

# Kerogen Type and Thermal Transformation of Organic Matter in the Miocene Monterey Formation

DANIEL M. JARVIE and L. LEE LUNDELL

## Abstract

Monterey Formation outcrop samples from Naples Beach, Santa Barbara–Ventura Basin, California, and Lions Head, Santa Maria Basin, California, were collected by the U.S. Geological Survey as part of the Cooperative Monterey Organic Geochemistry Study (Isaacs 1992; Isaacs et al. 1992, 1993; Isaacs et al., chapter 21, this volume). These samples were analyzed to determine basic geochemical characteristics including organic richness, petroleum potential, kerogen type, and maturity. On the basis of geochemical screening results, 12 of these samples were selected for detailed analyses including kerogen decomposition kinetics analysis and fingerprinting of the products formed during maturation under laboratory conditions. A core sample was also included in the screening and detailed analyses for control purposes.

The samples were subdivided into two groups based on the kinetic parameters, elemental data, and composition of the products formed during artificial maturation. One group of Monterey Formation samples (group 1), all from Naples Beach but also including the core sample, is characterized by having very broad kerogen decomposition profiles, high atomic oxygen-to-carbon (O/C) ratios, and conversion of organic matter at lower thermal thresholds than most other Type II marine kerogens. At a constant heating rate of 10 °C/million years (m.y.), the onset of generation, defined as 10% conversion of kerogen, ranges from 97 °C to 105 °C in this group of samples. The second group of Monterey Formation samples (group 2), all from Lions Head, is characterized by relatively narrow kerogen decomposition profiles, much lower O/C ratios, and calculated temperatures for the onset of generation of approximately 123–127 °C at 10 °C/m.y. Both groups contain Type II-S kerogens as defined by high sulfur-to-carbon (S/C) ratios (Orr 1986). Thus, the differences in the calculated onset of generation temperatures determined between the two groups do not appear to be related to sulfur content. However, there is a direct correlation between high O/C (>0.10) and early hydrocarbon generation.

The relative temperatures calculated for the onset of generation of the group 1 Monterey Formation samples are lower than for other labile Type II kerogens such as the Kimmeridge Shale. They are referred to as *early oil-generating kerogens*. The group 2 Monterey Formation samples have onset temperatures that are comparable to those of the Kimmeridge Shale and are referred to as *moderately early oil-generating kerogens*. Other kerogens such as the sulfur-lean Type II Woodford Shale and Type I Green River Shale have higher calculated temperatures for the onset of generation than either of these two and are referred to as *late oil-generating kerogens*.

It is known that thermal exposure and maturity differences exist between the group 1 and group 2 Monterey Formation samples. However, it is postulated that the differences represent two distinct organic facies. This assessment is based on differences in remaining hydrocarbon potentials and kinetic parameters, relatively constant S/C ratios, and maturity-decoupled compositional differences noted in selected peak ratios from fingerprints of the products formed during laboratory maturation. However, these two different organic facies could be the result of restructuring of organic matter during early maturation rather than different kerogen precursors.

Based on these data, it is proposed that these group 1 oxygen-rich Monterey Formation samples be identified as Type II-ONS kerogens because of their very high O/C and S/C ratios. Group 2 Monterey Formation samples have sufficiently high S/C ratios that their kerogens can be classified as Type II-S, but they are not as thermally labile as the group 1 Monterey Formation samples.

There is, also, a difference in the assessment of maturation level based on the classical interpretation of the peak pyrolysis temperatures ( $T_{max}$ ) in those samples having high O/C ratios and the very broad hydrocarbon generation profiles. For these oxygen-rich samples, kerogen conversion may reach 10% at  $T_{max}$  values as low as 400 °C, based on constant-heating-rate models and artificial maturation pyrolysis results from one Monterey Formation sample, KG-4. Open-system kerogen transformation experiments at a heating rate of 26.4 °C/min were used to show that this sample reaches 10% kerogen conversion at a peak pyrolysis temperature of 401 °C, 50% conversion at 429 °C, and 90% at 490 °C.

The Monterey Formation has been a subject of intense interest to a wide group of petroleum explorationists and scientists because of its high hydrocarbon potential and its nature as a source, carrier, and reservoir rock (Magoon and Isaacs 1983; Graham and Williams 1985). As of 1970 fractured Monterey shale reservoirs accounted for approximately 75% of the oil production in the Santa Maria Basin (Crawford 1971). The lithologic variability of the Monterey Formation has been described by various authors including Canfield (1939), Bramlette (1946), and Isaacs (1981, 1983).

The source rock potential of the Monterey Formation in the Los Angeles and Ventura Basins was described by Philippi (1965). In addition, he established the formation of the bulk of petroleum in these basins by thermal processes and reported that temperatures above 115 °C were required to convert the bulk of the kerogen to petroleum. His work also implied that decomposition kinetics play a role in hydrocarbon generation.

The decomposition kinetics of organic matter is dependent on the organic matter composition. The decomposition kinetics of coals was evaluated by van Krevelen, van Heerden, and Huntjens (1951); they demonstrated that the cracking of oxygen bonds in natural and synthetic compounds had significantly lower temperature requirements than the cracking of carbon-carbon bonds. Decarboxylation reactions, which are considered part of the kerogen formation process, take place at lower energy levels than does kerogen cracking (Vallentyne 1957, 1964; Johns and Shimoyana 1972). The loss of oxygen and water is a diagenetic step and occurs largely before, but also during, hydrocarbon generation. Reynolds, Burnham, and Mitchell (1995) have suggested some oxygen functionality as a potential source of early hydrocarbon generation. They also noted that Monterey Formation samples having the highest oxygen contents were the most reactive, not the

samples containing the highest amount of sulfur. Powell, Cook, and McKirdy (1975) suggested that kerogen derived from asphaltic precursors may decompose at lower thermal thresholds akin to a process intermediate between diagenesis and thermal decomposition of kerogen. Orr (1986) initiated a revised kerogen type to describe sulfur-rich Monterey kerogen termed Type II-S, which is Type II kerogen with atomic sulfur-to-carbon (S/C) ratios greater than 0.04 or containing more than 8% organic sulfur. He also suggested that these Type II-S kerogens generate petroleum at lower thermal thresholds than do sulfur-lean kerogens. This was attributed to cleavage of sulfur-sulfur bonds, which decompose more readily than carbon-carbon bonds. Baskin and Peters (1992) demonstrated via hydrous pyrolysis of a sulfur-rich Monterey sample that carbon loss was most intense during bitumen generation. This implied that bitumen decomposition was yielding the expelled oil in these experiments. Further, their data indicated that expelled oil was enriched in sulfur, which suggested that initial bitumen generation was due in part to sulfur-bond cleavage. They also suggested that low peak pyrolysis temperatures coupled with unusually high production indices were evidence of early generation. Hunt, Lewan, and Hennet (1991) published a scheme for predicting kerogen decomposition based on closed-system, hydrous-pyrolysis experiments on a range of Type II kerogens. Their scheme reflected variable levels of organic sulfur with higher sulfur content indicative of increased reactivity. Kerogens were described as Type II-A (the same as sulfur-rich Type II-S kerogens [Orr 1986]); kerogens with moderate sulfur contents, such as the Phosphoria Shale, were described as Type II-B; moderately sulfur-lean kerogens such as the Alum Shale were identified as Type II-C; and sulfur-lean kerogens such as the Woodford Shale were labeled Type II-D.

The hydrocarbon generation kinetics of the organic

matter in the Monterey Formation has been investigated and reported by a number of authors (Tissot, Pelet, and Ungerer 1987; Lewan 1989; Jarvie 1991; Reynolds and Burnham 1992; Reynolds, Burnham, and Mitchell 1995; Pepper and Corvi 1995). However, detailed analyses and description of the samples is modest and little control is available for comparison of these results.

The Cooperative Monterey Organic Geochemistry Study (CMOGS) provides an excellent opportunity to obtain both geochemical and geological controls to enhance our understanding of how various factors affect the generation of hydrocarbons from the Monterey Formation. In this chapter we discuss the results from open-system, constant-heating-rate pyrolysis experiments used to determine kinetic parameters on a number of Monterey Formation samples, as well as elemental data and fingerprints of products formed during laboratory maturation by closed-system pyrolysis of several of these samples. Kinetic data were extrapolated to geological time using an arbitrary, constant-heating-rate calculation appropriate for the high heat flow in this region. These results were compared with field data consisting of a geochemical database of the Monterey Formation where samples range from immature to late oil-window maturity.

## Experimental Section

### Samples

Thirty-three samples of the Monterey Formation from Naples Beach and Lions Head in the Santa Barbara-Ventura and Santa Maria Basins, respectively, were selected for analysis by the U.S. Geological Survey (figure 15.1). The stratigraphic column for the outcrop samples is shown elsewhere in this volume (Isaacs et al., chapter 21). Note that the stratigraphy includes samples from all members of the Monterey Formation as defined by Isaacs (1981). A core sample from the Petroleum Securities Rembush #1 well at 4925 ft, Santa Maria Valley, Santa Maria Basin, was included as a control sample to evaluate effects of weathering, if any.

### Analytical Program and Methods

Samples were prepared for analysis by grinding and passing through a 60-mesh (250  $\mu\text{m}$ ) sieve to insure homogeneous samples. Subsequently, the 33 outcrop samples and a single core sample were analyzed to determine organic richness, oil content, remaining hydrocarbon potential, and pyrolysis-based maturity parameters.



Figure 15.1 Sample location map with key fields and structures in the Santa Maria and Santa Barbara-Ventura Basins, California. Asterisks denote outcrop and control sample locations.

Samples were analyzed by a Rock-Eval™ plus total organic carbon (TOC) system (Delsi Instruments) to determine bulk thermal extraction and pyrolysis yields as well as total organic carbon contents. In this technique the sample was first heated to 300 °C for 5 min followed by nonisothermal pyrolysis at 25 °C/min to 600 °C. The pyrolyzed sample was subsequently transferred to a second oven where the remaining carbon was oxidized using air at approximately 580 °C (*note*: all temperatures and rates were nominal). The carbon dioxide generated during oxidation was trapped in a molecular sieve trap at 70 °C, which was later heated to 250 °C, causing the release of carbon dioxide into a thermal conductivity detector (TCD). Any carbon monoxide formed during oxidation was converted by hot copper oxide to carbon dioxide prior to trapping. Both pyrolysis and oxidation responses were calibrated and the total organic carbon content was calculated from both the bulk thermal extraction and pyrolysis yields, as well as the oxidation yields according to

$$\text{TOC (wt \%)} = 0.083 (S_1 + S_2) + 0.10 (S_3),$$

where  $S_1$  is the yield of free hydrocarbons vaporized at 300 °C in mg hydrocarbons/g rock,  $S_2$  is the yield of cracked hydrocarbons between 300 °C and 600 °C in

mg hydrocarbons/g rock, and  $S_4$  is carbon in carbon dioxide from oxidation in mg carbon/g rock.

This technique yields excellent correlation to Leco organic carbon determinations when proper care is taken in calibration of the instrument and when the linearity of the TCD is carefully monitored (see Laboratory 14 results for TOC data, chapter 25, this volume).

$T_{max}$  is the nominal temperature at which the maximum yield of  $S_2$  hydrocarbons occurs ( $T_{max}$  is the actual temperature at peak pyrolysis yields, and *true pyrolysis temperature* is the actual temperature at any given time in the pyrolysis process). Any carbon dioxide released between 300 °C and 390 °C (nominal) was trapped and subsequently detected by a TCD. It was recorded as the  $S_3$  value in mg carbon dioxide/g rock. It is defined as organic carbon dioxide, but inorganic interferences can occur (Katz 1983) because the oven temperature is actually 30–40 °C hotter (Espitalié 1985; Burnham, Braun, and Samoun 1988; Jarvie 1991) and certain labile carbonates will begin to decompose in the temperature range of 420–430 °C (actual).

Based on these screening results, 12 outcrop samples and the core sample were selected for evaluation by open-system pyrolysis to determine kinetic parameters. Kinetic parameters include a distribution of activation energies ( $E_a$ ) and a single Arrhenius factor ( $A$ ), which are used to calculate kerogen decomposition rates using rate equations and an assumed first-order reaction.

All samples selected for detailed analysis were first extracted for 24 h in a Soxhlet extractor utilizing a binary azeotropic mixture of chloroform and methanol to remove as much of the extractable organic matter (EOM) as possible. Each extracted sample was dried and reanalyzed for TOC and pyrolysis data to evaluate any changes in remaining potential ( $S_2$  value) due to loss of heavy EOM such as resins and asphaltenes.

The extracted rock samples were then used for determination of kinetic parameters. Whole-rock samples were not utilized because it is impossible to decouple cracking from vaporization of EOM in unextracted rock samples (Jarvie 1991). Data from the SR Analyzer (Humble Instruments & Services, Inc.) at six heating rates (analyzed in duplicate) from 250 °C to 900 °C were used in the automatic acquisition mode to construct kinetic data files consisting of time, true pyrolysis temperatures, and rate of kerogen decomposition. These files were processed in the Lawrence Livermore National Laboratory Kinetics program (Burnham 1989a) utilizing the rigorous discrete and Gaussian models as well as the Friedman model. A 1 kcal/mole

spacing was used in the discrete model, and the initial search range for the Arrhenius factor was  $10^2$  from the approximate value derived from the shift-in-peak-pyrolysis temperature.

Three samples (KG-1 and KG-4, which are from the carbonaceous marl member at Naples Beach, and KG-22, from the lower member at Lions Head) were demineralized, and the recovered kerogen was artificially matured utilizing a microscale sealed vessel (MSSV) system (GC2 Chromatography). The MSSV consists of a 40  $\mu$ l glass tube that is loaded with a small amount of kerogen (1–2 mg); the dead volume is filled with cleaned glass beads. The tube is subsequently purged with helium and sealed. After heating at constant temperatures ranging from 250 °C to 365 °C for 24–72 h, the tube is broken in a modified gas chromatographic injector for subsequent fingerprinting of the products formed during heating (Horsfield, Disko, and Leistner 1989). The products formed resemble a natural product in the gas chromatographic fingerprint, in other words, few or no alkenes are present. It is an excellent technique for evaluating the potential of a given petroleum source rock for gaseous and liquid products rather than relying strictly on hydrogen indices. Because it is a closed-system technique similar to hydrous pyrolysis but without added water, the cracked products are contained and allowed to react with other reactive species. Using an internal standard technique, quantitative results may be obtained. The gaseous and liquid hydrocarbon products formed during closed-system maturation were compared by means of gas chromatographic fingerprints to evaluate any compositional differences.

Each of the three Monterey Formation samples studied was heated at 300 °C and 350 °C for 24 h and 72 h in an attempt to decouple the effect of maturation on organic facies assessment. Because the Monterey Formation is essentially devoid of vitrinite, vitrinite reflectance data from a coal sample that was heated under the same time and temperature regime was measured and reported (Jarvie and Burgess 1993).

One sample, KG-4 (carbonaceous marl member), was artificially matured by open-system pyrolysis to evaluate the change in transformation ratio and peak pyrolysis temperature with increased thermal exposure. This was achieved by heating aliquots of the sample to 275, 325, 375, 425, and 475 °C at 26.4 °C/min (nominal temperatures). At these predetermined temperatures, the sample was lowered out of the pyrolysis oven but kept in a helium atmosphere to avoid oxidation. Each aliquot was subsequently analyzed to determine the remaining hydrocarbon potential,  $T_{max}$ , and TOC values.

These data were used to calculate the organic carbon mass balance and the decrease in hydrogen index with increasing thermal exposure (i.e., the calculated transformation ratio [TR]), based on the change in hydrogen indices from the original, whole-rock sample.

## Results and Discussion

### TOC Contents and Pyrolysis Results

TOC and pyrolysis data for the complete sample suite are shown in table 15.1, excluding sample KG-5, which was not analyzed. TOC values of the Monterey Formation samples range from 0.75% to 17.35%, with a mean value for 32 samples of 6.69%. The hydrogen indices (HI) range from 249 to 739 mg hydrocarbons/g TOC, with a mean value of 502 mg hydrocarbons/g TOC (figure 15.2). There is considerable variation in HI values, although samples from comparable members as described by Isaacs (1983) generally have very similar HI values. The lowest HI values (HI = 249 and 285 mg hydrocarbons/g TOC) measured for the Monterey Formation occur in a porcelanite from Naples Beach (KG-7) and a clayey dolostone from Lions Head (KG-18). There were no perceptible severe weathering effects observed in these samples or the geochemical data, particularly in comparison with the Rembush #1 core sample included for control purposes.

It is known that heavy hydrocarbons (high-molecular-weight waxes  $> n-C_{50}$ ), resins, and asphaltenes will affect the pyrolysis ( $S_a$ ) response (Clementz 1979) and must be removed to determine accurate hydrocarbon generation potentials. This is especially important in productive Monterey Formation horizons. Based on the whole-rock TOC values and petroleum potentials, 12 of the samples were extracted and reanalyzed (table 15.2; figure 15.3). The Naples Beach Monterey Formation samples have a wide range of remaining potentials (from 250 to 1900 barrels of oil/acre-ft), whereas the Lions Head samples exhibit a narrow range of remaining hydrocarbon potentials (800–1000 barrels of oil/acre-ft). The barrels per acre-foot calculation is based on conversion of pyrolysis yields, and the interpretive lines are based on Jones's (1984) kerogen classification scheme.

Based on classical interpretation of  $T_{max}$  values (Espitalié et al. 1977; Teichmüller and Durand 1983; Espitalié, Marquis, and Barsony 1984; Peters 1986), all samples are immature. However, there is a relatively high level of kerogen conversion based on the normalized oil contents ( $>10\%$ ) at low  $T_{max}$  values (figure 15.4). Although these elevated normalized oil contents

could result from migration of hydrocarbons into the rocks, it is perceived that they are rather derived from cracking of labile kerogen bonds and relatively high levels of preserved algal biomass that also decomposes at relatively low temperatures (Peters, Rohrback, and Kaplan 1981). The dotted lines in figure 15.4 suggest that pyrolysis maturity assessments should also be interpreted with regard to conversion levels, as indicated by normalized oil contents. For example, the Green River Shale can be immature at a  $T_{max}$  value of 442 °C, and a Permian cannel coal sample has been shown to be immature at 454 °C, based on low production index (PI) and measured vitrinite reflectance values (0.47%  $R_o$ ) (Jarvie and Burgess 1993). However, the cause of elevated normalized oil contents must be carefully investigated to insure that contamination from mud additives or migrated hydrocarbons is not inflating the free oil content of a rock. EOM is also reported to decrease  $T_{max}$  values of whole-rock samples by up to 16 °C (Kruge 1983). However, this phenomenon was not observed for most of the extracted samples in this study and is not a factor in the accurate assessment of maturity from calibrated peak pyrolysis temperatures.

Mineralogy (Isaacs et al. 1992; Isaacs et al., chapter 21, this volume) and biomarker data (Michael, chapter 14, this volume) indicate that the Lions Head exposure contains organic matter that is slightly more mature than Monterey Formation organic matter at Naples Beach. Note also that the Lions Head samples generally have higher peak pyrolysis temperatures than the Naples Beach samples, also confirming the slightly higher maturity of the Lions Head organic matter.

### Kinetic Analysis

Kinetic parameters—apparent activation energies ( $E_a$ ) and the associated Arrhenius factor ( $A$ )—were calculated from open-system pyrolysis of 12 of these Monterey Formation samples and the Rembush core sample. Many of the Monterey Formation samples contain organic matter that yields extremely broad pyrolysis peaks, resulting in a very broad distribution of activation energies. Certain samples (KG-1, KG-2, KG-4, KG-6, KG-7, KG-8, KG-10, KG-11, KG-30, all from Naples Beach, and the control sample) are characterized by a substantial fraction of their decomposition reactions occurring below 50 kcal/mole, although the principal  $E_a$  values are in the 51–56 kcal/mole range (figure 15.5a–g) (KG-7 and KG-8 not shown). Note that the core sample included for control purposes also has a very broad distribution of activation energies (figure

Table 15.1 Geochemical Screening Results on All CMOGS Monterey Formation Samples and Petroleum Securities Rembush #1 Core (Control) Sample.

Sample No.	Location	Lithologic Description	Total Organic Carbon (wt. %)	Oil Content (mg oil/g rock)	Oil Potential (mg oil/g rock)	T <sub>max</sub> (°C)	Potential Yield (bbls/acre-ft)	Hydrogen Index (HI) (mg hc/g TOC)
KG-1	Naples Beach	phosphatic foraminite	10.76	7.57	54.58	402	1194	507
KG-2	Naples Beach	phosphatic marl	17.36	9.34	86.43	408	1890	498
KG-4	Naples Beach	phosphatic mudstone	16.12	10.51	84.23	396	1842	523
KG-6	Naples Beach	siliceous mudstone	5.51	2.63	21.10	416	461	383
KG-7	Naples Beach	porcelanite	3.94	2.97	9.81	392	215	249
KG-8	Naples Beach	siliceous mudstone	5.99	4.02	18.40	407	402	307
KG-10	Naples Beach	siliceous-calcareous mudstone	4.63	2.30	19.85	412	434	429
KG-11	Naples Beach	calcareous-siliceous rock	2.92	1.27	11.66	414	255	399
KG-30	Naples Beach	diatomaceous mudstone	7.41	5.81	30.39	400	665	410
KG-31	Naples Beach	phosphatic calcareous diatomaceous shale	6.35	2.45	25.98	396	568	409
KG-32	Naples Beach	phosphatic calcareous diatomaceous shale	7.62	2.91	33.53	408	733	440
KG-33	Naples Beach	phosphatic calcareous diatomaceous shale	7.64	2.65	35.81	402	783	469
KG-34	Naples Beach	phosphatic calcareous diatomaceous shale	5.54	2.19	30.16	396	660	544
KG-35	Naples Beach	calcareous shale	4.38	1.12	17.46	419	382	399
KG-36	Naples Beach	calcareous-siliceous mudstone	5.01	1.75	24.64	414	539	492
KG-38	Naples Beach	calcareous-siliceous mudstone	4.01	1.56	17.35	410	379	433
KG-39	Naples Beach	calcareous-siliceous mudstone	4.98	1.80	24.32	412	532	488
KG-41	Naples Beach	phosphatic calcareous diatomaceous shale	16.35	5.78	91.48	399	2001	560
KG-14	Lions Head	mudstone	2.28	0.73	10.20	415	223	447
KG-15	Lions Head	porcelaneous shale	4.07	0.72	20.41	419	446	501
KG-16	Lions Head	dolomitic porcelaneous shale	5.82	4.72	38.92	417	851	669
KG-17	Lions Head	phosphatic calcareous shale	7.36	2.40	44.36	418	970	603
KG-18	Lions Head	clayey dolostone	0.80	0.11	2.28	421	50	285
KG-19	Lions Head	dolostone	0.75	0.32	4.17	419	91	556
KG-20	Lions Head	shale with prominent white bands	4.03	0.63	19.29	423	422	479
KG-22	Lions Head	siliceous calcareous mudstone	7.06	3.04	45.18	421	988	640
KG-24	Lions Head	siliceous shale	14.79	6.92	93.67	416	2049	633
KG-25	Lions Head	calcareous-siliceous shale	4.38	1.59	27.03	424	591	617
KG-26	Lions Head	phosphatic calcareous-siliceous shale	7.09	3.18	49.71	424	1087	701
KG-27	Lions Head	phosphatic calcareous-siliceous shale	6.52	2.98	47.24	421	1033	725
KG-42	Lions Head	siliceous shale	12.16	6.78	89.90	418	1966	739
KG-47	Lions Head	glassy chert	0.29	0.11	1.58	422	35	545
Pet. Securities Rembush #1	Santa Maria Valley	phosphatic mudstone?	5.45	6.17	35.63	421	779	654

Lithologic description from Isaacs et al. (1992, 1993); see also Isaacs et al., chapter 21, this volume.

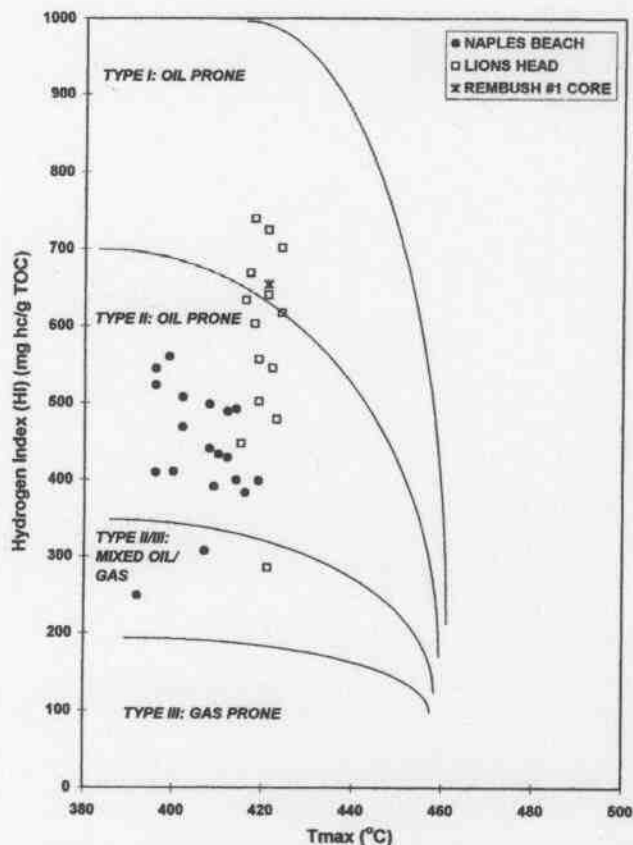


Figure 15.2 Kerogen type and maturity plot of all Monterey Formation samples from both Naples Beach and Lions Head. Most samples contain Type II oil-prone kerogen.

15.5h), suggesting that the Naples Beach samples are not altered by weathering. Three samples from Lions Head (KG-16, KG-22, and KG-27) have few or no reactions occurring below 50 kcal/mole (figure 15.6a-c) and have relatively narrow distributions of  $E_a$  values. These data suggest a higher onset-of-generation temperature but faster decomposition rates than the broadly distributed samples from Naples Beach once oil generation begins.

#### Calculated Geological Temperatures of Hydrocarbon Generation Using Kinetic Data

Kinetic data must be evaluated using both distributions of activation energies ( $E_a$ ) and the associated Arrhenius factor ( $A$ ). Kinetic data from experiments using different instruments and techniques can yield different  $E_a$  and  $A$  values. Because changes in  $E_a$  values are somewhat compensated by changes in  $A$  factors, it is not easy to compare relative reactivities by casual inspection of kinetic data. However, relative reaction rates can be compared by utilizing a constant-geologic-heating-rate calculation in order to compare calculated

transformation ratios, generation rates, and vitrinite reflectance. A constant-heating-rate calculation is used strictly to compare rates of kerogen decomposition using reasonable geologic heating rates, typically in the 1–12 °C/m.y. range.

In order to compare reaction rates (i.e., kerogen decomposition rates), both distributed  $E_a$  and  $A$  values were used to model conversion of kerogen at a reasonable geologic heating rate for the Monterey Formation. To determine what heating rate approximates more mature Monterey Formation samples found in the onshore Santa Maria Basin, well temperature and formation data were used to find reasonable heating rates for the comparison of kinetic results. The Exxon Hartnell 1–21 well in the Casmalia field, Santa Maria Basin, includes the top and base of the Monterey Formation at 4995 and 7210 ft, and corresponding ages of approximately 6 and 14 Ma, respectively, a geologic heating rate of 8.5–15 °C/m.y. is needed to reach present-day formation temperatures of approximately 120 °C. The Coastal Oil and Gas Corporation's Careaga #3 well in the deep San Antonio–Los Alamos Syncline of the Santa Maria Basin has a geothermal gradient of approximately 1.1 °C/100 ft. The geologic heating rates for the top and base of the Monterey Formation are calculated to be approximately 18 and 11 °C/m.y., respectively. Therefore, an average geologic heating rate of 10 °C/m.y. is a reasonable approximation to compare relative kerogen decomposition rates in the onshore Santa Maria Basin. These temperature data also indicate that the present-day Monterey Formation is at fairly high temperatures (>160 °C) at this locality. This is in reasonable agreement with the work of Williams et al. (1994), who reported an average geothermal gradient of 43.67 °C/km for the Sisquoc and Monterey Formations. At 43.67 °C/km the Monterey Formation in the Coastal Oil and Gas Corporation's Careaga #3 well would be at approximately 146–156 °C.

We arbitrarily define the onset of petroleum generation as the temperature at which the transformation of kerogen reaches 10%. Peak generation temperatures, which would be the geologic equivalent of  $T_{max}$  values of the generation rate curve at a given heating rate, are also used to compare reaction rates.

These definitions of the oil window are based on petroleum yields from the decomposition of kerogen rather than maturation parameters such as vitrinite reflectance (%  $R_o$ ) and, when properly correlated,  $T_{max}$  values. Maturation parameters are indicative of the maximum thermal exposure of a kerogen but do not account for transformation differences at a given temperature due to differences in kerogen conversion ki-

Table 15.2 Geochemical Screening Results on Extracted Rock Samples (Selected Samples Only)

Sample No.	Total Organic Carbon (wt. %)	Oil Content (mg oil/g rock)	Oil Potential (mg oil/g rock)	T <sub>max</sub> (°C)	Potential Yield (bbls/acre-ft)	Hydrogen Index (HI) (mg hc/g TOC)
KG-1	10.49	2.53	51.65	396	1130	492
KG-2	15.83	3.52	82.50	408	1804	521
KG-4	15.89	5.26	80.79	390	1767	508
KG-6	4.76	0.82	17.62	420	385	370
KG-7	3.41	0.86	8.29	385	181	243
KG-8	5.04	1.67	16.32	406	357	324
KG-10	4.23	0.49	15.91	417	348	376
KG-11	2.85	0.36	11.17	417	244	392
KG-30	5.80	1.56	23.39	412	512	403
KG-16	3.94	0.22	26.39	418	577	670
KG-22	4.90	0.16	30.43	421	666	621
KG-27	4.06	0.13	24.14	418	528	595
Pet. Securities						
Rembrush #1	1.89	0.40	9.62	408	210	509

See table 15.1 for location and lithology.

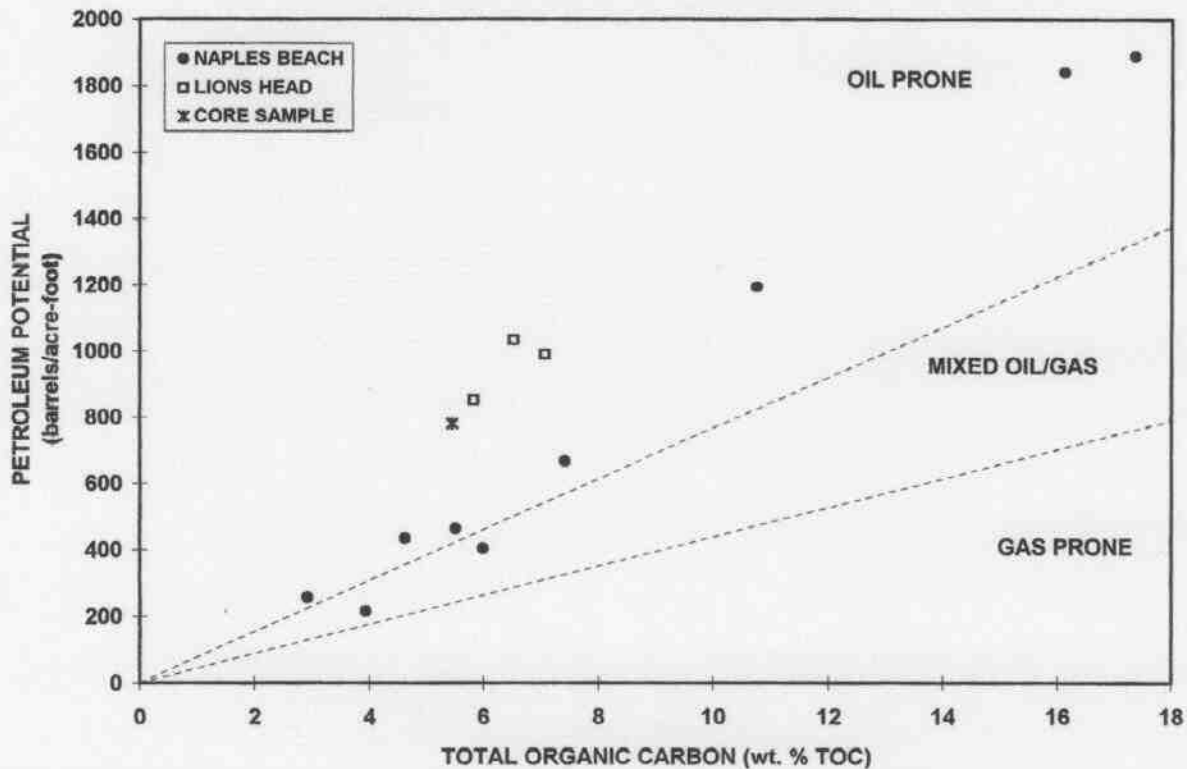


Figure 15.3 Cross-plot of relative petroleum potential and total organic carbon content of the Monterey Formation samples studied in detail. The Naples Beach samples have a broad range of petroleum potentials, whereas the three Lions Head samples are very similar to each other.

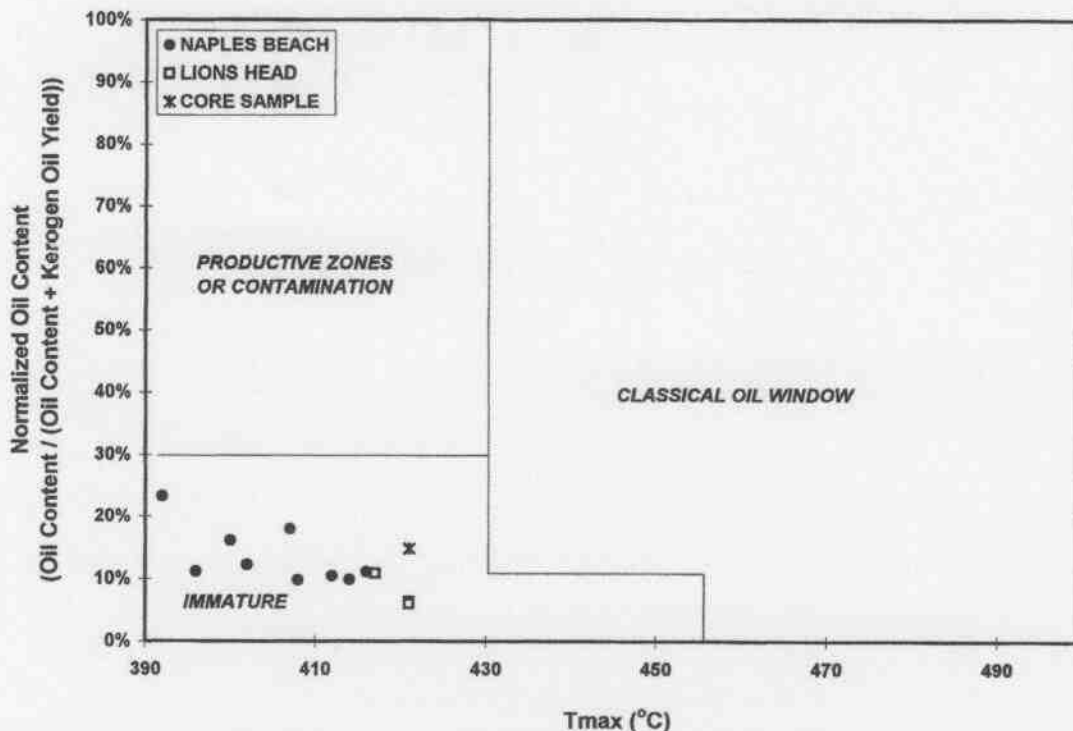


Figure 15.4 Comparison of normalized oil contents to  $T_{max}$  of selected Monterey Formation samples. Based strictly on the low peak pyrolysis temperatures, the samples would be judged to be immature. However, the normalized oil contents are  $\geq 10\%$ , which is indicative of unusually high amounts of oil at low maturity.

netics. For example, at a vitrinite reflectance of 0.70%, one kerogen may be 10% converted, whereas a second kerogen is 20% converted, strictly because of differences in reaction kinetics that result from inherent compositional differences in the organic matter. *These reactivity differences in the rates of kerogen decomposition can result in different levels of conversion at equivalent thermal exposure.* In turn, this may affect the timing of initial and peak petroleum generation. Therefore, a conversion-based definition of the onset of generation and peak generation has been utilized in this evaluation.

The calculated transformation rate curves using a  $10^\circ\text{C}/\text{m.y.}$  constant-heating-rate calculation for five selected Monterey Formation samples are shown plotted against temperature (figure 15.7). The three left-most transformation rate curves represent Naples Beach samples (KG-6, KG-1, and KG-11), all of which have both a broad pyrolysis profile and distribution of activation energies. These transformation rate curves represent the variability of Monterey Formation samples having a broad distribution of activation energies (see figure 15.5a-h), although KG-11 represents what we think is a maturity shift in this group. Organic matter in KG-11 is thought to be of higher maturity, based on

a higher  $T_{max}$  value and computed onset of generation temperature, while still having a broad distribution of activation energies. Note the similarity in the slopes of the transformation rate curve for sample KG-11 to those of KG-1 and KG-6. Sample KG-10 is similar to KG-11, representing more mature organic matter in this group. These two samples were included in CMOGS to represent siliceous-calcareous mudstones located within the lower calcareous-siliceous member (Isaacs et al. 1992). They are from the lower part of the Naples Beach section and consist of opal-CT mudstones below the opal-A/opal-CT transition zone (Isaacs et al. 1992; Isaacs et al., chapter 21, this volume).

Samples KG-16 and KG-22, representing Monterey Formation samples having a narrow decomposition profile and distribution of activation energies, have transformation rate curves that reach 10% conversion of kerogen at higher temperatures than the first group of Monterey samples (figure 15.6a-c). Samples in this group also have a steeper slope of the transformation rate curve, indicative of the narrower distribution of activation energies. Note that the KG-22 transformation rate curve intersects the KG-6 transformation rate curve at approximately 50% kerogen conversion. Ki-

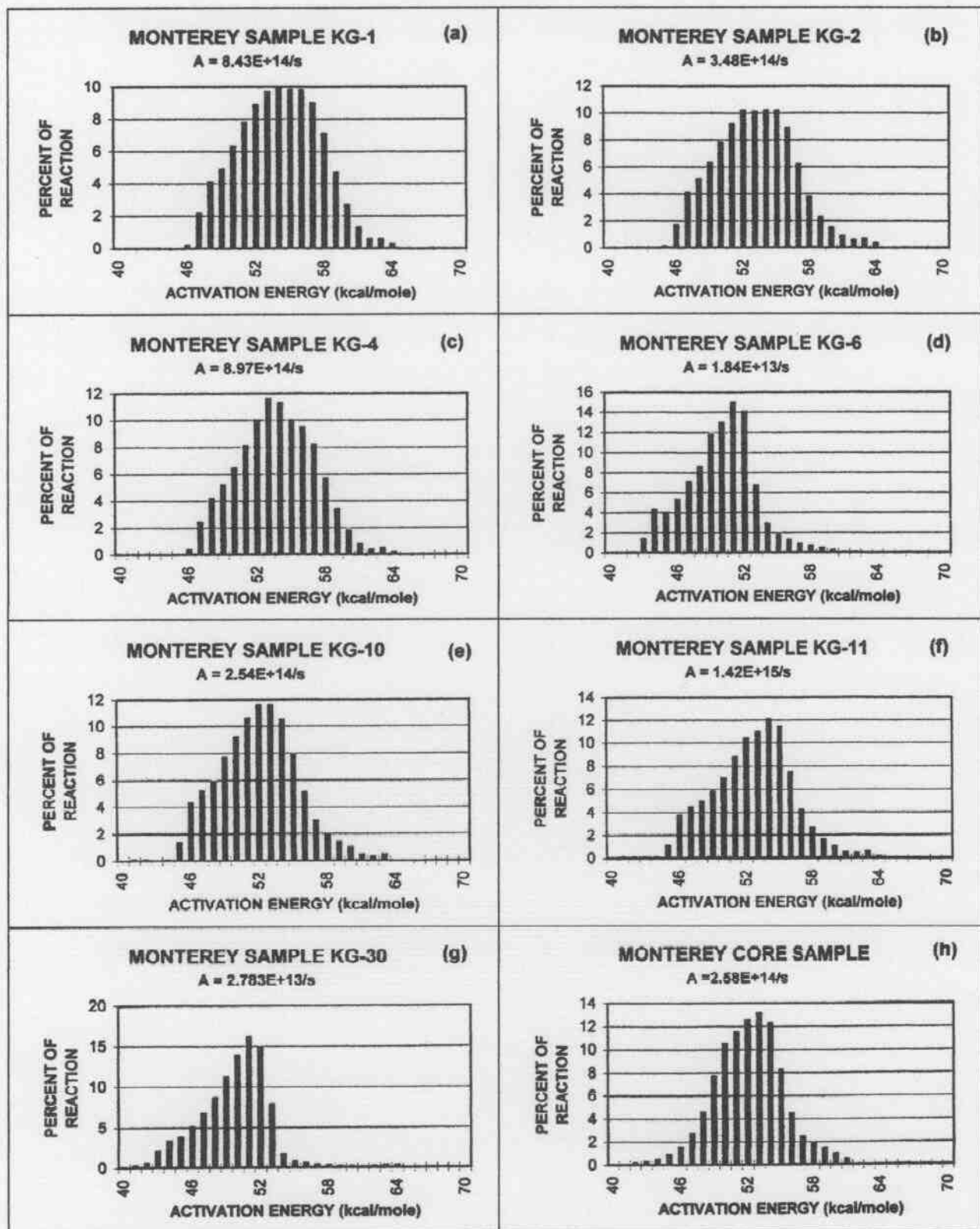


Figure 15.5 (a-h) Bar graphs of activation energy distributions and Arrhenius constants ( $A$ ) from open-system pyrolysis experiments on selected Monterey Formation samples. Naples Beach outcrop and the control core samples all have very broad distributions of activation energies, indicative of complex chemical composition and structure.

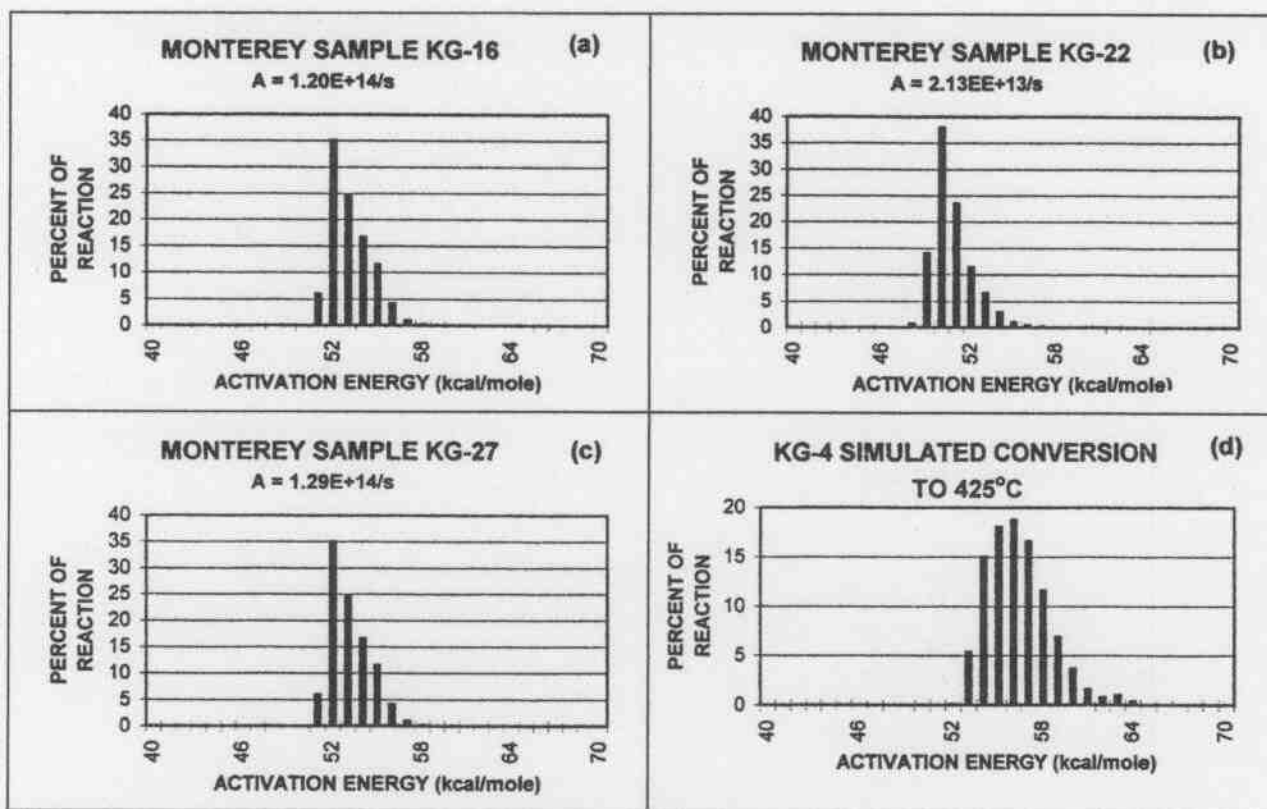


Figure 15.6 (a–c) Bar graphs of activation energy distributions and Arrhenius constants ( $A$ ) from open-system pyrolysis experiments on selected Monterey Formation samples from Lions Head. These samples have very narrow distributions of activation energies, which are more similar to classical Type II kerogens where over 70% of the reaction is described by two to four principal activation energies. (d) Distribution of activation energies for the Naples Beach sample KG-4 after simulated conversion to a  $T_{max}$  value comparable to the Lions Head Monterey Formation samples.

netic assessment of an asphaltene fraction of an oil from Santa Maria Valley field, where the Rembush control sample originated, follows the KG-6 transformation curve during the first part of the transformation, then shifts and follows the KG-22 transformation curve (Jarvie et al. 1999).

Both groups have similar peak generation temperatures, although there is approximately a 1 °C range among all samples studied at 10 °C/m.y. Calculated vitrinite reflectance values are also shown on this plot using the right  $y$  axis. Note that if lower heating rates were used (e.g., 1 °C/m.y.), the onset of generation and peak generation temperatures would be lower; if higher heating rates were used (e.g., 12 °C/m.y.), the calculated temperatures would be higher.

Broad generation rate curves are intuitively interpreted as resulting from kerogen with a high diversity of bond types and structural configurations. Generation occurs over a wide temperature range as the various bond types are broken. No single activation energy predominates in the distribution; but instead each 1 kcal/

mole increment comprises less than about 10–15% of the total distribution. Narrow generation rate curves are interpreted to be derived from less complex organic matter in terms of composition and structure. Generally, two or three  $E_a$  values describe more than 70% of the kerogen decomposition reaction. Decomposition of kerogen occurs over a narrower range of temperatures than in samples having a broad distribution of  $E_a$  values.

A comparison of rates of kerogen conversion of one sample from each Monterey Formation group to other petroleum source rocks is shown in figure 15.8. Monterey Formation sample KG-4 reaches the onset of generation and peak generation temperatures much earlier than samples of other kerogen types including other Type II kerogens such as those from the Monterey Formation at Lions Head (KG-16), Kimmeridge Shale, and Woodford Shale. This kerogen and the other broadly distributed kerogens in figure 15.5a–h are collectively identified as group 1 Monterey Formation samples and, more descriptively, as *early oil generators*.

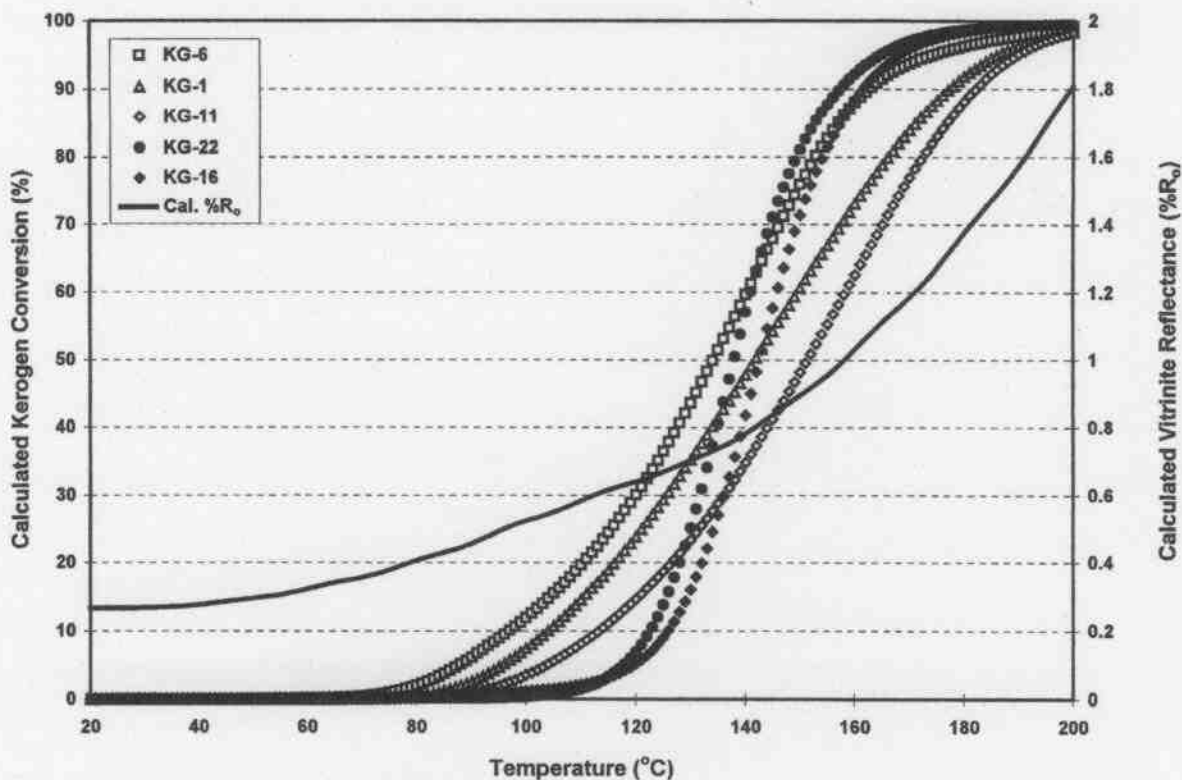


Figure 15.7 Relative kerogen transformation rate and temperature plot calculated from measured kinetic data using a 10 °C/m.y. constant-heating-rate calculation. A range of samples having a broad distribution of activation energies from Monterey Formation group 1, such as KG-1, KG-6, and KG-11 from Naples Beach, reach 10% conversion at lower temperatures than the Lions Head samples, which have a narrow distribution of activation energies, such as KG-16 and KG-22. Note the slope of the kerogen conversion profiles, which also reflect the decomposition rates. Calculated vitrinite reflectance values are plotted on the alternate y axis.

Lions Head sample KG-16, representative of the narrowly distributed kerogens of figure 15.6a-c, decomposes at a rate similar to that of other Type II kerogens such as those from the Kimmeridge Shale (similar to Type II-B defined by Hunt, Lewan, and Hennet [1991]). These samples are collectively identified as group 2 Monterey Formation samples and, descriptively, as *moderately early oil generators*. Other kerogens such as the Type II Woodford Shale (Type II-D defined by Hunt, Lewan, and Hennet [1991]) and the Type I Green River Shale are described as *late oil generators*. Note that all kerogen data reported in figure 15.8 are from open-system pyrolysis, and are discrete-model kinetic determinations.

Figure 15.9 summarizes the calculated onset of generation temperatures (10% conversion) and peak generation temperatures using a 10 °C/m.y. heating rate for all samples. We are suggesting that early oil generators be defined as any samples having calculated onset of generation temperatures of under 110 °C at this heating rate. The group 1 Monterey Formation

samples from Naples Beach (KG-1, KG-2, KG-4, KG-6, KG-7, KG-8, KG-10, KG-11, and KG-30) and the Rembush core sample reached 10% kerogen conversion at temperatures ranging from 97 °C to 114 °C. Interestingly, Kornacki (1993) suggested, from oil C<sub>7</sub> hydrocarbon data, that certain Monterey oils were expelled from the source rock at approximately 100 °C. This is in agreement with the data from the kerogen kinetic calculations even though the constant-heating-rate model is meant only to provide a generalized thermal history. Calculated oil expulsion temperatures from four oils analyzed by high-resolution C<sub>7</sub> gas chromatography in the CMOGS study (Oil 3 from the Orcutt field, Oil 4 from the Point Pedernales field, Oil 5 from the Lompoc field, and Oil 8 from the Zaca field; see detailed descriptions by Tennyson and Isaacs, chapter 12, this volume) have higher predicted expulsion temperatures that range from 110 °C to 115 °C (D. M. Jarvie, unpublished data, 1996).

Group 2, the moderately early oil generators, reach the onset of generation at temperatures between

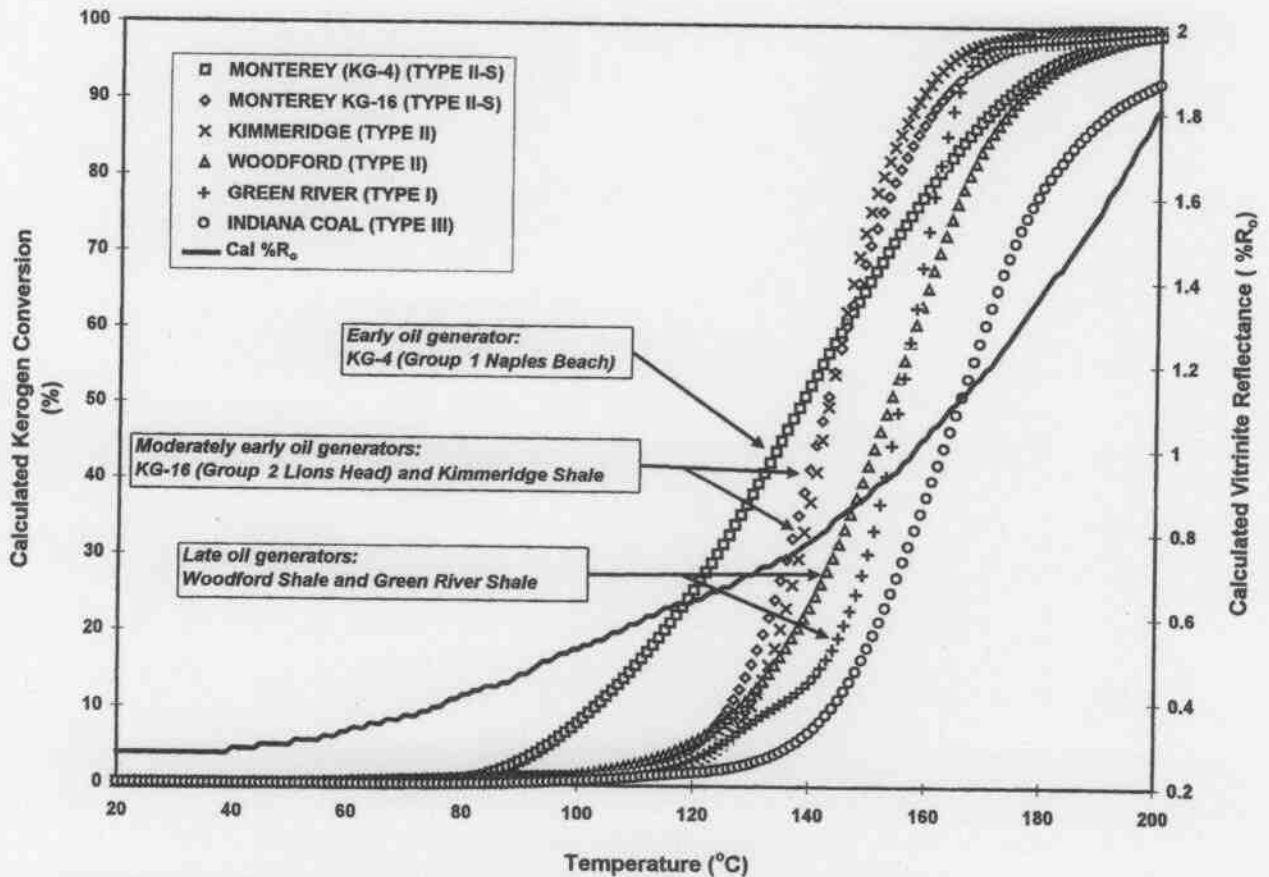


Figure 15.8 Comparison of the relative rates of kerogen conversion using a  $10^{\circ}\text{C}$  constant-heating-rate calculation for Types I, II, and III kerogens. The group 1 Monterey Formation samples are shown to convert at much lower thermal exposure than the other kerogens represented. The group 2 Monterey Formation samples are similar to more labile Type II marine kerogens such as those from the Kimmeridge Shale. Other Type I, II, and III kerogens require higher thermal exposure to crack. Calculated vitrinite reflectance values are plotted along the alternate  $y$  axis.

$120^{\circ}\text{C}$  and  $135^{\circ}\text{C}$  at a  $10^{\circ}\text{C}/\text{m.y.}$  heating rate. This group includes the Lions Head samples KG-16, KG-22, and KG-27, as well as other labile Type II kerogens such as the Kimmeridge Shale. Kornacki (1993) also found from oil  $C_7$  hydrocarbon data that other high-quality Monterey Formation oils were expelled from what he described as siliceous source rocks at approximately  $125\text{--}130^{\circ}\text{C}$  (i.e., at temperatures very similar to these group 2 Monterey Formation petroleum source rocks). Hornafius (1994) suggested that a temperature of  $127^{\circ}\text{C}$  is required to generate a  $20^{\circ}$  API oil, and  $166^{\circ}\text{C}$  to generate a  $30^{\circ}$  API oil. However, the Coastal Oil and Gas Co. Sharkey well in the San Antonio–Los Alamos Syncline produced  $38^{\circ}$  API oil with reservoir temperatures in the  $140\text{--}150^{\circ}\text{C}$  range.

More refractory Type II kerogens such as in the Woodford Shale reach the onset of generation at higher temperatures and are referred to as late oil generators. These reach the onset of generation at temperatures above  $135^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{m.y.}$  Lower

heating rates are probably more realistic for these other non-Monterey Formation source rocks such as the Kimmeridge Shale, but the  $10^{\circ}\text{C}/\text{m.y.}$  heating rate was used only to allow comparison of the relative reactivities of these different petroleum source rocks. If the Kimmeridge Shale or other source rocks were modeled at lower heating rates, they would reach the onset of generation at lower temperatures. For example, at  $1^{\circ}\text{C}/\text{m.y.}$ , the Kimmeridge Shale would reach 10% transformation at a temperature about  $8^{\circ}\text{C}$  lower, that is, at about  $118\text{--}122^{\circ}\text{C}$ .

There are two Monterey Formation samples from Naples Beach (KG-10 and KG-11) intermediate between the two Monterey Formation groups that reach the onset of generation between  $110^{\circ}\text{C}$  and  $120^{\circ}\text{C}$ . As stated previously, these samples are interpreted to represent slightly more mature or altered facies of the early oil generators and, as such, require slightly higher thermal exposure to crack.

Whether the differences in the group 1 early oil

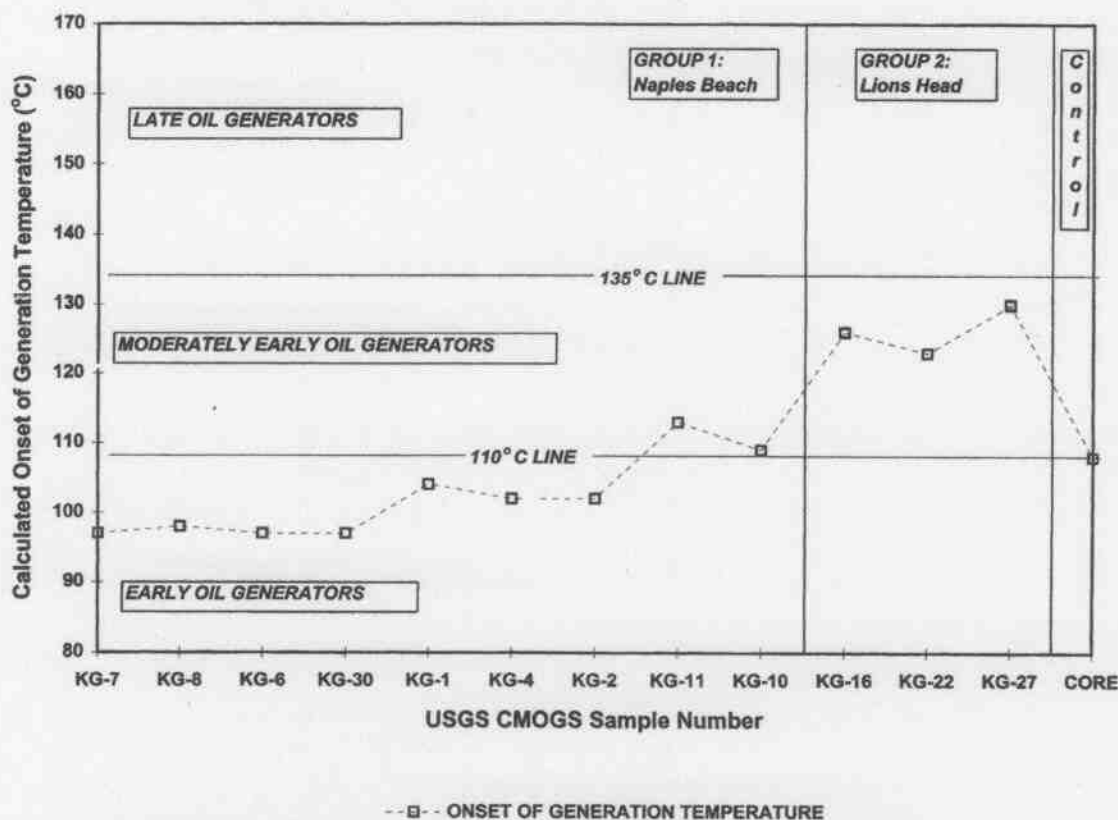


Figure 15.9 Calculated onset of generation temperatures (10% transformation) using a  $10^{\circ}\text{C}/\text{m.y.}$  constant-heating-rate calculation by sample location and stratigraphy. Samples reaching 10% conversion of kerogen at  $110^{\circ}\text{C}$  or less are denoted as *early oil generators*; samples reaching 10% conversion between  $110^{\circ}\text{C}$  and  $130^{\circ}\text{C}$  are denoted as *moderately early oil generators*. The Type II Woodford Shale and the Type I Green River Shale samples reach 10% conversion at temperatures above  $130^{\circ}\text{C}$  at this heating rate and would be labeled as *late oil generators*.

generators and the group 2 moderately early oil generators are indicative of differences in organic facies or due to maturity differences is a key issue. An apparent difference in facies could result from a restructuring of kerogen during maturation as carbon and oxygen are lost, primarily as carbon dioxide. This would cause an apparent enrichment in hydrogen-to-carbon (H/C) ratios, whereas oxygen-to-carbon (O/C) ratios would decrease. Restructuring would probably result in a slightly more refractory kerogen having different chemical composition, structure, and properties. If this were the case, group 1 Monterey Formation kerogens, after losing much carbon dioxide to reach an O/C value  $< 0.10$ , would be restructured such that they would then behave as group 2 Monterey Formation samples.

### Elemental Analysis

Rates of kerogen decomposition calculated from kinetic data reflect kerogen composition and structural differences. As the complex kerogen or even protokerogen (Peters, Rohrback, and Kaplan 1981) moiety

cracks to form petroleum, the weakest bonds are broken first. If the organic matter is relatively homogeneous, the decomposition of kerogen occurs over a narrow temperature range. This is reflected in the kinetic parameters for the Green River Shale, which in a kinetic assessment has over 80% of the kerogen decomposition reaction occurring at a single activation energy. Note also the steep slope of the transformation rate curve for the Green River Shale in figure 15.8. Broader decomposition profiles as seen in the Naples Beach samples and the Rembush core sample are suggestive of a more complex chemical composition including higher concentrations of oxygen, sulfur, and nitrogen in the kerogen.

Sulfur has been widely suspected to play a key role in early oil generation (Orr 1986), and sulfur content has been postulated as one potential indicator of an early oil-generating kerogen. A plot of atomic S/C ratios and calculated onset of generation temperatures at  $10^{\circ}\text{C}/\text{m.y.}$  from the kinetic data for a few of these Monterey samples is shown in figure 15.10. The S/C ratio

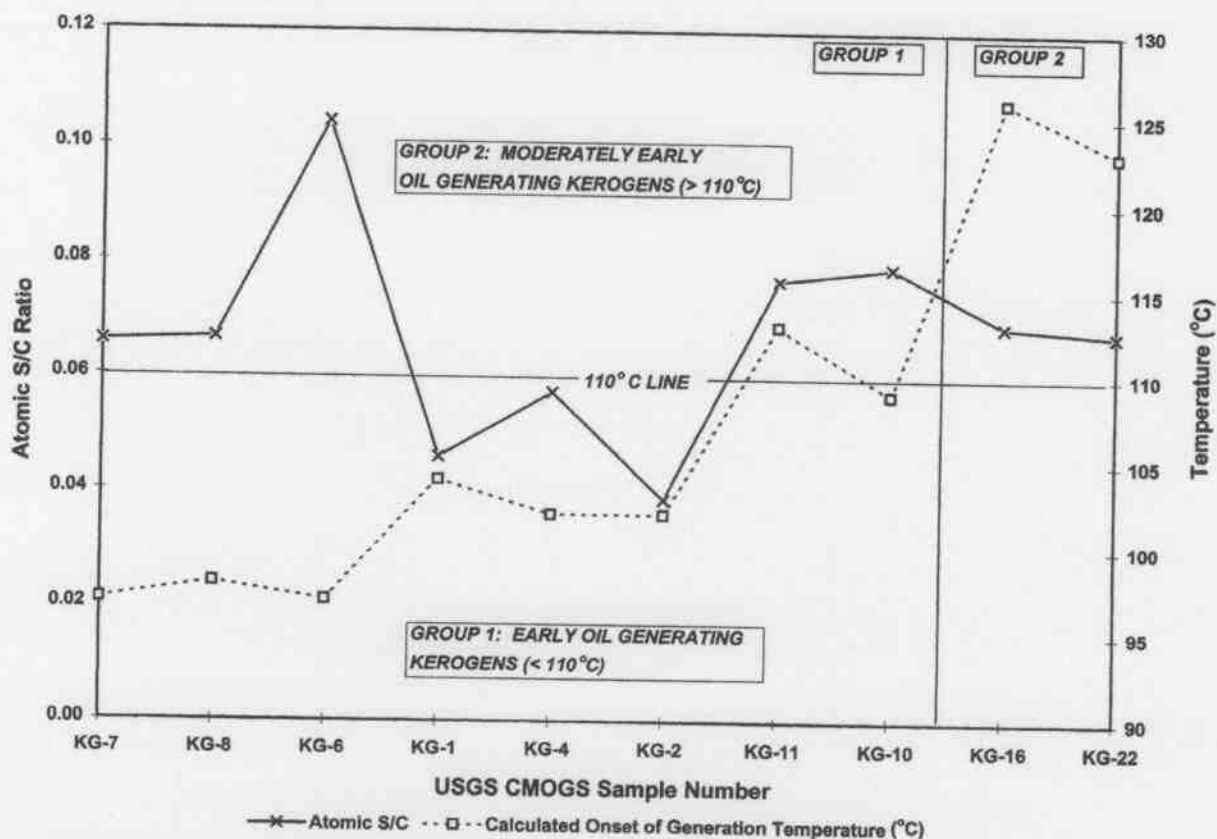


Figure 15.10 A plot of atomic S/C ratios and calculated onset of generation temperatures (alternate *y* axis) by sample (in stratigraphic sequence by location) illustrates that most samples evaluated in this study would be classified as Type II-S using the 0.04 cutoff of Orr (1986). A relationship between sulfur content and early oil generation is not evident from these data. Atomic S/C ratios are from Laboratory 13 in table 25.10 (Rullkötter et al., chapter 25, this volume).

is plotted on the left *y* axis, and the calculated onset of generation temperature is on the right *y* axis versus sample designation. Samples are arranged according to their stratigraphic positions at Naples Beach and Lions Head. Although most samples would be classified as sulfur-rich Type II-S kerogens, note the lack of correlation of S/C ratios to the calculated onset of generation temperatures for both groups. This lack of correlation would hold true regardless of the heating rate utilized. However, this is not to say that sulfur does not play a role in the rate of kerogen decomposition of other petroleum source rocks, but it does not explain the differences in rates of kerogen decomposition between the group 1 and group 2 Monterey kerogens described in this study.

On the other hand, atomic O/C ratios show good correlation to calculated onset of generation temperatures by sample (figure 15.11). Group 1 samples, which all have a broad distribution of activation energies and whose kerogen would be predicted to decompose at lower temperatures, have very high O/C ratios. The group 2 samples from Lions Head, which have tem-

peratures indicative of moderately early oil generation and have a narrower distribution of activation energies (KG-16 and KG-22), have much lower O/C ratios. Thus, there appears to be a direct relationship between the oxygen content and early transformation of kerogen.

Though not as obvious, the nitrogen content also tracks the calculated onset of generation temperatures. Stankiewicz et al. (1996) noted that  $C_1$ - $C_5$  alkylpyrroles were major products in flash-pyrolysis gas chromatographic-mass spectrometric analysis of a Naples Beach kerogen. Although there is variation in the elemental data reported by various laboratories participating in this study, the relative relationship of these atomic ratios or total organic sulfur contents to the calculated onset of generation temperature remains consistent.

The group 1 early oil-generating Monterey kerogens probably should be referred to as Type II-ONS kerogens, reflecting (1) their much higher oxygen contents as well as slightly higher nitrogen contents, both of which appear to be directly related to early kerogen conversion, and (2) their higher sulfur contents. How-

