormally low bitumen and HC coefficients of this sample (fig. 1).

However, these low values could also be from partial loss of this fractionated-oil phase to the drilling mud during the rock trip up the wellbore in drilling operations. This HC loss is discussed in Price and LeFever (1992) and Price (1994). During the rock trip uphole, HC gases cogenerated and present with the fractionated oil, expand in volume from the large pressure decreases from depth to surface. These gases explode into the drilling mud, blowing fractionated oil in the rock's cracks and parting laminae into the mud. This can result in the loss of sig-

nificant amounts of generated HCS to the drilling mud before mature source rocks ever arrive at the laboratory for analysis.

Features of the whole-rock chromatogram of figure 2 suggest that such a loss has occurred in this sample. Note the two dashed lines on the whole-rock chromatogram (fig. 2) connecting the $C_{12}$ to $C_{17}$ n-paraffins and the $C_{13}$ to $C_{18}$ isoprenoid HCS. Such regular decreases in concentration with decrease in carbon number result from leaching by solution mechanisms or from evaporation. Bell-shaped chromatograms, such as that of the whole-rock gas chromatogram of figure 2, also result from a gas-assisted loss of generated HCS to the drilling mud.

The HC loss to the drilling mud has been found to be larger from cuttings chips than from core because of the larger surface area of cuttings chips (L. C. Price, unpub. data). This observation is manifested in the data of figure 1.

Of the 27 samples of figure 1, all are core except two, which are picked cuttings chips (shales) from the 6,324.3 m (20,750 ft) Apex Central Core Hole-1, the deepest well in the Los Angeles Basin. These two cuttings-chip samples are labeled AC (Apex-1 chips) at 176° and 198°C (fig. 1). The 5 deepest samples of figure 1 are all core from the Apex well, and a sample at 183°C (labeled ACO) between the two cuttings-chips samples is also an Apex-1 core sample. The 183°C core sample was identical to the two contiguous cuttings chip samples (at 176° and 198° C, fig. 1), regarding OM facies and mineralogy, except that it was core. Note that the amount of extractable bitumen and HCS for the two Apex-1 cuttings-chip samples fall far off their respective curves, curves largely defined by Apex-1 core at depth in figure 1. This observation is attributed to a greater loss of generated HCS to the drilling mud from the cuttings chips versus core. Moreover, this loss strongly affects qualitative characteristics of the remaining HCS in the two Apex-1 cuttings-chips samples.

Saturated and aromatic HC gas chromatograms of the three samples under discussion (176°, 183°, and 198°C) are in figure 3, the chromatogram from the core being in the middle and those from the cuttings chips being on the top and bottom. Note the "rounded" bell-like shape of the peaks above the hump and the expanded humps in the four chromatograms from cuttings chips compared to the chromatograms from core. The saturated HCS from the core have higher concentrations of higher and lower molecular weight material compared to the cuttings chips, which have a post-escape "residue" concentrated over n-$C_{16}$ to n-$C_{21}$. As discussed the aromatic-HC gas chromatogram of the core is dominated by peaks of alkylated-benzenes, alkylated-naphthalenes, and alkylated-phenanthrenes and resembles a moderately mature oil. In contrast, these peaks are less pronounced in the aromatic-HC gas chromatograms from cuttings chips. The rounded bell-shaped gas chromatograms of figure 3 have been observed in other unrelated studies of this author and are believed to be characteristic of rocks with significant HC losses to drilling mud (Price and Le Fever, 1992). As discussed, the HC losses are due to a decrease of confining pressure as core and cuttings chips ascend the wellbore during drilling operations. Also note in figure 3 that the carbon-normalized saturated- and aromatic-HC concentrations of the two cuttings-chip samples are significantly lower than that of the core: 32.7 and 45.8 percent less saturated HCS and 31.0 and 41.4 percent less aromatic HCS for the 198° and 176°C (18,255-18,451 ft and 16,337-

16,641 ft) samples, respectively, compared to the equivalent values from the core sample. Data from Price and others (1999) demonstrate that the OM over this burial interval in the Apex-1 was all the same. Thus, these differences in amounts of saturated HCS are not due to facies variations.

## Variable OM Hydrogen Richness

In figure 1, samples shallower than 94°C generally have lower hydrogen indices (76.8-128) compared to deeper samples between 95° and 200°C (hydrogen indices = 116-282, with one exception at 159°C, "LBA", hydrogen index = 87.4). This distribution of hydrogen indices is in part due to an increase in silts and sands, and a decrease in kerogen hydrogen richness, with decrease in depth (and rock age) in the Los Angeles and Ventura Basins (Price and others, 1999), partly because these basins "sanded-up" in the late Pliocene and Pleistocene. Thus, shallower sediments were deposited in more oxygen-rich settings, had more terrestrial OM deposited with them, and their OM was more strongly diluted with mineral matter, all compared to deeper sediments. The increase in hydrogen indices with increase in depth is also partly due to increasing kerogen hydrogenation by water with increasing depth (Price and others, 1999).

The "LBA" (Long Beach Airport-1) sample at 159°C in figure 1 with a hydrogen index of 87.4 and 1.74 percent TOC has discordant (low) HC and bitumen coefficients. A hydrogen index of 87.4 is tending towards type IV OM (inertinite). This explains the low HC and bitumen coefficients, because per unit weight, type IV OM has less capacity for HC generation than types III or III/II OM. Thus, another reason for the scatter in bell-shaped HC generation curves (fig. 1) can be variable original kerogen hydrogen richness, even within rocks of seemingly uniform OM.

## HC-Rich Immature Shales

In figure 1, four samples at burial temperatures <120°C have unexpectedly high HC and bitumen coefficients (107/1.36 (53°C), 112/0.88V (57°C), 215/1.65 (94°C), 176/1.56V (120°C)). In fact, two of these samples have values characteristic of the deeper zone of mainstage-HC generation. These four samples, and probably to a lesser extent several other samples of figure 1, typify an observation applicable to fine- (and coarse-) grained rocks of the southern California petroleum basins: abnormally high bitumen concentrations can exist in these rocks at immature ranks. This observation was also made by both Katz and Royale (1993) and Katz and Elrod (1983) for offshore southern California sediments. As discussed in Price and others (1999), ROCK-EVAL analyses of coarse-grained rocks in these basins often demonstrated significant staining, an observation supported by Soxhlet extractions of several of the stained rocks (not discussed here). It appears that many (most?) porous rocks in and around southern California oil fields have moderate to significant levels of oil staining. Innumerable petroleum-geochemical analyses of coarse-grained rocks from California petroleum basins by UNOCAL support this observation (Bruce Bromley, UNOCAL, oral commun., 7/94). Such staining in
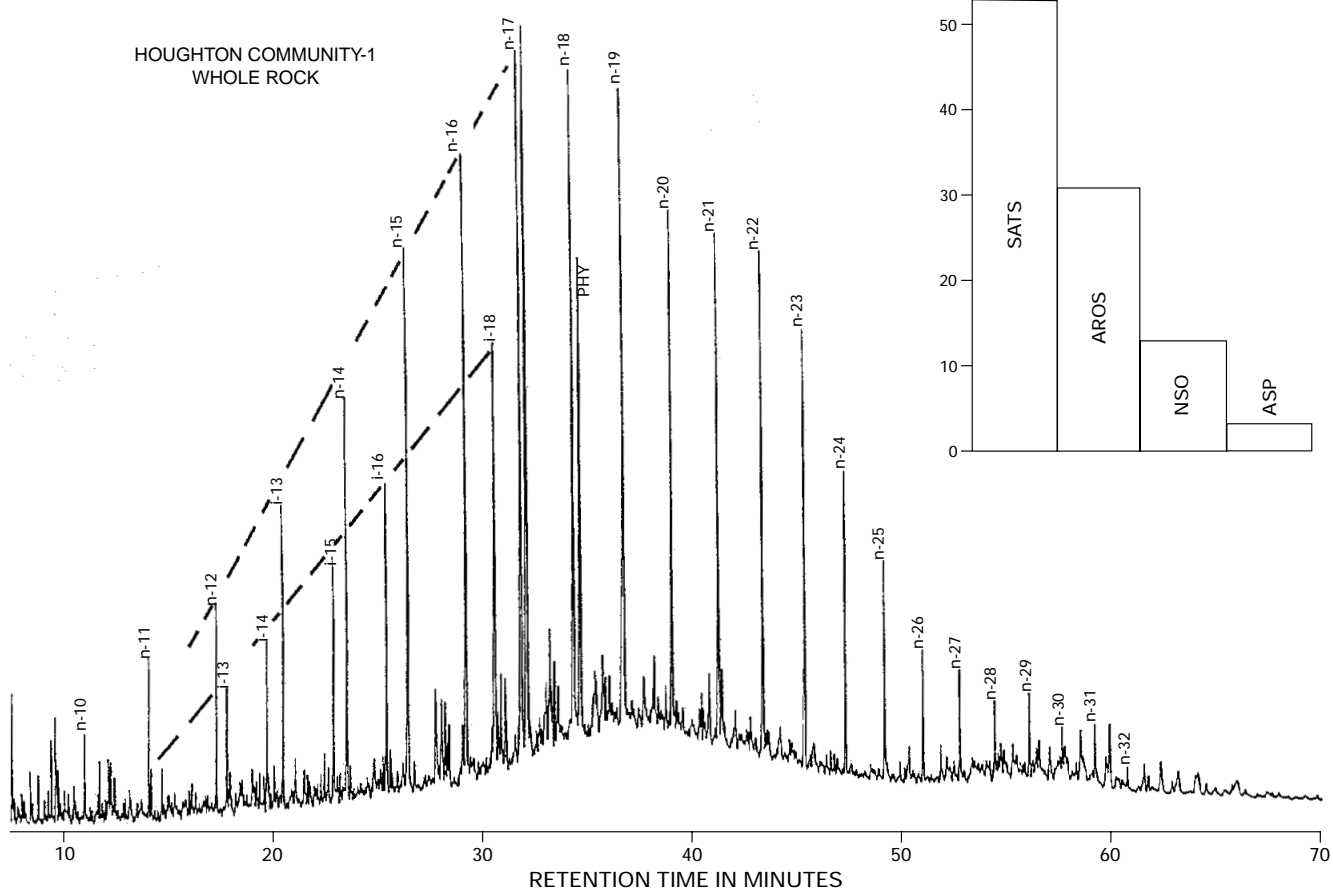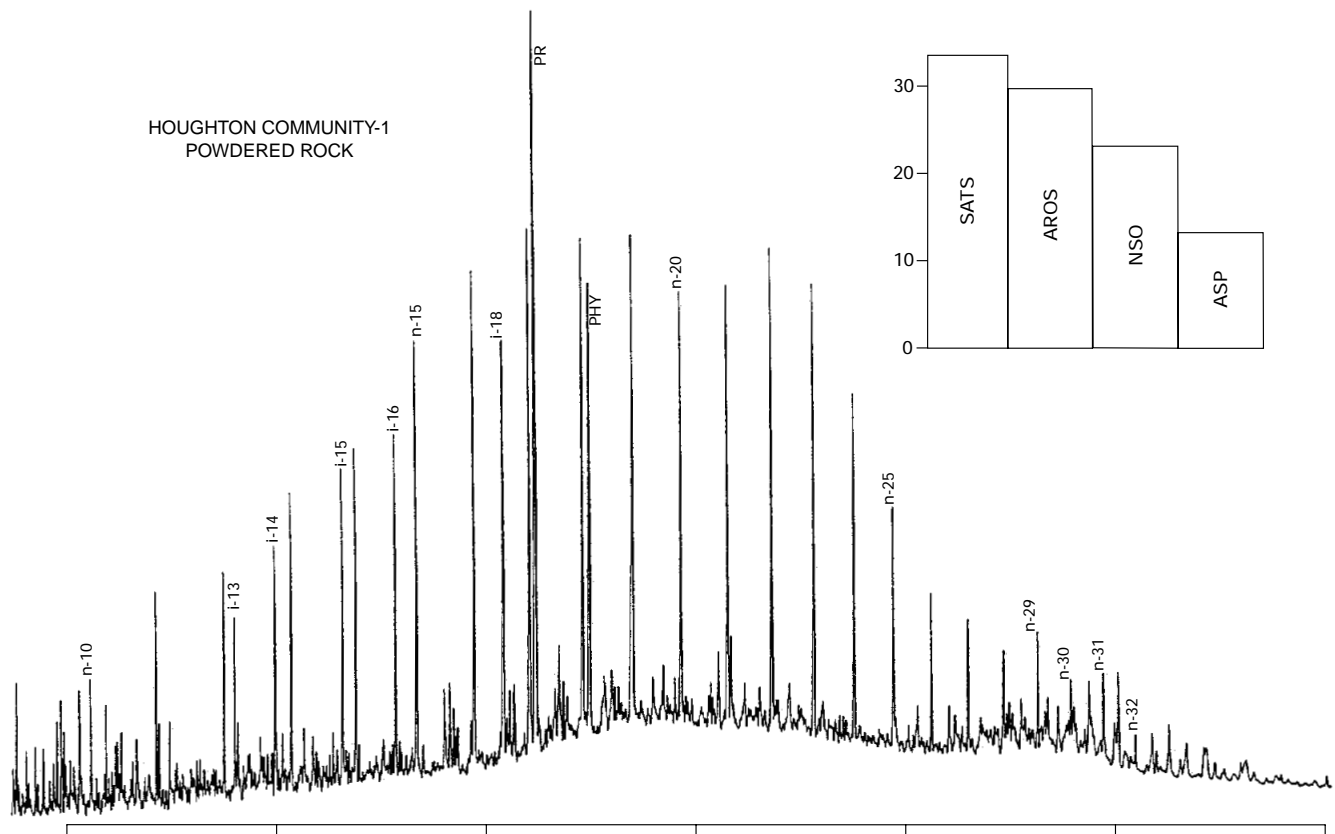
HOUGHTON COMMUNITY-1
POWDERED ROCK

HOUGHTON COMMUNITY-1
WHOLE ROCK

RETENTION TIME IN MINUTES

**Figure 2 (previous).** Saturated-HC gas chromatograms from solvent extractions of whole and powdered rock of the Houghton Community-1, 12,875-12,890 ft sample. The n-paraffins are designated by n- and their respective carbon numbers, isoprenoid HCS by i- and their respective carbon numbers, PR is pristane and PHY is phytane. Dashed lines connect the tops of the n-paraffin and isoprenoid HC peaks. Use the whole-rock chromatogram as an index for the powdered-rock chromatogram. Histograms show the normalized percentages of $C_{13+}$ saturated (SATS) and aromatic (AROS) HCS, resins (NSO), and asphaltenes (ASP) for both extracts.

these coarse-grained rocks would originate from migrating oil, either derived from shales adjacent to the sands or from more deeply buried shales.

The origin of occasional high bitumen and HC concentrations in immature fine-grained rocks with all OM types in the California basins is more problematical. Many causes are possible; however, we envision only three likely explanations: (1) abnormally large amounts of either HCS or HC precursors in kerogen with weak bonds, originally deposited with the shales; (2) migrating oil, from deeper more mature rocks, moving into shallower fine-grained rocks; and (3) HC cap-rock leakage from oil-fields with gas-assisted vertical migration through microfracture networks over the fields. Each explanation has flaws. Conversely, qualitative evidence within the saturated and aromatic HCS of the "stained" samples suggests each mechanism operable, while concurrently demonstrating that no mechanism operates universally. In figure 4, saturated- and aromatic-HC gas chromatograms are shown for five immature shales, four of which are "stained", as delineated by abnormally high saturated-HC coefficients determined by Soxhlet extraction. The top saturated-HC chromatogram (fig. 4, Reyes-1) is representative of immature "unstained" samples for all OM types: (1) low concentrations of $C_{14}$- and $C_{22+}$ n-paraffins; (2) high pristane/n-$C_{17}$ and phytane/n-$C_{18}$ (and other i-C/n-C) ratios; (3) most of the saturated HCS composed of n-$C_{14}$ to n-$C_{20}$ molecular weight material; and (4) prominent biomarker peaks, compared to adjacent n-paraffins. Blowups of the biomarker region are in the upper right of each saturated-HC chromatogram.

The Reyes-147 and Taylor-315 (second and fourth) chromatograms (fig. 4) both have elevated concentrations of saturated and aromatic HCS, and thus by quantitative considerations would appear to be "stained". However, the saturated-, and aromatic-HC gas chromatograms of both these samples are typical of immature "unstained" samples of all OM types, and thus also serve as representative examples of chromatograms from immature samples. For example, within the aromatic HCS for these two samples: (1) there is a pronounced $C_{15+}$ hump; and (2) there are large, but not dominate, peaks of methyl-, dimethyl-, and trimethyl- naphthalenes, and methyl- and dimethyl- phenanthrenes. Note in contrast that the $C_{15+}$ hump in the Reyes-1 aromatic HCS (first right-hand chromatogram) is suppressed by uncharacteristically high concentrations of alkylated benzenes. High concentrations of HCS and bitumen with immature characteristics in immature rocks, such as the Reyes-147 and Taylor-315 examples, account for most examples of "stained" samples of fine-grained rocks in this study. As discussed below, these cases are attributed to generation occurring over low temperatures (40° to 90°C), from HC and bitumen precursors in kerogen with very weak bonds.

The WC533 shale (bottom chromatograms, fig. 4) has low saturated- and aromatic- HC concentrations, and by quantitative considerations would be considered unstained. However, the saturated HCS from this sample have very mature characteristics for their burial temperature (73.5°C): (1) elevated n-C/i-C ratios, (2) elevated concentrations of $C_{14}$- and $C_{19+}$ material, and (3) high n-paraffin peaks compared to adjacent biomarkers. Within the aromatic HCS: (1) there is a reduced hump, (2) significant $C_{15}$- material, and (3) much of the sample is composed of alkylated benzenes and naphthalenes. The relatively elevated amounts of $C_{15}$- HCS in this sample preclude either surface staining of the core by oil during drilling or co-deposition of the HCS with the shale, because loss or evaporation of the $C_{15}$- HCS would occur in both cases. Instead, these low carbon-normalized concentrations of mature HCS appear to have been "implanted" in the shale after burial. A gas-assisted vertical migration of oil (gas solution) from a more deeply buried reservoir could account for the low concentrations of mature HCS in the WC533 sample. Microseepage of thermogenic HC-gas occurs at all surface localities in petroleum-bearing basins, including sites laterally removed from production (Price, 1986, 1993a). Moreover, Leith and others (1993) demonstrated a gas-assisted vertical migration of oil into microfractured shales for as much as 400 m above the Snorre field in the North Sea and discussed other such cases documented by workers in other areas. Similar vertical HC movement through caprocks above oil fields would be expected, and is documented, in the structurally intense southern California basins, and thus also helps to explain the scatter in the figure 1 data, including the scatter in the bell-shaped HC generation curve.

The WD107 shale sample has high concentrations of biodegraded saturated (and aromatic) HCS (third chromatograms, fig. 4). Biodegradation requires an open-fluid system for both nutrient and oxygen influx to the microbes and for waste-product removal. This is not possible in a shale. Perhaps the WD-107 HCS were co-deposited with the shale, from macroseeping oil being degraded at the depositional interface. However, the WD-107 biodegraded HCS could have also have originated from a gas-assisted vertical migration, from a deeper biodegraded oil reservoir, through microfractured caprocks.

Curiale and others (1985) also reported biodegraded HCS extracted from two samples of Antelope shale from the Miocene Monterey Formation in the Midway-Sunset oilfield, San Joaquin Valley Basin. They tentatively concluded that the biodegradation occurred either in the water column before deposition or at the sediment-water interface after deposition. They did not believe that these biodegraded HCS were emplaced by oil staining because these samples had some of lowest extractable organic-matter contents of their entire sample set, and they (logically) concluded that oil-staining should result in high bitumen coefficients. However, the bitumen coefficients of their two samples were, in point of fact, moderately high (117.9 and 141.5 mg/g OC), especially for their shallow burial depths (675.4 and 932.0 m, respectively). Moreover, the WC533 sample (last chromatograms, fig. 4) must be oil-stained, yet it has very low saturated- and aromatic-HC coefficients (8 and 3 mg/g OC, respectively). Thus, staining does not necessarily appear to result in high HC concentrations. Because the highly structured Midway-Sunset field would be prone to vertical HC leakage
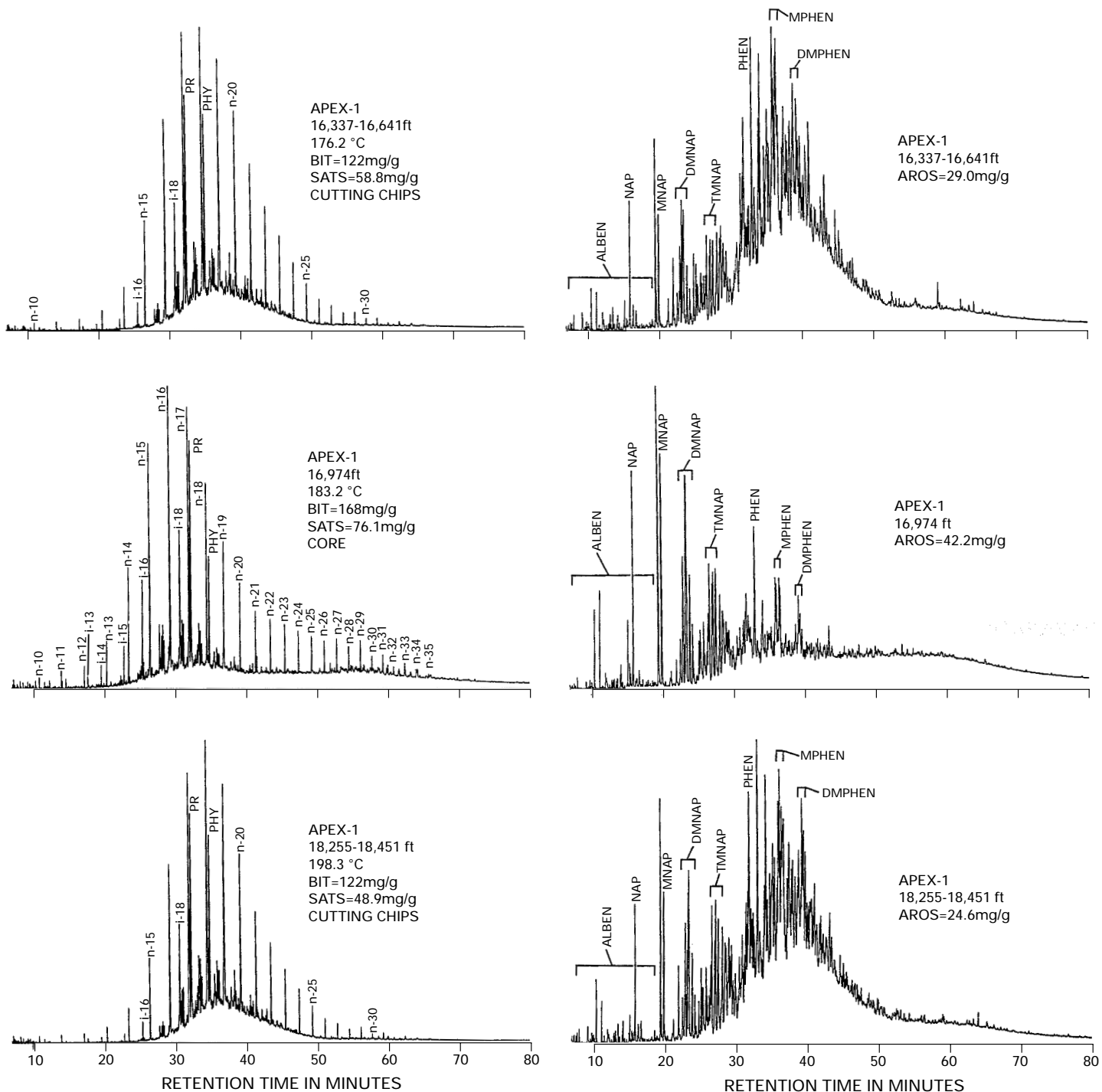
**Samples and Methods** 9

**Figure 3.** Saturated and aromatic HC gas chromatograms for two cuttings-chip samples (16,337-16,641 ft and 18,255-18,451 ft) and one core sample (16,974 ft) from the Apex-1 wellbore. In the saturated-HC chromatograms, n-paraffins are designated by n- and their respective carbon number, iso-prenoid HCS by i- and their respective carbon number, PR is pristane, and PHY is phytane. Use the 16,974 ft chromatogram as an index for unlabeled peaks in the other saturated-HC chromatograms. Sample depth is in feet, burial temperature is in °C, bitumen coefficients, or the milligrams of bitumen per gram of organic carbon (BIT = "x" mg/g), and saturated-HC coefficients (SATS = "y" mg/g) are given for each saturated-HC chromatogram. In the aromatic HC chromatograms: ALBEN are alkylated benzenes; NAP is naphthalene; MNAP, DMNAP, and TMNAP are the methyl-, dimethyl-, and trimethyl-naphthalenes; PHEN is phenanthrene, and MPHEN and DMPHEN are the methyl- and dimethyl-phenanthrenes. Aromatic HC coefficients (AROS = "x" mg/g) and sample depths (in feet) are given for each aromatic HC chromatogram.
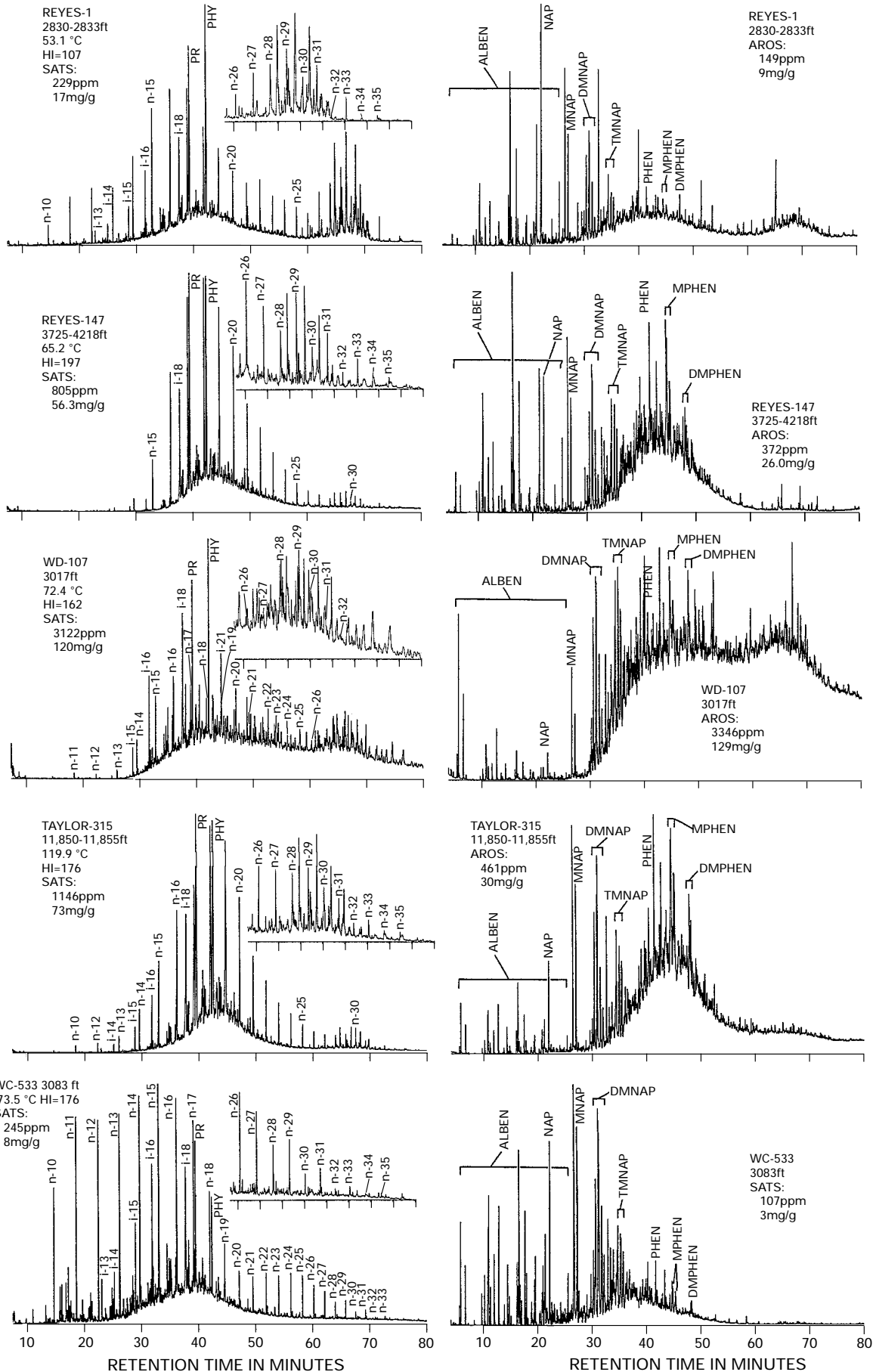
REYES-1
2830-2833ft
53.1 °C
HI=107
SATS:
  229ppm
  17mg/g

REYES-1
2830-2833ft
AROS:
  149ppm
  9mg/g

REYES-147
3725-4218ft
65.2 °C
HI=197
SATS:
  805ppm
  56.3mg/g

REYES-147
3725-4218ft
AROS:
  372ppm
  26.0mg/g

WD-107
3017ft
72.4 °C
HI=162
SATS:
  3122ppm
  120mg/g

WD-107
3017ft
AROS:
  3346ppm
  129mg/g

TAYLOR-315
11,850-11,855ft
119.9 °C
HI=176
SATS:
  1146ppm
  73mg/g

TAYLOR-315
11,850-11,855ft
AROS:
  461ppm
  30mg/g

WC-533 3083 ft
73.5 °C HI=176
SATS:
  245ppm
  8mg/g

WC-533
3083ft
SATS:
  107ppm
  3mg/g

RETENTION TIME IN MINUTES

RETENTION TIME IN MINUTES

**Figure 4 (previous).** Saturated and aromatic HC gas chromatograms from five immature shales. In the saturated HCS, n-paraffins are designated by n- and their respective carbon numbers, isoprenoid HCS by i- and their respective carbon numbers, PR is pristane, and PHY is phytane. Use the WC-533 3,083 ft saturated HC chromatogram as an index for unlabeled peaks in the other chromatograms. Sample depth (in feet), burial temperature (in °C), the ROCK-EVAL hydrogen index (HI), and saturated-HC concentrations in ppm (by rock weight) and as normalized to TOC (mg/g) are given for each saturated HC chromatogram. An expanded chromatogram of the biomarker region ($n$-$C_{26}$ to $n$-$C_{36}$) is also provided wherein the n-paraffins are labeled by their respective carbon numbers. In the aromatic-HC chromatograms, ALBEN are alkylated benzenes; NAP is naphthalene; MNAP, DMNAP, and TMNAP are the methyl-, dimethyl-, and trimethyl-naphthalenes; PHEN is phenanthrene; and MPHEN and DMPHEN are the methyl-, dimethyl-phenanthrenes. Aromatic-HC concentrations are also given in ppm (by rock weight) and as normalized to TOC (mg/g).

through its fractured anticlinal crest, the two biodegraded samples Curiale and others (1985) reported on could be due to oil staining.

Examples of immature fine-grained rocks with unusually high HC concentrations are common in the southern California basins. These HCS have multiple origins and help to obfuscate interpretation of quantitative and qualitative characteristics arising from HC generation, such as the data of figure 1.

### Bitumen Compositions

Normalized bitumen percentages are plotted in figure 5 for the samples of figure 1 along with TOC-normalized extractable HCS (left-hand number) and the ROCK-EVAL hydrogen index (right-hand number). Over no temperature range in figure 5, is there a correlation between maxima or minima in the compound classes with either the HC coefficient or the hydrogen index. To wit, a relatively high percentage of saturated HCS does not consistently correlate with relatively high (or low) hydrogen indices or HC coefficients. However, there is a trend, with scatter, of a progressive increase in the percentage of saturated HCS of the total bitumen versus a continuous decrease in the resins, with increasing burial temperature. In contrast, aromatic HCS, and to a lesser extent, asphaltenes, remain relatively constant versus temperature. The 90° to 180°C range covers most of the mainstage HC generation zone (fig. 1). Over these temperatures in figure 5, all compound classes remain somewhat constant, with one exception near 140°C ("56/217"). Thus, it appears that in the case of hydrogen-poor OM, the HCS and resins plus asphaltenes are being cogenerated with each other, unlike the case with hydrogen-rich OM, wherein resins and asphaltenes are generated first and later thermally decompose to HCS (Lewan, 1991; Price and Wenger, 1992). In other words, reaction pathways may be different between these different OM types.

### Saturated-HC Gas Chromatograms

Qualitative changes in the saturated HCS from HC generation in hydrogen-poor OM are evident in figures 4 and 6. The Reyes-1, Reyes-147, and Taylor-315 saturated-HC chro-
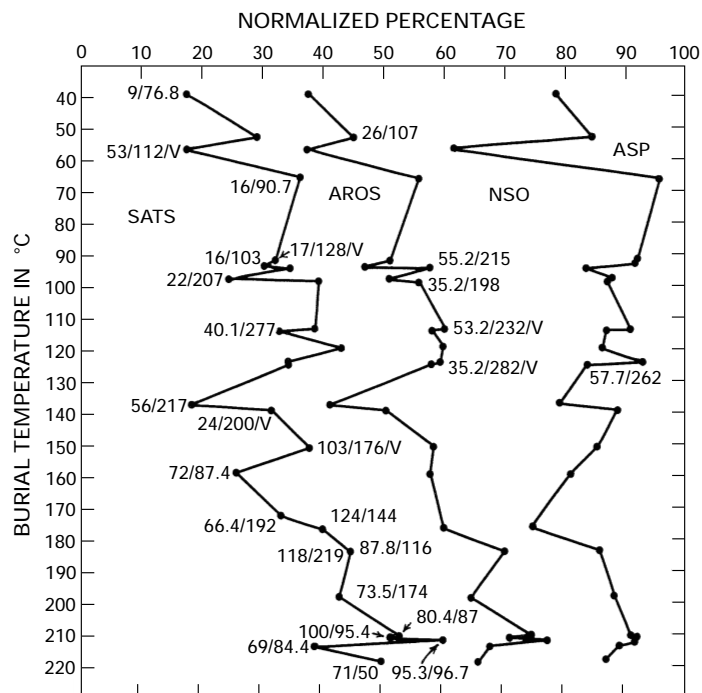


**Figure 5.** Normalized percentages, versus burial temperature, of saturated (SATS) and aromatic (AROS) HCS, resins (NSO), and asphaltenes (ASP) in bitumen from rocks with hydrogen-poor OM from the Los Angeles-Ventura Basins. The left-hand number of each sample is the HC coefficient (mg saturated plus aromatic HCS/g TOC) and the ROCK-EVAL hydrogen index is the right-hand number. Ventura Basin samples are marked by "V".

matograms of figure 4 (first, second, and fourth chromatograms, left side), and the La Mirada 46-1 chromatogram of figure 6 (upper left chromatogram), represent examples from immature samples. These chromatograms (1) are principally concentrated over the 16 to 22 carbon number range; (2) have a pronounced naphthenic hump; (3) have low, but variable, concentrations of $C_{15}$- and $C_{23+}$ n-paraffins; (4) have moderate to prominent biomarker peaks; and (5) have moderate isoprenoid HC to n-paraffin (i-C to n-C) ratios. The first and second characteristics are distinguishing. In contrast, early stages of HC generation (refer to Sup. Lim .-1 13,080 ft and La Mirada 46-1 11,988 ft; second and third left chromatograms respectively; fig. 6) are generally characterized by (1) moderate to significant increases in the relative concentrations of $C_{15}$- and $C_{21+}$ compounds; moderation of the naphthenic hump; (3) pronounced biomarker peaks with relatively small adjacent n-paraffins; and (4) higher i-C to n-C ratios, relative to more immature samples. The increased relative concentrations of $C_{15}$- compounds demonstrates that the hydrogen-poor OM of these basins generates these compounds, an important point of discussion below.

Samples in the middle of mainstage HC generation and beyond, as expected, demonstrate increased maturity. For example, the Baldwin Hills-1 12,406 ft chromatogram (upper right chromatogram, fig. 6) has a smoother $C_{17+}$ n-paraffin profile, greatly reduced biomarker peaks, and lower i-C/n-C ratios, all relative to more immature samples. However, saturated HCS from rocks with hydrogen-poor OM at this, and higher, ranks invariably have low or reduced concentrations of $C_{14}$- HCS and

smoothly decreasing n-paraffin profiles with decreasing carbon numbers (dashed lines in the Baldwin Hills-1 and Apex-1 16,974 ft and Apex-1 20,219 ft (three right-hand chromatograms, fig. 6). As discussed below, this feature is not from either analytical procedures or HC loss during core storage. Instead we attribute the feature to a preferential loss of $C_{14}$- saturated HCS either to expulsion or to the drilling mud.

The maturity of the Apex-1 16,974 ft chromatogram is advanced relative to the Baldwin Hills-1 chromatogram, as is that of the Apex-1 20,219 ft chromatogram relative to the Apex-1 16,974 ft chromatogram (three right-hand chromatograms, fig. 6): smoother n-paraffin profiles; greatly reduced biomarker peaks; lower i-C/n-C ratios, and so forth. However, the Apex-1 16,974 ft sample also has reduced concentrations of both $C_{14}$- peaks (dashed line) and $C_{19}+$ n-paraffins relative to the Apex-1 20,219 ft sample, features also attributed to a significant loss of these compounds either to expulsion or to the drilling mud. The $C_{15}+$ portion of the 20,219 ft chromatogram has the mature characteristics expected for its 213.9° C burial temperature. However, this sample has also lost significant amounts of $C_{15}$- HCS (dashed line).

## Southern San Joaquin Valley

### Introduction

Selected shales from the Paloma field in the central syncline of the Southern San Joaquin Valley were chosen for Soxhlet extraction to confirm the ROCK-EVAL analyses for this area (Price and others, 1999), and for comparison with the extractable OM from rocks with hydrogen-poor OM from the Los Angeles-Ventura Basins. The extensively cored 21,306 ft (6,493.8m) Ohio Oil KCL "A" 72-4 wellbore (Paloma Field) has a well defined HC generation profile (Price and others, 1999, figs. 12, 13). One sample (257/1.67, 101°C, fig. 7) is from the Canal field about 12.9 km (8 mi) north of the Paloma field and was used to fill in a temperature gap in the Paloma field samples.

### HC Generation

In figure 7, the solid line and dots are the HC coefficient (mg HCS/g OC), and the long-dashed line and triangles are the bitumen coefficient (mg bitumen/g OC) for shales from the Paloma field. Hydrogen indices (left number) and TOC contents (right number) are given for each sample. Between burial temperatures of 70° to 90°C, most of the shales had low TOC contents with very hydrogen-depleted OM (Price and others, 1999, fig. 12). This prevented determination of pre-generation $C_{15}+$ bitumen and HC baseline concentrations in figure 7. Thus, the short-dashed lines in the 70° to 120°C portion of both curves are interpretations accommodating the extraction data from the low TOC rocks of this interval. Based on the ROCK-EVAL data for this area (Price and others, 1999; their figs. 12, 13), the solid and long-dashed lines are believed to best represent trends which would be in rocks with TOC contents of 1-3 percent (if such rocks were present): gradually increasing HC and bitumen concentrations from low-level HC generation occurring before mainstage HC generation. A shallow (70-120°C) zone of intense HC generation, as portrayed by the short-dashed lines, is not a preferred explanation. Rather, we attribute the elevated HC and bitumen coefficients over this interval to the low TOC values of two of the samples (0.19 and 0.32 percent) and to elevated amounts of indigenous (pre-generation) HCS and bitumen in the 2.57/1.67 sample, which, as noted, is from the Canal field, north of the Paloma field.

Mainstage HC generation is interpreted to begin at 135°C in figure 7 (in the middle of the Antelope shale of the Miocene Monterey Formation) and to maximize by 180°C. These are lower temperatures for these events than those of the much larger ROCK-EVAL data base for this area (150° and 203°C, respectively, figs. 12 and 13 in Price and others, 1999). By comparison, Kruge (1983), from both analyses of Monterey rocks at the Lost Hills oilfield and time-temperature modeling, concluded that intense HC generation would only begin at 140°C in the Southern San Joaquin Valley Basin, an estimate in agreement with the analyses of this study. The temperatures at Paloma for beginning mainstage HC generation (135°C) and maximum of generation (180°C) are significantly higher than for the same two events in the Los Angeles Basin rocks with hydrogen-poor OM (90° to 95° C and 150° to 160°C, respectively, fig. 1). This divergence is attributed to the hypothesis of Price and others (1999) that the Los Angeles Basin has cooled significantly in the recent geologic past. Thus, HC generation there actually took place at higher burial temperatures than present-day values.

### Non-Generation Controls

Parameters besides HC generation have significant control over quantitative and qualitative aspects of the bitumen from shales of the Paloma field. For example, the apparent shallow trends in the bitumen and HC coefficients (short-dashed lines, fig. 7) are inferred as due to very low TOC values in two samples and to abnormally high contents of immature indigenous bitumen in one sample. As another example in figure 7, one sample (590/2.26 at 150°C) has values far greater than the trends of the curves and two samples (94/2.97, 180°C; and 39.6/2.02, 214°C) have values far less than the curves. The 590/2.26 sample has a bitumen coefficient of 376, which plots off scale. As discussed below, the saturated- (and aromatic-) HC gas chromatograms of this sample (Anderson 56-35, 13,905 ft) have immature characteristics. Thus the high HC concentrations in this rock are not from oil staining. Instead, the very large bitumen (376) and HC coefficients (228) of this sample are another example of the high contents of indigenous bitumen possible at pre-HC-generation ranks in rocks in the California petroleum basins. Moreover, the hydrogen index decreased from 590 to 223 when this sample was Soxhlet extracted, demonstrating that the rock contains type III, and not type II, OM.

Comparison of the two samples with low HC and bitumen coefficients (94/2.97, 180°C; and 39.6/2.02, 213°C) in figure 7 with samples at equivalent temperatures and on the curves (227/1.66, 180°C; and 95.6/1.14, 214°C; respectively), yields insights into the reasons for these low values. Saturated- and aromatic-HC gas chromatograms are given in figure 8 for the four samples under discussion. The saturated-HC chromatograms for the
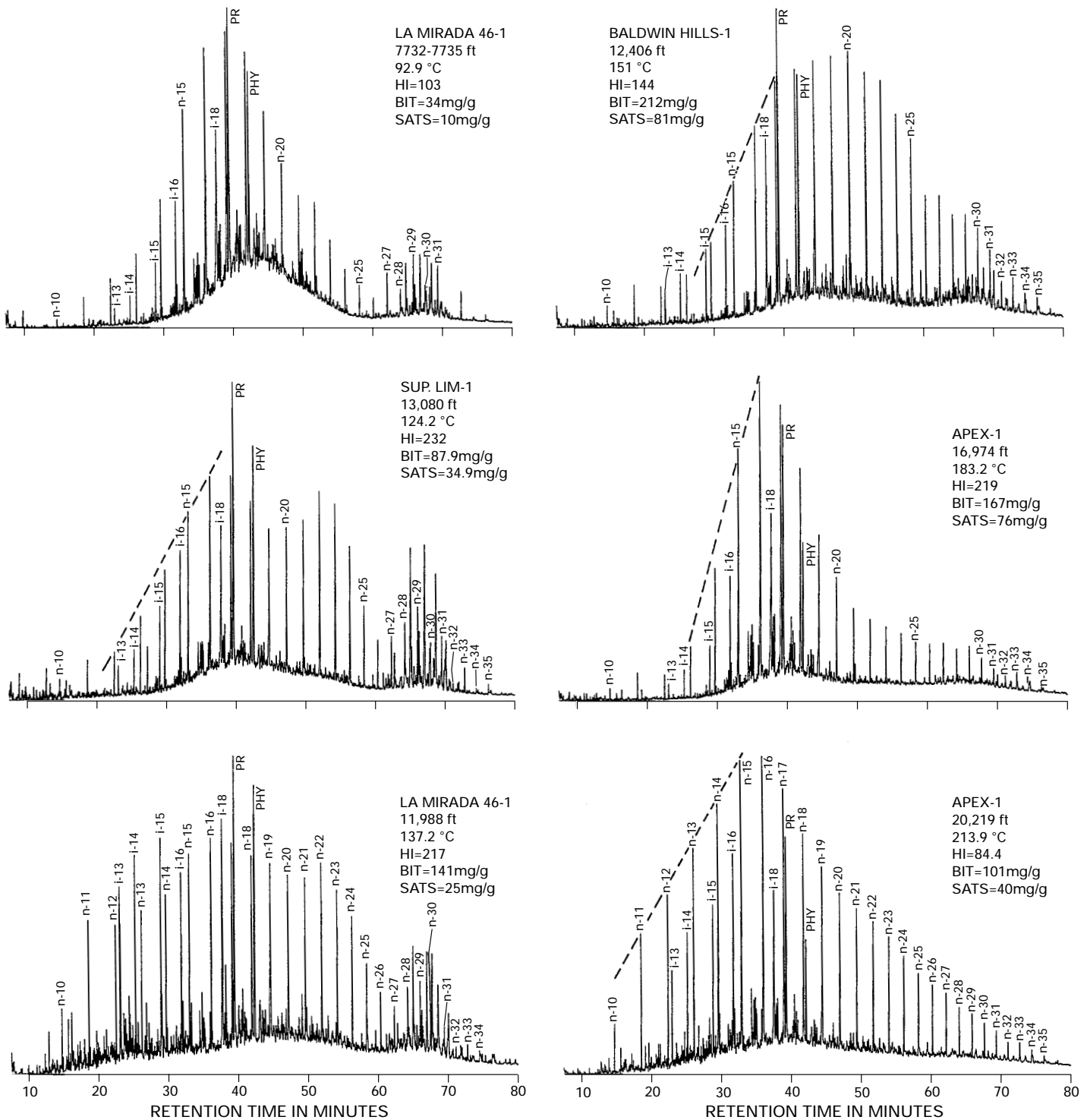
**Figure 6.** Saturated-HC gas chromatograms from Los Angeles-Ventura Basin samples, demonstrating qualitative (maturity) changes from HC generation in hydrogen-poor OM. See figure captions 2-4 for explanation of labeling on chromatograms.

KLC "A" 72-4 samples at 179.6° (17,160 ft, "94/2.97") and 180.6°C (17,269-17,272 ft) samples are similar (two top left chromatograms, fig. 8). Those of the aromatic HCS are less similar (top two right chromatograms, fig. 8), partly because higher methyl-naphthalene concentrations suppress the 179.6°C (17,160 ft) sample's aromatic hump. The lower methyl-naph-thalene concentration in the 180.6°C sample is from a moder-ately greater loss of lighter HCS in this sample compared to the

179.6°C sample. This loss is also manifested by the greater slope of the dashed line in the $C_{15-}$ portion of the saturated HC-chromatogram of the 180.6°C sample compared to the 179.6°C sample (upper two left chromatograms, fig. 8). Otherwise, these two saturated-HC chromatograms are almost identical.

ROCK-EVAL analysis of these samples after Soxhlet extraction revealed approximately equivalent hydrogen indices (82 for the 179.6°C sample, and 127 for the 180.6°C sample).

**Figure 7.** Plot of the HC coefficient (dots, solid line) and bitumen coefficient (triangles, long-dashed line) versus burial temperature in ° C and depth in kilometers for shales from the Paloma Field, Southern San Joaquin Valley Basin. Thus, there are two data points for each sample. Left-hand number for each sample is the ROCK-EVAL hydrogen index, right-hand number is the TOC. See figure 1 caption for further explanation. The "590/2.26" sample (at about 140°C) has an offscale bitumen coefficient of 376.

The originally higher hydrogen index (227) of the 180.6°C sample was from resins and asphaltenes, in the abundant bitumen of this sample (228 mg/g OC), contributing to the $S_2$ peak (Clementz, 1979). Thus, these two shales were originally of equivalent organic richness and the much higher bitumen and HC contents in the 180.6°C sample can not be from more hydrogen-rich OM. Nor can loss of generated HCS to the drilling mud explain the difference, because the 180.6°C sample, with higher bitumen and HC concentrations, has actually had the greater loss to the drilling mud, as demonstrated by the dashed slanted lines (top two left chromatgrams, fig. 8). Thus more efficient HC expulsion from the 179.6°C sample is the only apparent remaining explanation for the lower HC concentrations in that sample.

The chromatograms from the 214.2°C (20,922-20,925 ft) and 214.3°C (20,930 ft) samples are strikingly different from each other (bottom four chromatograms, fig. 8). The 214.3°C saturated and aromatic HCS have the mature characteristics expected for this sample's burial temperature. However, the 214.2°C saturated HCS have very immature characteristics: (1) high pristane/n-$C_{17}$, phytane/n-$C_{18}$, and other i-C/n-C ratios; (2) a pronounced naphthenic hump; and (3) being largely composed of $C_{16}$-$C_{23}$ material. The 214.2°C aromatic-HC chromatogram also appears quite immature compared to that of the 214.3°C sample. Neither the qualitative nor quantitative differences of these two samples are related to original richness of their OM, because ROCK-EVAL analysis of the two Soxhlet-extracted shales revealed that they had equivalent hydrogen indices, 30.6 for the 214.2°C sample and 23.5 for the 214.3°C sample. The higher original hydrogen index of the 214.2°C sample (95.6 unextracted versus 30.6 extracted) is again due to resins and

asphaltenes contributing to the $S_2$ peak (Clementz, 1979). Thus, the OM in the two samples is equivalent.

The 214.2°C core had obvious visual fractures and slickenslides. It is possible that this rock, when buried, was along an oil-migration path and that significant amounts of nonindigenous oil were stored in the cracks of this rock. This would account for the high saturated-HC and bitumen coefficients of the 214.2°C sample relative to the 214.3°C sample (81 and 122 versus 21 and 27, respectively). Moreover, the cracks and fractures of the 214.2°C sample would have allowed loss of much of this nonindigenous oil to the drilling mud, resulting in the leached and highly immature appearance of that sample's saturated- and aromatic-HC chromatograms. Whatever the cause, the qualitative aspects of the 214.2°C sample's saturated and aromatic HCS are most unusual and unexpected.

As an aside, the KCL "A" 72-4 20,930 ft saturated- (and aromatic-) HC gas chromatograms, were the only chromatograms in this study from rocks with hydrogen-poor OM, at 150°C or higher, which did not have a significant loss of $C_{15}$-compounds (fig. 8). Different factors unrelated, or only indirectly related, to HC generation and (or) maturity appear to result in both significant scatter in the bell-shaped generation curves of hydrogen-poor OM (figs. 1, 7) and in profound qualitative differences in saturated- and aromatic-HC gas chromatograms (figs. 2, 3, 4, 6, 8, 10). These factors include variable efficiency of HC expulsion, loss of HCS to the drilling fluid during drilling operations, subsurface migrating HCS, possibly variable original organic richess even within one OM type, and no doubt yet-unrecognized controls.

### Bitumen Composition

Normalized bitumen percentages are plotted in figure 9 for the Paloma field samples along with the HC coefficient (left-hand number) and hydrogen index (right-hand number) for each sample. Beyond 135°C (beginning of intense HC generation), the percentage of saturated HCS progressively increases, whereas that of the resins (NSO) continuously decreases, especially above 180°C. This is analogous to the trends observed in the Los Angeles Basin (fig. 5). Also, as in figure 5, the percentages of aromatic HCS and asphaltenes, with scatter, remain roughly constant. Thus, as with the hydrogen-poor OM in the Los Angeles Basin, in the hydrogen-poor OM at Paloma, the HCS, resins, and asphaltenes are cogenerated with each other, and the resins appear to preferentially thermally decompose above 180°C. The minimum in the saturated-HC percentage (13.5 percent) in the "33/452" sample at 137°C cannot be attributed to this sample having hydrogen-rich OM (hydrogen index = 452), because the next shallowest sample ("31/164") also has a low percentage of saturated HCS (17.5 percent), yet it contains type III/IV OM (hydrogen index = 164).

### Saturated-HC Gas Chromatograms

Satrated-HC gas chromatograms from immature rocks at Paloma, somewhat resemble those of the Los Angeles-Ventura Basins, with large naphthenic envelopes and a limited carbon
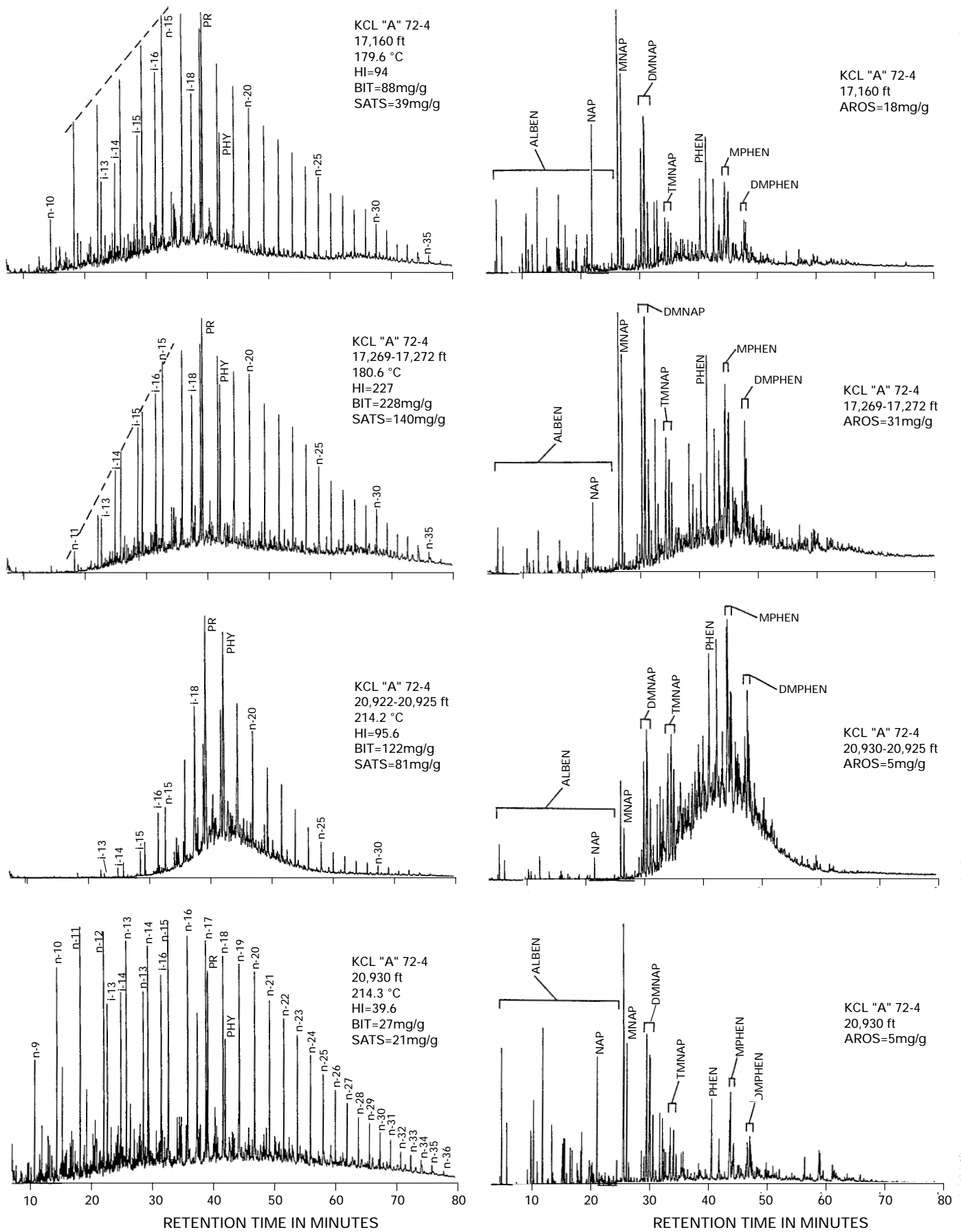
**Figure 8.** Saturated and aromatic HC gas chromatograms for four deep core samples from the Paloma KCL"A" 72-4 wellbore. See figure 3 caption for explanation of labels on the chromatograms. Dashed lines on two chromatograms connect the top of the n-paraffin peaks.

number range ($C_{15}$ to $C_{24}$) over which most saturated HCS occur (Ohio A-1, 6,750 ft sample; second chromatogram from top, left side; fig. 10). However, differences can also exist between immature samples from the two basins as seen in the Ohio A-1 4,574-4,583 ft sample (top left chromatogram, fig. 10), to wit: higher concentrations of n-paraffins at Paloma, a wider carbon-number range over which most saturated HCS occur, and strong odd n-paraffin preferences over n-$C_{23}$ to n-$C_{33}$. We attribute these differences to slightly different starting OM (a stronger influence of terrestrial OM at Paloma) and possibly to different depositional conditions in the rocks deposited shallower than 8,600 ft (2,620 m) at Paloma (Pliocene San Joaquin Formation and younger rocks) compared to Los Angeles and Ventura basin rocks. The saturated HCS from rocks deeper than 8,600 ft (2,620 m) at Paloma (Pliocene Etchegoin Formation and older rocks) were similar to, or indistinguishable from, those of Los Angeles and Ventura Basin rocks at similar maturities. For example, compare the KCL "A" 21-14 8,608 ft sample (101°C, third chromatogram on left, fig. 10) with the La Mirada 46-1 7,732-7,735 ft sample (top left chromatogram, fig. 6).

ROCK-EVAL data (Price and others, 1999) suggest that low-level HC generation occurs at Paloma before mainstage HC generation, as interpreted by the inferred gradually increasing HC and bitumen coefficients between 30° to 130°C in figure 7. This inference is supported by changing qualitative characteristics of the saturated HCS in figure 10 from 100° to 140°C, which corresponds to a rank of pre-mainstage HC generation (fig. 7). For example, in the KCL "A" 21-14 8,608 ft sample (third chromatogram on left, fig. 10) and the KCL-F-71-10 12,028 ft sample (top right chromatogram, fig. 10): (1) the size of the naphthenic envelope is suppressed from generation of acyclic HCS and n-paraffins, (2) the biomarker peaks become prevalent, and (3) the pristane/n-$C_{17}$ and phytane/n-$C_{18}$ ratios increase significantly, all compared to shallower samples. These qualitative differences could be attributed to an OM-type shift with depth at Paloma. However, visual-kerogen analyses (unpub. data, L. C. Price) demonstrate a uniform OM type in these rocks. Moreover, as discussed above, these same peculiar qualitative changes were also observed in saturated HCS from Los Angeles and Ventura Basin rocks at these same maturity levels (pre-mainstage HC generation). This observation suggests that basically the same starting OM is present in equivalent-age rocks from the three basins, at least for the hydrogen-poor OM. This hypothesis is supported by carbon-isotopic analyses of the saturated and aromatic HCS from mid Miocene rocks with hydrogen-poor OM from the three basins (L. C. Price, unpub. data). To wit, saturated HCS have a narrow range of $\delta^{13}C$ values (-25.0 to -23.5) as do aromatic HCS (-24.7 to -23.0), with no apparent differences between samples from the three basins

With the commencement and progression of mainstage-HC generation at Paloma, as judged by the Anderson 56-35 13,905 ft, and KCL "A" 72-4 15,293-15,302 ft samples (second and third chromatograms on right respectively, fig. 10): (1) biomarker peaks decrease and adjacent n-paraffins become increasingly dominant; (2) increasing amounts of $C_{14}$- and $C_{22}$+ material are generated; (3) i-C/n-C ratios decrease as does the naphthenic hump; and (4) n-paraffin profiles become more regular. With further burial, these maturity changes continue (17,160 ft and 17,269-17,272 ft samples (two top left chromatograms, fig. 8);
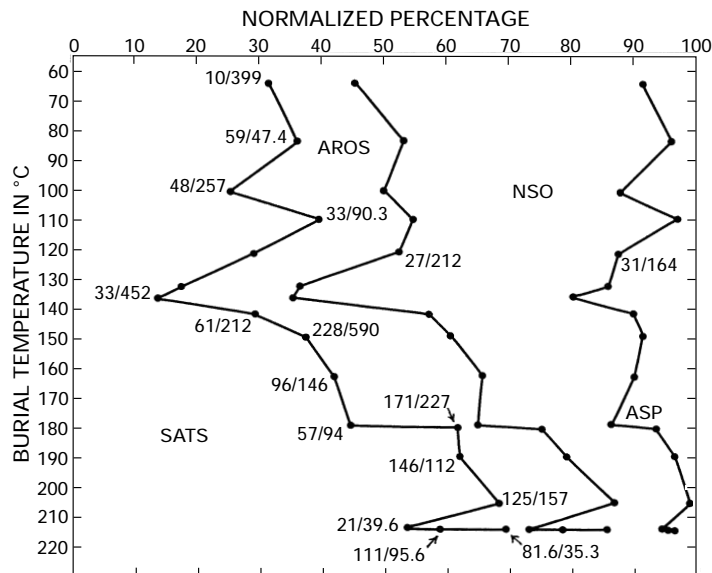


**Figure 9.** Normalized percentages, versus burial temperature, of saturated (SATS) and aromatic (AROS) HCS, resins (NSO), and asphaltenes (ASP) in bitumen from rocks from different wells in the Paloma Field, Southern San Joaquin Valley Basin. Samples at 162.5°C and higher are from the KCL"A" 72-4 wellbore. The HC coefficient (mg saturated plus aromatic HCS/g TOC, left-hand number) and ROCK-EVAL hydrogen index (right-hand number) are given for each sample.

and 18,286-18,297 ft sample (bottom right chromatogram, fig. 10). The deepest samples have the mature characteristics expected at these 214°C burial temperatures (the 20,930 ft sample (bottom left chromatogram, fig. 8).

The qualitative changes in the Paloma saturated HCS during mainstage-HC generation are indistinguishable from those from the hydrogen-poor OM of the Los Angeles-Ventura Basins over the same ranks. That the saturated HCS from the different areas cannot be discriminated from one another, at any rank above 95°C, suggests the same starting OM or similar depositional conditions, or both, for these areas. Lastly, it is noteworthy that the saturated HCS become oil-like only at about 180°C and above for the hydrogen-poor OM of both areas.

## Hydrogen-Rich OM

### HC Generation

Figure 11 is a plot of the HC (dots and solid line) and bitumen (triangles and dashed line) coefficients versus burial temperature for rocks with hydrogen-rich OM, mainly from the Los Angeles Basin. All samples had ROCK-EVAL hydrogen indices of at least 350, many with higher values, several with values characteristic of type I OM. Hydrogen indices (left-hand number) and TOC contents (right-hand number) are given for each sample.

Two features are immediately apparent in figure 11. First, two shallower samples at 72.5° and 90.5°C (243E/2.35E and 363E/1.58E, respectively) have very high HC (215 and 249) and bitumen (323 and 372) coefficients. The previously discussed 243E/2.35E sample (fig. 4, third chromatogram on left, WD-
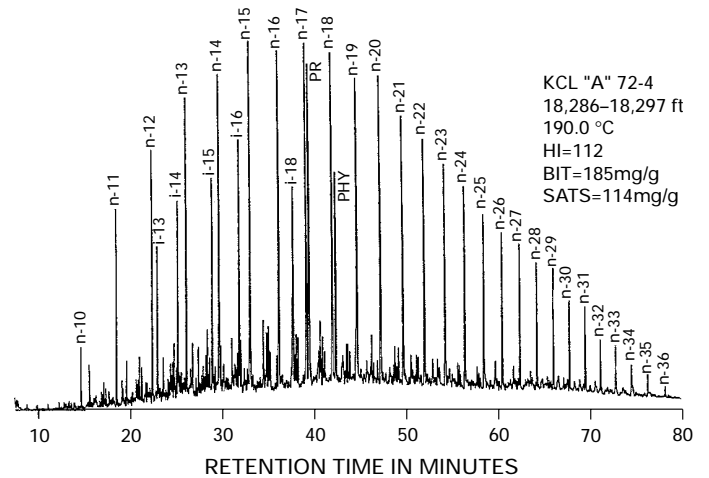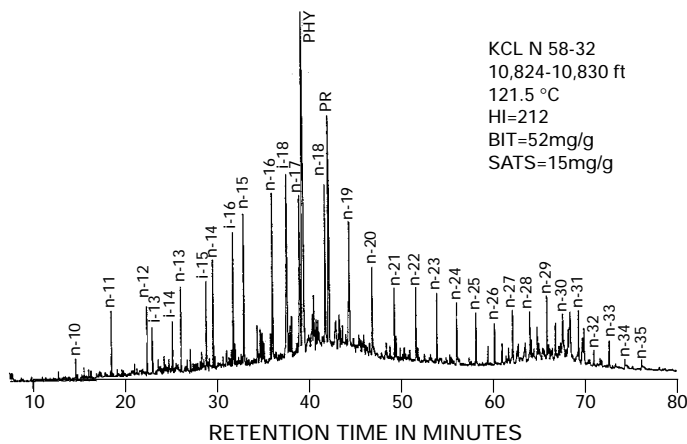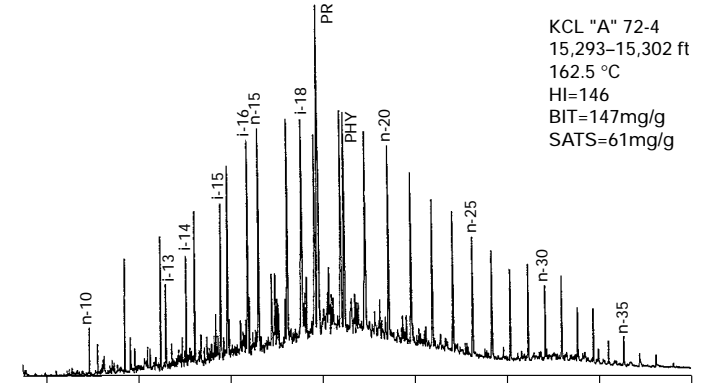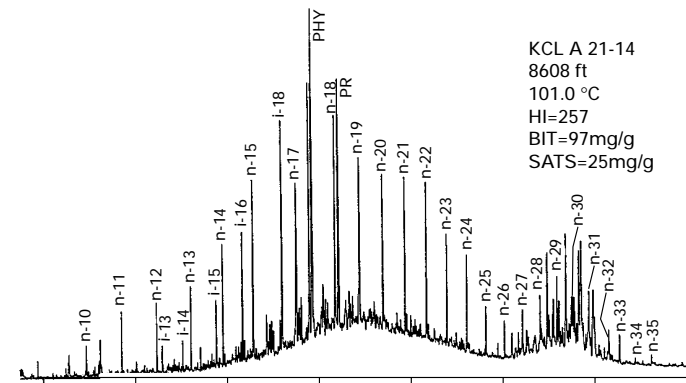
**OHЮ A-1**
4574-4583 ft
64.1 °C
HI=399
BIT=23mg/g
SATS=7mg/g

**KCL F 71-10**
12.028 ft
132.5 °C
HI=164
BIT=66mg/g
SATS=10mg/g

**OHIO A-1**
6750 ft
84.0 °C
HI=47.4
BIT=111mg/g
SATS=40mg/g
(T.O.C.=0.19)

**ANDERSON 56-35**
13,905 ft
149.7 °C
HI=590
BIT=376mg/g
SATS=140mg/g

**KCL A 21-14**
8608 ft
101.0 °C
HI=257
BIT=97mg/g
SATS=25mg/g

**KCL "A" 72-4**
15,293–15,302 ft
162.5 °C
HI=146
BIT=147mg/g
SATS=61mg/g

**KCL N 58-32**
10,824-10,830 ft
121.5 °C
HI=212
BIT=52mg/g
SATS=15mg/g

**KCL "A" 72-4**
18,286–18,297 ft
190.0 °C
HI=112
BIT=185mg/g
SATS=114mg/g

RETENTION TIME IN MINUTES

RETENTION TIME IN MINUTES

18    Organic Metamorphism in the California Petroleum Basins

**Figure 11.** Plot of the HC coefficient (dots, solid line) and bitumen coefficient (triangles, dashed line) versus burial temperature in °C for shales with hydrogen-rich OM (hydrogen index >350) from the California petroleum basins. Left-hand number at each sample point is the ROCK-EVAL hydrogen index, right-hand number is TOC; "E" after these numbers refers to Soxhlet-extracted samples. SSJV is a Southern San Joaquin Valley Basin sample. All other samples are from the Los Angeles Basin.

107, 3,017 ft) was hypothesized to be a biodegraded oil which migrated into the shale from a deeper reservoir with biodegraded oil, via caprock leakage. This fact and the lower hydrogen index (243) of the extracted, versus the unextracted (372), sample (table 1) would suggest that this rock contains type III, and not type II/III, OM. Saturated- and aromatic-HC gas chromatograms of the other sample (363E/1.58E) are immature. Thus, the high HC concentrations of this sample are due neither to "oil staining" nor to mainstage HC generation. The 363E/1.58E sample is yet another example of high concentrations of immature bitumen and HCS which are occasionally present in immature shales from the California basins. Based on ROCK-EVAL analyses (Price and others, 1999), other immature rocks with hydrogen-rich OM from these basins at burial temperatures below 120°C also have abnormally high bitumen contents. Gas chromatography suggests that the slightly elevated HC coefficients, and significantly elevated bitumen coefficients, of the 388/3.63 and 404/3.54 samples (fig. 11, both about 162°C) appear to be due to low-level HC generation. Gas chromatography could not be performed on the 551/5.27 sample (about 132°C, fig. 11) and thus the cause of the slightly elevated HC, and moderately elevated bitumen, coefficients of that sample is unknown.

The second obvious feature of figure 11 is that it lacks even an ill-defined bell-shaped curve at 120°C and above, temperatures where HC generation is expected from the data of Philippi (1965), Price and others (1999), and figures 1 and 7. One might argue for a vague bell-shaped curve for the bitumen coefficient (dashed line) from 105° to 161.5°C with a sharp drop thereafter. However, the high hydrogen indices (500-700) of the rocks between 164° to 197°C argue against mainstage-HC generation occurring here. Moreover, the HC coefficient (solid line) with scatter, remains essentially invariant from 105° to 197°C, and the three deepest samples of figure 11 have some of the lowest values of the entire sample base.

In figure 1, which shows rocks from the same areas as figure 11 but with hydrogen-poor OM, intense HC generation begins by 100°C, maximizes by 165°C and is largely complete by 210°C. At Paloma (fig. 7), intense HC generation commences in rocks with hydrogen-poor OM by 135°C, maximizes by 180°C, and is also largely complete by 210°C. In contrast, in figure 11, the persistent high hydrogen indices in samples at 150° to 198°C, and the lack of defined increases in either the bitumen or especially the HC coefficients, both dictate the conclusion that mainstage-HC generation has not even begun by 198°C in these rocks. As discussed in Price (1988), an equivalent situation exists with the 21,500 ft (6,552.9 m) Shell Taylor 653 wellbore, Ventura Avenue Field, Ventura Basin. This well, with a 210°C bottom-hole temperature, encountered the Miocene Santa Margarita Formation at about 16,000 ft (4,987 m), at a burial temperature of 155°C. All measured maturity indices were suppressed in these 2 to 5 percent TOC rocks with hydrogen-rich OM from 155° to 210°C and the threshold of intense HC generation was not recognized in these rocks to total
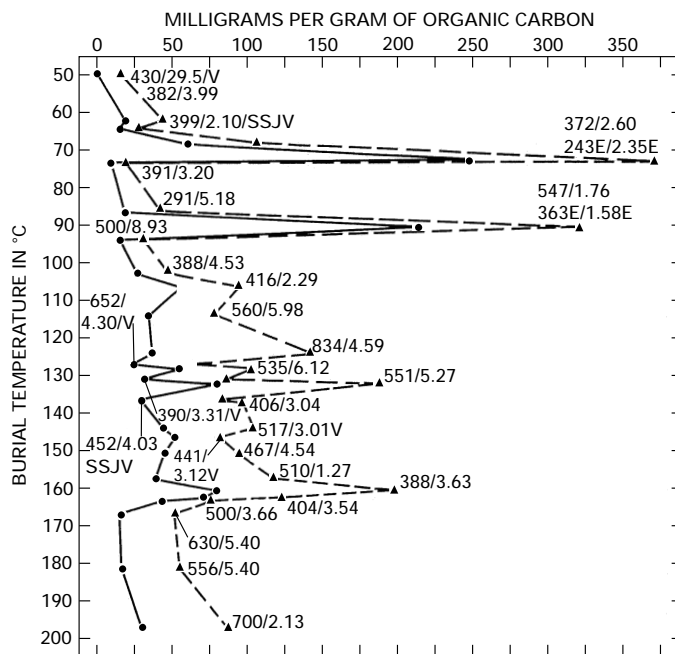
depth (John Castaño, Shell Oil, oral commun., 11/5/1985). Unpublished analyses carried out in 1999 on the rocks of this well with hydrogen-rich OM by the author demonstrate that mainstage $C_{15}+$ HC generation actually commences in this well at 196.7°C and 6,218 m. This paradox of high-temperature generation with hydrogen-rich OM is unexpected by existing paradigm. Moreover, because intense HC generation has not yet begun by 200°C in figure 11, the declines from the maxima of the bell-shaped curves of figure 1 beyond 150°C, and of figure 7 beyond 180°C, cannot be from HC destruction.

## Bitumen Composition

The normalized compositional percentage of the bitumen from the samples of figure 11 are given in figure 12, where profoundly different trends are present compared to the two equivalent plots for hydrogen-poor OM (figs. 5 and 9). The shallowest sample in figure 12 is a 29.6 percent TOC shale with type II-S OM from the Monterey Formation, Ventura Basin. This unweathered quarry sample from Naples Beach, Ventura Co., Calif., (supplied by M. D. Lewan, U.S. Geological Survey, sample ML-91-16) has never been hotter than 40°-50°C (Caroline Isaacs, U.S. Geological Survey, oral commun., 6/94). The low content of saturated HCS (4.0 percent) in the shallowest sample is because of the sample's extreme immaturity, and agrees with the normalized percentages of saturated HCS (1.03 to 6.03 percent) that Katz and Elrod (1983) reported in bitumens

extracted from 23 Middle Miocene to Lower Pliocene immature rocks (1,236 to 3,306 ft, 377.2 to 1,007.5 m burial depths) with type II OM from offshore California (fig. 16, discussed below). Thus, the 2.70/430 V sample is representative of immature hydrogen-rich OM in the California petroleum basins. Between 50° and 68°C, in figure 12, the saturated-HC percentage sharply increases to 44 percent at 68°C, the second highest percentage of the sample set. Considering both the data of Katz and Elrod (1983) and of this study, this increase can only be due to early HC generation between 40° and 70°C from cracking of weak bonds (perhaps acids, alcohols) to saturated HCS.

These profound qualitative changes in bitumen composition from 40° to 70°C are paralleled by equally profound qualitative changes in saturated-HC gas chromatograms. This is evidenced by comparing chromatograms from the most immature samples of this paper with those (not shown here) from the very immature offshore California shales of both Katz and Elrod (1983, fig. 5) and Claypool and others (1979, fig. 1). The Claypool and others (1979) and Katz and Elrod (1983) chromatograms completely lack n-paraffins, with the only peaks being acylic saturated HCS, or biomarkers, or simply naphthenic humps. B. Katz (Texaco, written commun., 11/13/1995) notes recent data suggesting that in some of the Cooperative Monterey Organic Geochemical Study (CMOGS) Naples Beach samples, more than 80 percent of the saturated HCS may be made up by the biomarker bisnorhopane (also evident in the data of Katz and Elrod, 1983). However, saturated-HC chromatograms of this study from even the most immature rocks with hydrogen-rich OM (see the WD-401, 2,411 ft sample, burial temperature 62.1°C, top left chromatogram, fig. 13) had a complement of n-paraffins and a much more "mature" appearance. Isaacs and others (1993) report that by inorganic thermometers, the maximum burial temperatures reached by the Naples Beach section were 40° to 50°C, whereas the Lions Head section was exposed to 85° to 100°C. Bitumen from Lions Head samples of the CMOGS study, although still immature, is significantly more mature in appearance than that from Naples Beach samples. For example, Lions Head bitumen has significantly higher n-paraffin concentrations than bitumen from the Naples Beach sample suite (Barry Katz, Texaco, written commun., 11/13/95). Thus, data from other investigators support the observations of this study regarding profound qualitative changes in the bitumen from rocks with hydrogen-rich OM over burial temperatures of 40° to 70°C. These strong qualitative differences in chromatograms between such low-temperature samples can only be caused by low temperature (40°-70°C) generation processes which also cause the strong qualitative changes in the bitumen over these temperatures (fig. 12). However, this is a temperature interval which usually does not receive attention in petroleum-geochemical studies, often because of a lack of samples.

From 68°C to the deepest samples of figure 12, with scatter, the percentage of saturated HCS decreases. In fact, the second hottest sample (181.4°C) has the second-lowest saturated-HC content (6.7 percent). Beyond 90°C, the percentages of aromatic HCS and resins remain roughly constant. In contrast, beyond a minimum at 68°-75°C, the percentage of asphaltenes increases with scatter. The compositional changes over the entire temperature range in figure 12 suggest that, contrary to the quantitative data (fig. 11), some type of low-level HC generation is occurring with increasing burial. Moreover, the much different bitumen compositional trends versus burial temperature in figure 12, compared to bitumen compositional trends for hydrogen-poor OM (figs. 5, 9), dictate that the reaction path of the hydrogen-rich OM is markedly different than that of hydrogen-poor OM.

Lewan (1991) observed the reaction pathway: kerogen --> asphaltenes + resins--> HCS in hydrous-pyrolysis experiments on the shale of the Upper-Devonian to Lower-Mississippian Woodford Formation (type II OM). He also noted that this reaction pathway has long been observed in oil-shale retorting and also has been previously suggested for natural HC generation. Furthermore, Lewan has observed this reaction pathway for other rocks with hydrogen-rich OM (M. D. Lewan, U.S. Geological Survey, oral commun., 4/94). This reaction pathway also occurred in rocks with hydrogen-rich OM in the experiments of Wenger and Price (1991), and thus appears applicable to all hydrogen-rich OM. Therefore, that the percentage of saturated HCS is still decreasing at 198°C (fig. 12), supports the conclusion drawn from the figure 11 data that mainstage HC generation has not yet begun in these rocks with hydrogen-rich OM at temperatures as high as 198°C.

### Saturated-HC Gas Chromatograms

Eight representative saturated-HC gas chromatograms from the samples of figures 11 and 12 are shown in figure 13. Saturated-HC chromatograms from immature rocks with hydrogen-rich OM (WD-401, 2411 ft, top left chromatogram, fig. 13) have the same characteristics as those with type III OM (Reyes-147 and Reyes-1 samples, top left two chromatograms, fig. 4), namely: (1) most of the saturated HCS concentrated over $C_{14}$ to $C_{21}$; (2) a pronounced naphthenic envelope over limited carbon ranges ($C_{13}$ to $C_{20}$); (3) a lack of significant concentrations of $C_{22}$+ n-paraffins with an almost complete absence of $C_{27}$+ (waxy) n-paraffins; (4) a noticeable lack, or reduced concentrations, of $C_{13}$- HCS (the WD-401, 2,411 ft sample, top left chromatograms fig. 13, is an exception); and (5) moderate i-C/n-C ratios.

Although several exceptions existed, primarily between burial temperatures of roughly 95° to 145°C, saturated-HC chromatograms from rocks with hydrogen-rich OM (fig. 13) had the same qualitative changes as in chromatograms from rocks over the same temperature interval with hydrogen-poor OM from the Los Angeles-Ventura (fig. 6) and Southern San Joaquin Valley (fig. 10) Basins. These changes included (1) relative increases in $C_{20}$ to $C_{26}$ n-paraffins and $C_{15}$- compounds; (2) a moderation of the naphthenic envelope from generation of $C_{15}$ to $C_{20}$ n-paraffins and acyclic saturated HCS; (3) increases in i-C/n-C ratios especially pristane/n-$C_{17}$ and phytane/n-$C_{18}$; and (4) a dramatic increase in biomarker peak heights. For example, compare Seal Beach, 6,045-7,901 ft (103.4°C, second left chromatogram from top, fig. 13) with both La Mirada 46-1, 7,732-7,735 ft (92.9°C, top left chromatogram, fig. 6) and with Shell KCL "A" 21-14, 8,608 ft (101.0°C, third left chromatogram from top, fig. 10). Also compare WD-102, 6,071 ft (124.3°C, third left chromatogram from top, fig. 13) with Sup.
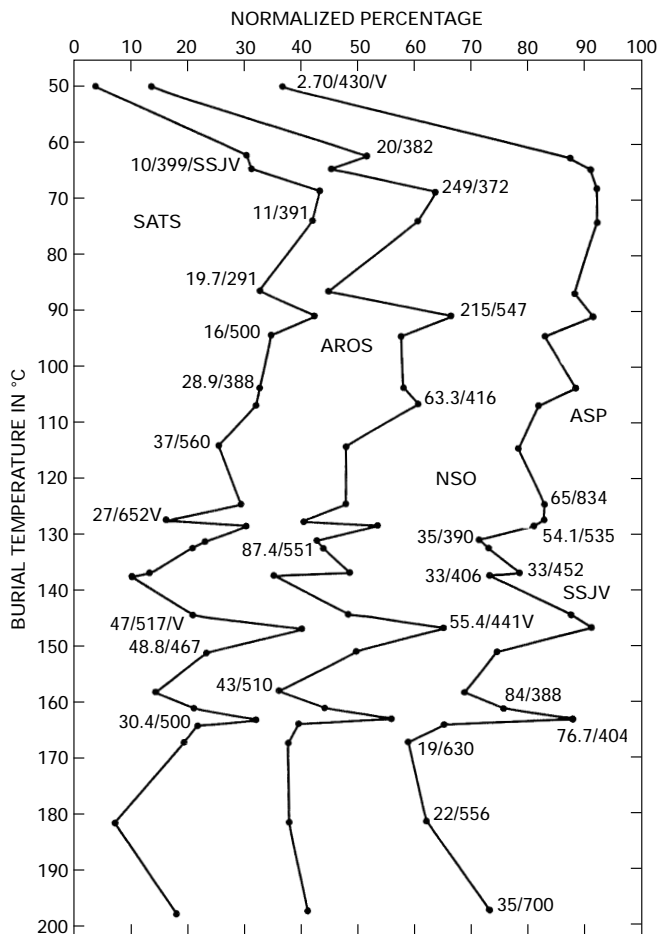
**Figure 12.** Normalized percentages, versus burial temperature of saturated (SATS) and aromatic (AROS) HCS, resins (NSO), and asphaltenes (ASP) in bitumen from rocks with hydrogen-rich OM (hydrogen index >350) from the California (principally Los Angeles-Ventura) petroleum basins. The HC coefficient (mg saturated plus aromatic HCS/g OC, left-hand number) and the ROCK-EVAL hydrogen index (right-hand number) are given for each sample. See figure 11 caption for explanation of letters next to samples.

Lim.-1 13,080 ft (124.2°C, second left chromatogram from top, fig. 6) and Ohio KCL-F-71-10, 12,028 ft (132.5°C, top right chromatogram, fig. 10). All these chromatograms have the same characteristics in spite of significant OM-type and geographic variations. This observation suggests that the same starting OM was present both in these different basins and in different depositional settings of these basins.

The hypothesis that all (or most of) the southern California basin Miocene kerogens had the same, or nearly the same, starting OM, in spite of widely different ending OM types, is supported by carbon-isotopic analyses of the saturated and aromatic HCS extracted from these rocks. Whether the OM is hydrogen-rich, or hydrogen-poor, both the saturated and aromatic HCS have a narrow range of $\delta^{13}C$ values (-25.0 to -23.5 and -24.7 to -23.0, respectively). Moreover, kerogens from different locations in these basins also have a narrow range of $\delta^{13}C$ values (-21.00 to -22.80), with no differences between hydrogen-rich and hydrogen-poor OM.

Curiale and others (1985) noted a similarity in biomarker distributions among Miocene Monterey oils and rock extracts from the Los Angeles, Ventura, Santa Maria, and San Joaquin

Valley Basins. This similarity was surprising to them, given the different basins, field locations, and the diverse lithology of the Monterey rocks. Those authors also concluded that a similar starting OM was present in these different locations. Caroline Isaacs, on the basis of data generated by the Cooperative Monterey Organic Geochemical Study (CMOGS), concluded that all the OM in Monterey rocks was the same, despite widely variable depositional settings for the different CMOGS samples (C. Isaacs, then U.S. Geological Survey, written commun., 12/1/95).

If indeed, all (or most of) the Miocene kerogens in southern California basin shales started from the same OM, irrespective of the final hydrogen richness of the kerogens, then depositional conditions must have played the major role in determining final organic facies in these basins.

In figure 13, the biomarker peaks in the Lloyd-185, 14,990-15,074 ft (146.4°C)(bottom left chromatogram) sample are moderated compared to the two shallower chromatograms (second and third chromatograms on left, fig. 13), an observation applying to most other shallower samples with burial temperatures between 80° to 140°C and with hydrogen-rich OM. This trend was also observed in saturated HCS from hydrogen-poor OM over the same burial temperatures. For example, compare the Lloyd-185 (146.4°C) chromatogram (bottom left chromatogram, fig. 13) with the Anderson 56-35, 13,905 ft (149.7°C) chromatogram (second chromatogram from top right, fig. 10). Again, the two are remarkably similar, suggesting the same starting OM both in the different basins and in different depositional settings in the basins.

Between 145° and 197.7°C to (the highest-temperature sample studied), saturated-HC chromatograms from rocks with hydrogen-rich OM had significant qualitative differences compared to chromatograms from lower-temperature rocks with hydrogen-rich OM (fig. 13). This observation demonstrated that continuing low-level HC generation was occurring in these deeper rocks. A most notable characteristic was increased $C_{14}$- and $C_{22}+$ material relative to $C_{15}$ to $C_{21}$ range compounds. Consequently, the higher-temperature chromatograms (four right chromatograms, fig. 13) always had more uniform n-paraffin distributions relative to lower-temperature samples (four left chromatograms, fig. 13). However, the highest-temperature samples with hydrogen-rich OM still had irregular n-paraffin profiles compared to those from high-temperature samples with hydrogen-poor OM. Thus, compare the n-paraffin profiles of the WC-403 9,412 ft and 10,387 ft samples (bottom two right-hand chromatograms, fig. 13, hydrogen-rich OM) with those of the 18,286-18,297 ft (bottom right chromatogram, fig. 10), 20,219 ft (bottom right chromatogram, fig. 6), and 20, 930 ft (bottom left chromatogram, fig. 8) samples, all with hydrogen-poor OM.

In rocks with hydrogen-rich OM, between 145° and 197.7°C, within the saturated HCS, certain maturity indices could reverse themselves, with no index constantly increasing and remaining elevated. For example, selected i-C/n-C ratios, could have significantly more mature values than other indices in the same chromatogram, or the relative heights of biomarker peaks compared to adjacent n-paraffins could reverse themselves between samples. Also note that even though they are at equivalent burial temperatures, the Alamitos 48-A 158°C chromatogram (top right chromatogram, fig. 13) appears more mature
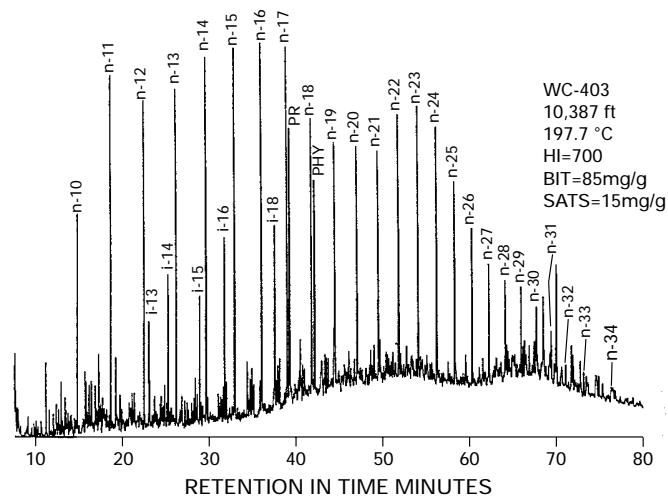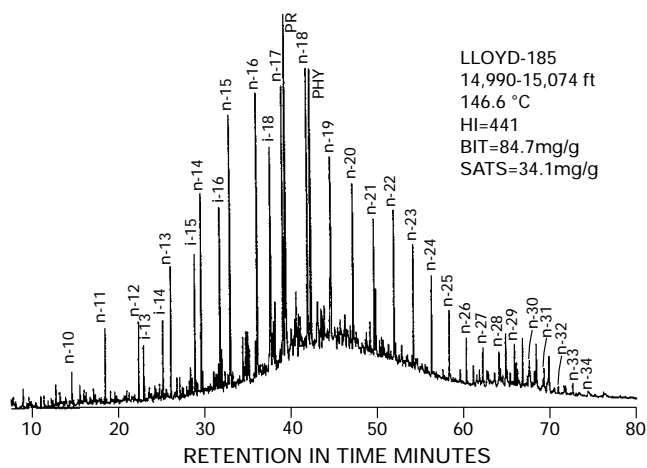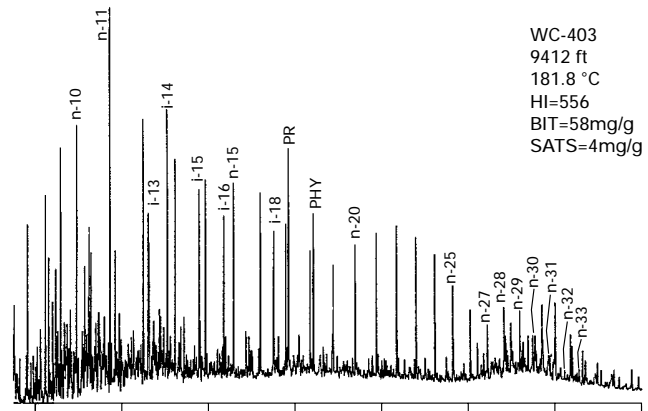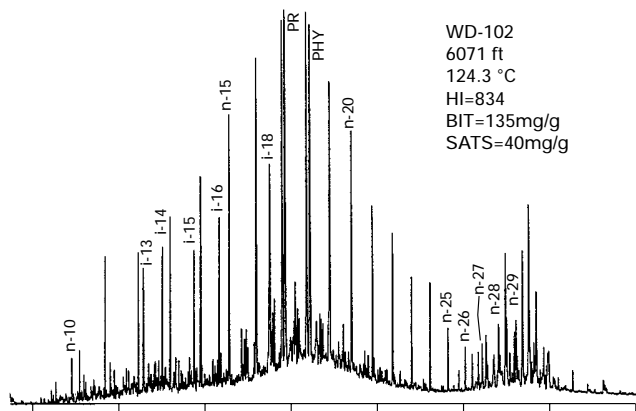
WD-401
2411 ft
62.1 °C
HI=382
BIT=38mg/g
SATS=12mg/g

ALAMITOS 48-A
12,655-12,664 ft
158 °C
HI=510
BIT=119mg/g
SATS=11mg/g

SEAL BEACH
6045-7901 ft
95.0-117.7 °C(103.4 °C)
HI=388
BIT=49.8mg/g
SATS=16.4mg/g

LLW-1
10,250-10,254 ft
161.29 °C
HI=388
BIT=189mg/g
SATS=40mg/g

WD-102
6071 ft
124.3 °C
HI=834
BIT=135mg/g
SATS=40mg/g

WC-403
9412 ft
181.8 °C
HI=556
BIT=58mg/g
SATS=4mg/g

LLOYD-185
14,990-15,074 ft
146.6 °C
HI=441
BIT=84.7mg/g
SATS=34.1mg/g

WC-403
10,387 ft
197.7 °C
HI=700
BIT=85mg/g
SATS=15mg/g

RETENTION IN TIME MINUTES

RETENTION IN TIME MINUTES
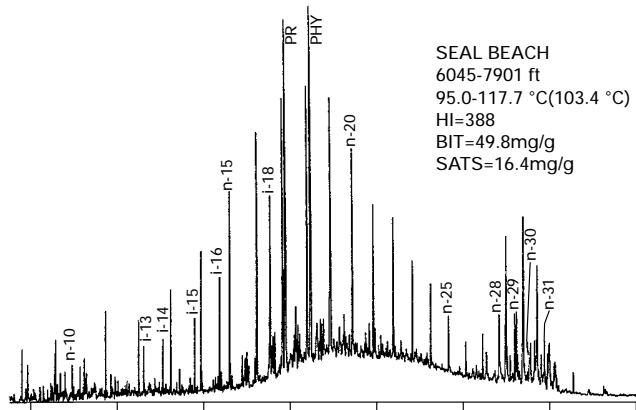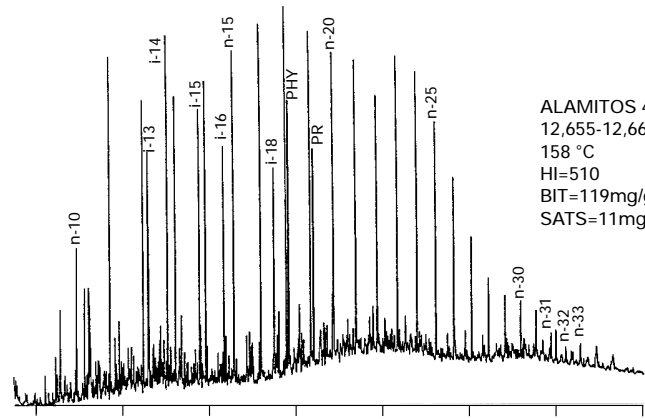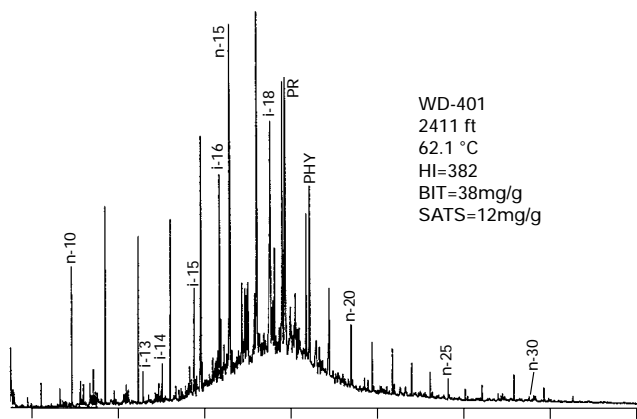
Saturated-HC gas chromatograms from rocks with hydrogen-rich OM of the Los Angeles-Ventura Basins demonstrating qualitative (maturity) changes versus burial temperature. See figure captions 2-4 for explanation of labeling on chromatograms.

than the LLW-1 161.2°C chromatogram (second chromatogram from top right, fig. 13) which has significantly higher i-C/n-C ratios and more prominent biomarker peaks. On the other hand, note the prominent i-$C_{14}$ peak in the Alamitos 48-A 158°C chromatogram. Thus, no saturated HC-chromatogram from a rock with hydrogen-rich OM had an overall mature appearance, no matter what the burial temperature.

All saturated-HC chromatograms from rocks with hydrogen-rich OM at and above 150°C had three characteristics (fig. 13): (1) elevated concentrations of $C_{14}$- material compared to all but one example (20,930 ft sample, bottom left chromatogram, fig. 8) from rocks with hydrogen-poor OM at equivalent temperatures; (2) irregular (ragged) n-paraffin profiles; and (3) overall immature appearances, although some maturity indices in the chromatogram could have "mature" values.

The changes in qualitative characteristics of the saturated-HC-chromatograms from rocks with hydrogen-rich OM versus increasing burial temperature (fig. 13), like the bitumen compositions of figure 12, demonstrate that some form of HC generation is occurring in these rocks. However, the high hydrogen indices (as much as 700), the low saturated-HC coefficients (4 to 15 mg/g OC), and the low normalized percentages of saturated HCS in the bitumen of these rocks, all demonstrate that mainstage HC generation has not commenced in these rocks, contrary to the situation in rocks with hydrogen-poor OM at equivalent temperatures. This observation may explain why rocks with hydrogen-rich OM at temperatures of 150°C and greater have $C_{14}$- saturated HCS. That is because these rocks have not entered mainstage-HC generation and thus have not yet generated significant amounts of HC gas. Therefore, there is little gas to cause a loss of what $C_{14}$- HCS have been generated, either to expulsion or to the drilling mud during drilling operations.

The presence of $C_{14}$- saturated HCS almost exclusively in the rocks of this study at or above 150°C, but only with hydrogen-rich OM, is an important observation. Moreover, the abundant $C_{14}$- material in the KCL "A" - 72-4, 20,930 ft chromatogram (bottom left, fig. 8) demonstrates that the general lack of $C_{14}$- material in high-temperature rocks with hydrogen-poor OM cannot be due to a lack of generative capability for these compounds from hydrogen-poor OM. Lastly, saturated-HC gas chromatograms from rocks at high temperatures, and with hydrogen-rich OM, retain an overall immature appearance simply because these rocks have not yet entered mainstage-HC generation.

## Discussion

### Suppression of Organic Metamorphism in Hydrogen-Rich OM

Figure 14 is another example of the significant suppression of organic metamorphism always observed in rocks with hydro-

gen-rich OM at elevated temperatures in the southern California basins. In figure 14, data are plotted from samples with burial temperatures between 158.0° to 176.2°C, thus HC generation should be underway. These samples also have a wide hydrogen-index range. The best indication of HC generation is direct measurement of generated HCS, e.g., the HC coefficient. This parameter, and the percentage composition of the extracted bitumen, for seven different samples are plotted in figure 14, all versus hydrogen index. As the hydrogen index increases, the HC coefficient strongly decreases, from values of around 100 mg/g OC for samples with hydrogen indices of 100-150, to 19 mg/g OC for a hydrogen index of 630. Concurrently, elevated percentages (60 percent and above) of total HCS in the extracted bitumen in low-hydrogen-index rocks strongly decrease with increasing hydrogen index (fig. 14).

Comparison of individual sample pairs with widely different hydrogen indices, but at similar elevated burial temperatures (>150°C), invariably demonstrates that the high-hydrogen-index sample is significantly less mature in appearance. For example, compare the hydrogen-rich OM WC-403, 9412 ft sample (181.8°C, second right-hand chromatogram from bottom, fig. 13) with hydrogen-poor OM samples at equivalent temperatures: Apex-1, 16,974 ft (183.2 ° C, middle right chromatogram, fig. 6); KCL "A" 72-4, 17,160 ft and 17,269-17,272 ft (179.6°C and 180.6°C respectively, top two left chromatograms, fig. 8). Also, compare the hydrogen-rich OM WC-403, 10,387 ft sample (197.7°C, bottom right chromatogram, fig. 13) with hydrogen-poor OM samples at slightly lower or higher temperatures: KCL "A" 72-4, 18,286-18,297 ft sample (190.0°C, bottom right chromatogram, fig. 10), KCL "A" 72-4 20,930 ft sample (214.3°C, bottom left chromatogram, fig. 8) or the Apex-1, 20,219 ft sample (213.9°C, bottom right chromatogram, fig. 6). Lastly, compare the hydrogen-rich OM LLW-1 (161.2°C, second chromatogram from right top, fig. 13) and Alamitos 48-A (158.0°C, top right chromatogram, fig. 13) samples, with the hydrogen-poor OM KCL "A" 72-4, 15,293-15,302 ft sample (162.5°C, third chromatogram from right top, fig. 10). In these cases, and others not shown, the hydrogen-rich OM sample was always significantly less mature in appearance than the hydrogen-poor OM sample as judged by: (1) more irregular n-paraffin profiles, (2) more prominent biomarker peaks, (3) large, irregular, or bimodal naphthenic envelopes, and (4) higher i-C/n-C ratios.

In this study, the $C_{25}+$ portion of saturated-HC gas chromatograms was the most consistent and best index to monitor maturity changes versus temperature. It is well known that with increasing HC generation, the n-paraffin peaks over this carbon-number range become significantly larger than adjacent biomarker peaks. In all cases examined, for sample pairs at equivalent temperatures, the chromatogram from more hydrogen-rich OM was always less mature (higher biomarker peaks relative to adjacent n-paraffins) than that from hydrogen-poor OM at temperatures of 150°C and higher. Three examples are given in figure 15. The hydrogen-poor OM Baldwin Hills sample at 151.0°C clearly has a more mature appearance than the 467 hydrogen index Bryant Estate sample also at 151.0°C (two top chromatograms, fig. 15). This observation is also true for the other two sample pairs. Moreover, the 16,974 ft Apex-1 sample (bottom left, fig. 15), with hydrogen-poor OM is in the middle
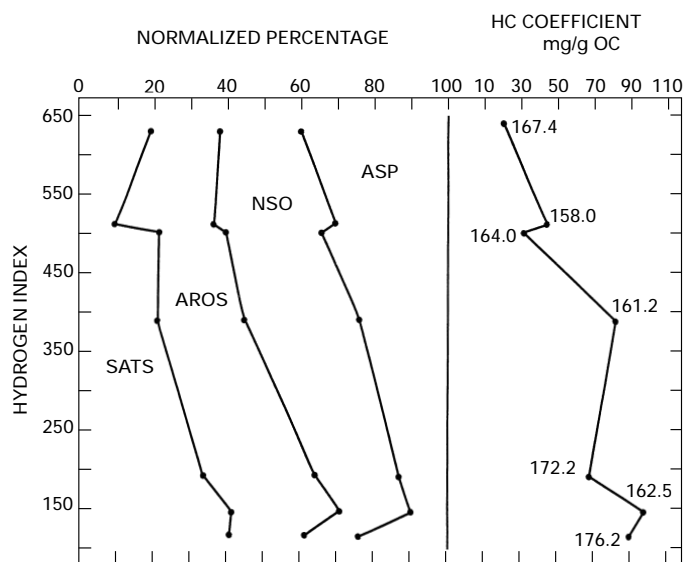
**Figure 14.** Plots of normalized bitumen composition and the HC coefficient (mg of saturated plus aromatic HCS/g TOC) versus the ROCK-EVAL hydrogen index for samples of this study at burial temperatures of 158.0° to 176.2°C. In the normalized-percentage (bitumen composition) plot, SATS are saturated HCS, AROS are aromatic HCS, NSO are resins, and ASP are asphaltenes. Burial temperatures (in °C) are given for each data point in the HC coefficient plot.

of mainstage HC generation, and has a high saturated-HC coefficient (76.1 mg/g). By contrast, the hydrogen-rich member of this sample pair (WC-403, 9,412 ft, 181.8°C, bottom right, fig. 15) has not yet begun mainstage generation and consequently has a low saturated HC coefficient (4 mg/g), in spite of its high burial temperature.

Significant differences between the reaction kinetics of other examples of hydrogen-rich OM and more thermally labile hydrogen-poor OM has been previously discussed (Price, 1988, 1991). Numerous examples of these differences have also been presented both in Price and others (1999) and this paper. These differences are also apparent in the data of Wenger and Price (1991). This divergence in reactivity manifests itself by $R_o$ suppression in hydrogen-rich OM (Price and Barker, 1985). However, in this study, all aspects of organic metamorphism, including mainstage HC generation, are suppressed in hydrogen-rich OM, compared to hydrogen-poor OM, due to, among other controls, the stronger bonds in hydrogen-rich OM. This significant suppression of HC generation has strong exploration implications.

## Origin of High Concentrations of Immature HCS

As discussed above, the Reyes-147 and Taylor-315 samples (second and fourth chromatograms on left, fig. 4) have unexpectedly high HC concentrations for their burial temperatures, yet the saturated and aromatic HC chromatograms for these samples are quite immature in appearance. Because this is characteristic of most immature samples of this study with abnormally high HC concentrations, such samples cannot have a significant component of oil from staining.

Other investigators have also found abnormally high concentrations of extractable HCS and bitumen in immature shales in California. For example, Claypool and others (1979), in their study of Pliocene and Miocene shales from the outer continental shelf OCS-CAL 78-164-1 wellbore reported very high HC coefficients (81 to 187 mg/g OC) and very high bitumen coefficients (159 to 346 mg/g OC) in some of their immature samples. Because these bitumens and HCS had very immature appearances, they could not have originated from staining by oil. Claypool and others (1979) concluded that the OM in the shales they studied could generate large amounts of HCS at very immature ranks. However, other immature shales in their sample set had, for their maturity, normal HC (11 to 34 mg/g OC) and bitumen (29.7 to 80 mg/g OC) coefficients, seemingly contradicting this hypothesis. Taylor (1976, p. 25) also noted that shales from offshore southern California could have abnormally high carbon-normalized extractable bitumen and HCS. Telnaes and others (in press) also observed high contents of extractable bitumen (bitumen coefficients of 100-460 mg/g OC) in very immature shales of the lower Pliocene Sisquoc and upper Miocene Monterey Formations in the OCS-315-1 (offshore Santa Maria Basin) wellbore. Kruge (1983) noted very high contents of extractable bitumen in some immature Monterey shales that he studied from the Lost Hills oil field, San Joaquin Valley Basin. He attributed these high concentrations to migrated HCS, although he noted some could also be indigenous. Curiale and others (1985) examined Monterey shales (and oils) from the Santa Maria Valley, San Joaquin Valley, Ventura, and Los Angeles Basins. They found high bitumen coefficients (118 to 437 mg/g OC) in immature shales at shallow to moderately shallow burial depths (675 to 2,179 m). Deeper samples also had elevated bitumen coefficients, but immature biomarker distributions in these samples suggested that mainstage-HC generation, if commenced at all, was not advanced.

Much of this previous work which was just discussed involved Monterey shales, and thus most of the above investigators concluded that the occurrence of abnormally high bitumen concentrations at immature ranks is peculiar to Monterey Formation rocks. However, high bitumen concentrations at immature ranks were also found in rocks other than the Monterey Formation in some of these studies. Moreover, Monterey rocks, and the OM therein, have highly variable lithologies, and thus were deposited under highly variable conditions in the different basins examined in the above studies. Thus, abnormally high bitumen concentrations cannot be ascribed as a feature unique to Monterey deposition. Lastly, this study found abnormally high concentrations of immature bitumen and HCS in all age rocks examined and in all basins studied. This phenomenon is characteristic of all rocks and all OM types of late Neogene deposition in the California basins. Abnormally high bitumen concentrations have also been observed in immature sediments from the Sea of Japan and the Bohai Basin (Barry Katz, Texaco, written commun., 11/13/95). However, it is unclear from whence these elevated concentrations of immature HCS originate. For example, were they incorporated into the shales at deposition or were they generated from kerogen moities with low activation energies?

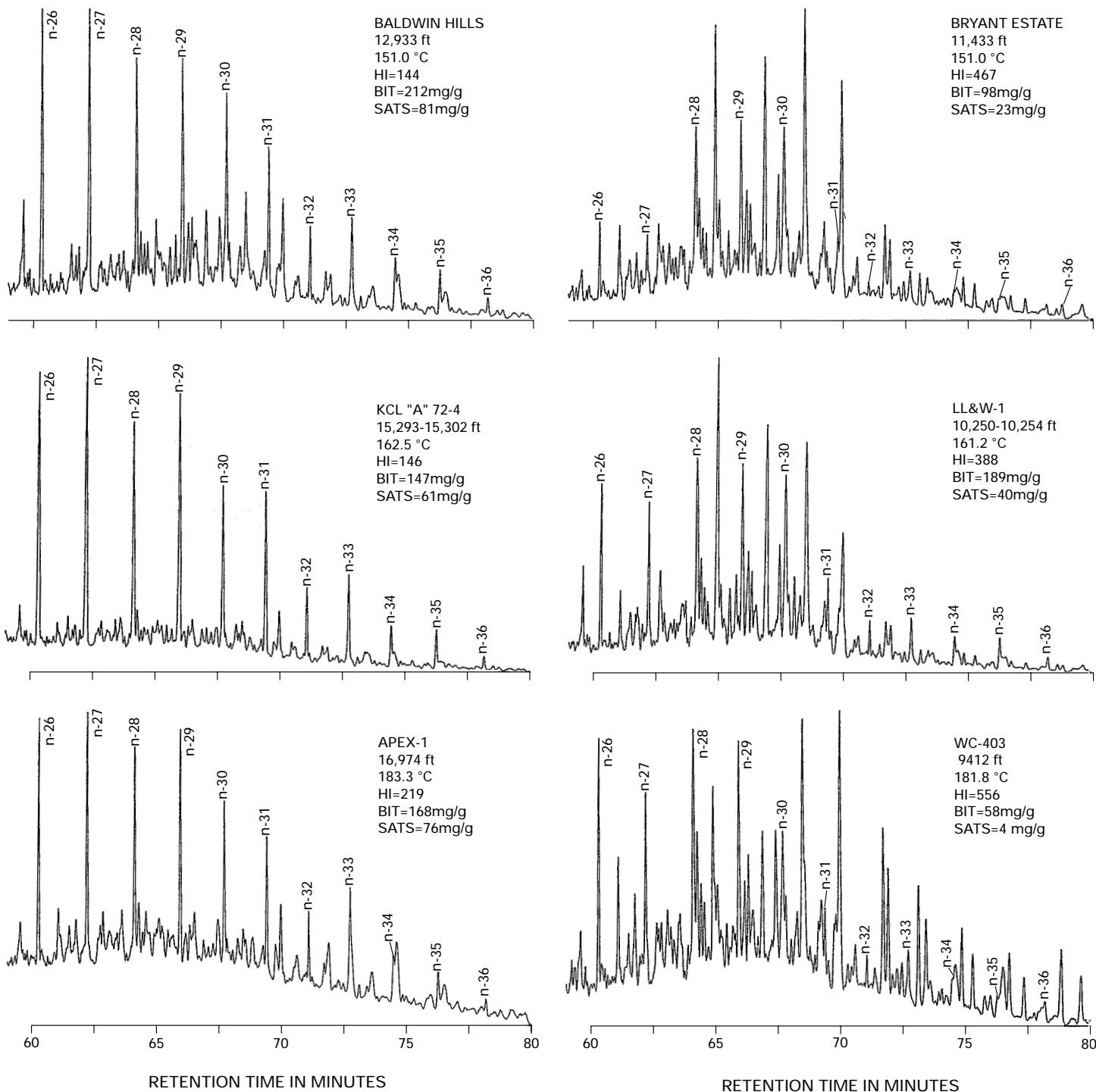Data from Katz and Elrod (1983) add insight to this question. They analyzed 23 shallow (377.2 to 1,007.5 m) mid-

**Figure 15.** Saturated-HC gas chromatograms of three sample pairs (hydrogen-rich versus hydrogen-poor OM) at equivalent burial temperatures over the $C_{26}$ to $C_{36}$ interval. The n-paraffins are labeled by their respective carbon number. See figure captions 2-4 for explanation of labeling on chromatograms.

Miocene to lower-Pliocene organic-rich shales from the Deep Sea Drilling Project (DSDP) Site 467, offshore southern California. Some of their data are in figure 16. The TOC contents for these shales ranged from 1.71 to 9.69 percent (averaging around 3 percent, fig. 16). Kerogen elemental hydrogen to carbon (H/C) ratios for 19 of the 23 shales so analyzed ranged from 1.26 to 1.40, values characteristic of type II OM. The HC coefficients calculated from the Katz and Elrod (1983) data are low, ranging

from 3.25 to 15.2 mg/g OC, and total HCS compose less than 15 percent of the extractable OM in all samples, with saturated-HC percentages ranging from 1.03 to 4.68 percent for all but one sample (fig. 16). Resins, and especially asphaltenes, comprise most of the extractable OM. Most bitumen coefficients are moderately high to high (fig. 16, 72.5 to 152.8 mg/g OC). However, these are misleading values because most of the bitumens are asphaltenes (55.14 to 86.91 percent). Moreover, in

these samples, bitumen coefficients increase with increasing percentages of asphaltenes. In point of fact, these samples have low to normal carbon-normalized contents of total HCS and, in some cases, resins.

Because no accurate burial temperatures are available for DSDP Site 467, such temperatures will have to be estimated. Based on well-established geothermal gradients for other southern California offshore areas, a gradient of 25° to 30°C per km would be reasonable, as would a temperature of about 11°C at the sediment-seawater interface. Thus, the shallowest Katz and Elrod (1983) samples would have been exposed to temperatures of 20.4° to 22.3°C, with the deepest samples at 36.2 to 41.2°C. The OM in these samples appears to be representative of hydrogen-rich OM in the rocks of the coastal onshore California Basins (Barry Katz, Texaco, oral commun., 7/95). However, none of these samples has the high carbon-normalized concentrations of immature HCS found in some onshore rocks. Thus, we may speculate that the high HC concentrations of some onshore rocks were not incorporated at deposition, but rather arose from cracking of weak kerogen bonds (perhaps alcohols or acids) above 41°C but before mainstage-HC generation. The pronounced compositional changes in bitumen from rocks with type II OM between 40° and 64°C (figs. 12, 16), and the profound qualitative changes in saturated-HC gas chromatograms from 40° to 70°C (discussed above), both demonstrate that some type of low-temperature HC generation is occurring, before mainstage-HC generation begins.

This hypothesized low-temperature HC generation, which must be from very weak kerogen bonds, always results in qualitative changes in the extractable bitumen. However, whether or not this low-temperature HC generation results in significant quantitative changes in bitumen and HC concentrations depends on the percentage of kerogen originally made up by the hypothesized weak bonds. Thus, we speculate that immature rocks with high concentrations of immature HCS and bitumen, originally had an abnormally high percentage of weak bonds in their kerogen. Such early HC generation, if it exists, and the possibility that such early generated HCS could form commercial oil deposits, have exploration implications as significant as the highly suppressed mainstage-HC generation observed in hydrogen-rich OM (discussed above).

## Bell-Shaped HC-Generation Curves

Bell-shaped HC-generation curves (figs. 1, 7) are invariably observed for coals and shales with hydrogen-poor OM, where maturity ranges are large enough, e.g., $R_o = 0.4$ to 1.5-2.0 percent (Price, 1989). However, such curves are uncommon in source rocks with both hydrogen-rich OM and TOC contents >5-7 percent. For example, Price and others (1984) observed no measurable increase in bitumen concentrations in the shales of the Upper Devonian to Lower Mississippian Bakken Formation, even though that rock went completely through mainstage-HC generation (conservatively, starting average TOC contents and hydrogen indices respectively are 15-17 percent and 550-650, versus ending average values of 7-9 percent and 50-150). Price and others (1984) attributed this lack of a HC-concentra-
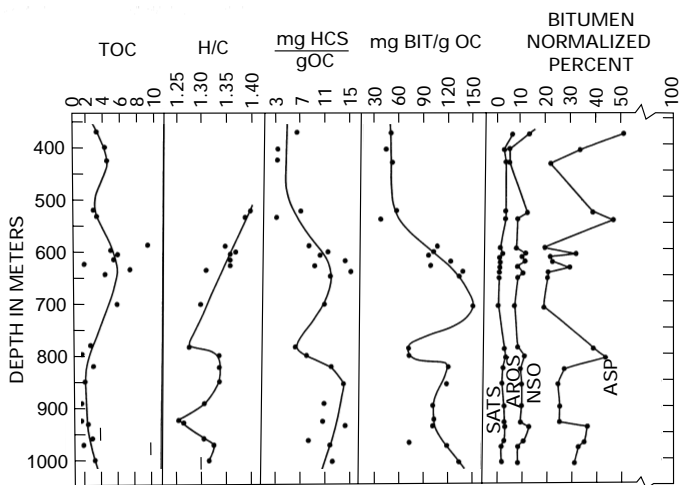


**Figure 16.** Plots of total organic carbon (TOC), kerogen elemental hydrogen to carbon ratios (H/C); the saturated plus aromatic HC coefficient (mg HCS/g OC); the bitumen coefficient (mg BIT/g OC); and normalized bitumen percentages, all for the data of Katz and Elrod (1983). In the normalized-bitumen plot, SATS are saturated HCS, AROS are aromatic HCS, NSO are resins, and ASP are asphaltenes. There is a scale break between 50 and 100 percent in the asphaltene field.

tion buildup in the Bakken shales to efficient source-rock expulsion. Larter (1988, p. 193) commented on this general lack of a HC-concentration buildup in source rocks with hydrogen-rich OM; "In the author's view, the development of a visible generative window in source rock sections is an infrequent occurrence." Larter (1988) also attributed this lack of a HC-concentration buildup to efficient expulsion.

However, Tissot and others (1971) reported significant HC and bitumen concentration increases with depth from HC generation in the early Toarcian shales (hydrogen-rich OM) of the Paris Basin, also reflected in ROCK-EVAL data on the same samples (Espitalié and others, 1985; their figure 20). Substantial variation thus exists in HC-concentration increases during HC generation for different rocks. Reasons for this variance can be hypothesized.

Firstly, at immature ranks, rocks with hydrogen-poor OM usually have lower TOC contents and lower contents of indigenous (pre-generation) bitumen than rocks with more hydrogen-rich OM. Also, many rocks with hydrogen-rich OM at moderately low ranks, and beyond, have low (or no) matrix porosity (for example, the Bakken shales, Price and LeFever, 1992). However, lower TOC rocks with type III OM can have elevated porosities (10-20 percent) even when deeply buried (see Price, 1976, figs. 12, 13). Thus, the presence, or absence, of bell-shaped HC-concentration curves in fine-grained rocks can be attributed partly to storage capacity. Organic-rich rocks with low (or no) porosities and elevated concentrations of indigenous HCS cannot easily store newly generated HCS. Thus, these HCS are expelled either to adjacent organic-poor rocks or to a secondary-migration path. Another significant loss is oil stored in cracks and parting laminae in source rocks (Price and Clayton, 1992) to the drilling mud (Price and Le Fever, 1992).

Conversely, higher-porosity, lower-TOC rocks with hydrogen-poor OM have lower original contents of indigenous HCS

and significantly greater storage capacity for newly generated HCS, allowing bell-shaped HC concentration curves to build up during  HC generation.  (The reasons for some of the quantitative variation in the bell-shaped portion of these curves has been discussed above.)  The decline from the maximum of bell-shaped curves is classically attributed to $C_{15}+$ HC thermal destruction (Albrecht and others, 1976).  However, this explanation is contradicted by both the data from high-temperature samples with type II OM of this study and by the data of Price (1993b).  Instead, we attribute such declines to movement of generated HCS from these organically mature rocks, resulting from the rock matrix having finally become satiated with $C_{15}+$ HCS from increasing HC generation and decreasing porosity, both from increasing burial.  The organic-rich Paris Basin Toarcian shales appear to be an exception to the above hypotheses, but this is not the case.  The Toarcian shales, even during mainstage HC generation, unlike most other high TOC fine-grained rocks with hydrogen-rich OM, retain elevated porosities, up to 10 percent (B. Krooss, Institute of Petroleum and Organic Geochemistry, Jülich, Germany; and J. Burrus, Institut Francais du Pétrole, Paris, France; oral communs., 10/94).  J. Burrus attributed the HC-concentration buildups during HC generation in the Toarcian shales to the elevated porosities of that rock compared to the low porosities, and lack of HC concentration buildups, in the Bakken shales (J. Burrus, oral commun., 10/94), a point of agreement here.

The absence of bitumen and HC-concentration buildups in the hydrogen-rich OM of this study is not, however, from the conditions outlined in the above discussion for rocks with hydrogen-rich OM.  Rather, their absence is because intense HC generation has not commenced in these rocks at any of the burial temperatures examined.

## Conclusions

1.  Bell-shaped HC-generation curves are present in rocks with hydrogen-poor OM in the Los Angeles and Southern San Joaquin Valley Basins.  In the Los Angeles Basin, HC generation commences at 90°C and maximizes by 165°C.  Above 165°C, HC and bitumen concentrations and hydrogen indices all strongly decrease to low values by 220°C, where HC generation is largely complete.  In the San Joaquin Valley Basin, HC generation commences at 135°C and maximizes by 180°C.  Above 180°C, HC and bitumen concentrations and hydrogen indices all strongly decrease to low values by 214°C.  In the Ventura Basin, intense HC generation has not begun in rocks with hydrogen-poor OM by 140°C.  The significant differences in burial temperatures at commencement of HC generation for the same OM type between the different areas is attributed to recent cooling in the Los Angeles Basin. HC generation in the Los Angeles Basin is thus assumed to have taken place at higher burial temperatures in the geologic past.

2.  Scatter in the bell-shaped portion of the HC-generation curves observed in this study for hydrogen-poor OM are attributed to variable original hydrogen indices, a non-

uniform loss of generated HCS to either the drilling mud or to source-rock expulsion, and to some shales having very high relative amounts of extractable bitumen and HCS, long before HC generation begins.

3.  In bitumen from rocks with hydrogen-poor OM, the percentage of saturated HCS progressively increases with increasing burial.  Moreover, resins and asphaltenes appear to be cogenerated with the HCS.  Above 140° to 150º C, resins appear to preferentially thermally decompose.

4.  Although saturated HCS from hydrogen-poor OM become increasingly mature with  burial, they become oil-like only at temperatures above 180°C in the Los Angeles and Southern San Joaquin Valley Basins.  Above 140° to 150°C, saturated HCS from hydrogen-poor OM usually have their qualitative (and quantitative) characteristics  altered by expulsion and (or) HC loss to the drilling mud, especially loss of $C_{15}$- HCS.  A lack of such alterations and no loss of $C_{15}$- HCS in rocks with hydrogen-rich OM to temperatures of at least 198°C is attributed to low concentrations of HC gas in these rocks from the lack of commencement of mainstage-HC generation.

5.  In the southern California basins, coarse-grained rocks in or around existing oil fields, where such rocks are not commercial oil reservoirs themselves, often have very high bitumen concentrations, from oil-staining.

6.  Data from this and other studies document that profound qualitative changes occur in the bitumen and HCS over 40° to 70°C in rocks with hydrogen-rich OM in the southern California basins, presumably from low-temperature HC generation processes.

7.  In rocks with hydrogen-poor OM in the California basins, above 40°C  and before mainstage generation, low-temperature HC generation also appears to occur, resulting in significant qualitative, but often no measurable quantitative, changes in the bitumen and HCS.  This low-temperature HC generation in rocks with all OM types in these basins may result from weak (15-40 kcal/mole) kerogen bonds.

8.  Fine-grained, immature (pre-mainstage HC generation), late Neogene rocks in the southern California petroleum basins of all OM types, including sulfur-poor OM, occasionally have abnormally high concentrations of indigenous immature HCS and bitumen.  Different lines of evidence suggest that this material may result from low temperature (40° to 120°C) generation from kerogens which originally have abnormally high contents of weak bonds (15-40 cal/mole).  Such a low-temperature generation could have strong exploration implications.

9.  Profound suppression of mainstage-HC generation, and all aspects of organic metamorphism, is present in rocks with hydrogen-rich OM in the southern California basins, compared to rocks with hydrogen-poor OM buried under the same conditions.  For example, mainstage-HC generation is largely complete, and extracted bitumen is mature in appearance, in rocks with hydrogen-poor OM by 200°C.  Conversely, mainstage HC generation has not even begun in rocks with hydrogen-

rich OM by 198°C at the Wilmington field and has begun only at 197°C at the Ventura Avenue Field. Moreover, extracted bitumens from such rocks still have an immature appearance at these high temperatures. This suppression of organic metamorphism in source rocks with hydrogen-rich OM has profound exploration implications.

10. Trends in bitumen composition versus burial temperature suggest that hydrogen-rich OM follows different reaction pathways, in addition to having different reaction kinetics, than hydrogen-poor OM. In the hydrogen-poor OM of this study, saturated and aromatic HCS, resins, and asphaltenes are all cogenerated; and at temperatures above 150°C, saturated HCS increasingly make up a greater percentage of the bitumen, while resins preferentially thermally decompose. By contrast, hydrogen-rich OM first generates resins and asphaltenes, which later thermally decompose to HCS.

11. From 60° to 145°C, saturated-HC gas chromatograms from all OM types demonstrate the same peculiar qualitative changes, versus temperature, in rocks from different sites in the three basins of this study. Moreover, these same changes are evident in other studies of southern California shales. These peculiar similarities suggest that the same, or similar, starting OM exists in many of the late Neogene rocks throughout southern California. Differences in hydrogen-richness, and reaction pathways and kinetics between the different OM types must then be due to different depositional conditions at different sites affecting the same starting OM.

12. The presence or absence of bell-shaped HC-generation curves in fine-grained rocks with adequate maturity ranges are hypothesized as due to organic richness and rock-storage capacity (porosity). With exceptions, organic-rich shales with hydrogen-rich OM typically have low porosities and high original bitumen concentrations by rock weight. Thus, such rocks cannot build up HC and bitumen concentrations significantly elevated over their original values. However, less organic-rich rocks with hydrogen-poor OM typically have higher porosities and lower original bitumen and HC concentrations (by rock weight), and thus invariably build up bitumen and HC concentrations from HC generation.

13. The decline in the concentration maxima at 150° and 180°C for the two bell-shaped HC generation curves for hydrogen-poor OM in this study cannot be due to HC cracking. This is because HC generation in hydrogen-rich OM only occurs at temperatures of 197°C or higher in the same basins. Instead, we attribute the declines in the bell-shaped HC-generation curves to source-rock expulsion and loss of generated HCS to the drilling mud during drilling operations.

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