1986

Biomarker Geochemistry of the Miocene Monterey Formation, West San Joaquin Basin, California: Implications for Petroleum Generation

Michael A. Kruge
krugem@mail.montclair.edu

MSU Digital Commons Citation

Kruge, Michael A., "Biomarker Geochemistry of the Miocene Monterey Formation, West San Joaquin Basin, California: Implications for Petroleum Generation" (1986). *Department of Earth and Environmental Studies Faculty Scholarship and Creative Works*. 59.
https://digitalcommons.montclair.edu/earth-environ-studies-facpubs/59

Preprint:
Michael A Kruge,
Biomarker geochemistry of the Miocene Monterey Formation, West San Joaquin Basin, California: Implications for petroleum generation. Organic Geochemistry, Volume 10, Issues 1–3, 1986, Pages 517-530.
https://doi.org/10.1016/0146-6380(86)90050-1.
(http://www.sciencedirect.com/science/article/pii/0146638086900501)

Biomarker geochemistry of the Miocene Monterey Formation, West San Joaquin Basin, California: Implications for petroleum generation

Michael A Kruge

Department of Geology and Geophysics
University of California, Berkeley, CA 94720, U.S.A.

Present address: Sohio Petroleum Co., Petroleum Geochemistry Group,
4440 Warrensville Center Rd., Cleveland, OH, 44128 U.S.A.

Abstract: Much of the Miocene Monterey Formation of California is rich in biogenic sediment, especially organic matter and silica. Because of the geologic structure, the Monterey in the subsurface near Lost Hills in the San Joaquin Basin forms a natural laboratory for the study of the diagenetic responses of these materials. Rocks of similar age and lithology are buried to depths ranging between 500 and 3500 m, and are thus exposed to a temperature range of 45–130°C. The diagenetic progression of silica from opal-A to opal-CT to microquartz is well-documented in Monterey burial history studies. However, diagenetic indicators need to be established below the depth of complete conversion of opal-CT to quartz, which may be very shallow (1500 m or less at Lost Hills). Conventional maturity indicators are problematic. The scarcity of vitrinite in many Monterey samples hampers reflectance measurements. In addition, values that are measured may be anomalously low. Maximum pyrolysis temperatures are depressed, due in part to high heavy bitumen content. Biomarker geochemistry provides effective alternative maturity indicators. Of particular interest are the stereochemical variations observed in the assemblages of steranes and triterpanes extracted from oil well core samples. For example, the 20S/20R ratio of 5α(H), 14α(H), 17α(H)-24-ethylcholestane increases from 0.09 to 0.56 over the depth range cited. Samples from petroleum accumulation zones are distinguished by anomalously mature biomarker assemblages considering their depth of burial. This indicates that these bitumens are as mature as the deepest non-production zone sample (3430 m), even though they are from much shallower depths (580–1572 m). Other maturity (and/or migration) indicators confirm this, such as the relative increases in amounts of 14β(H), 17β(H)-steranes, rearranged steranes and tricyclic terpanes. Thus, it appears that any immature indigenous bitumen in production zone samples is overwhelmed by a mature component, which presumably migrated updip, from deeper, warmer strata. Since much oil is produced from shallow, organic-rich fractured Monterey shales, early in situ generation has previously been hypothesized. However, while both source and reservoir rock are lithologically similar and lie within the same formation, biomarker geochemistry indicates that substantial generation occurs only in deeply buried Monterey shales.

Keywords: California; Monterey Formation; steranes; hopanes; maturity indicators; San Joaquin Basin; Lost Hills oil field; diasteranes; tricyclic terpanes; diagenesis

INTRODUCTION

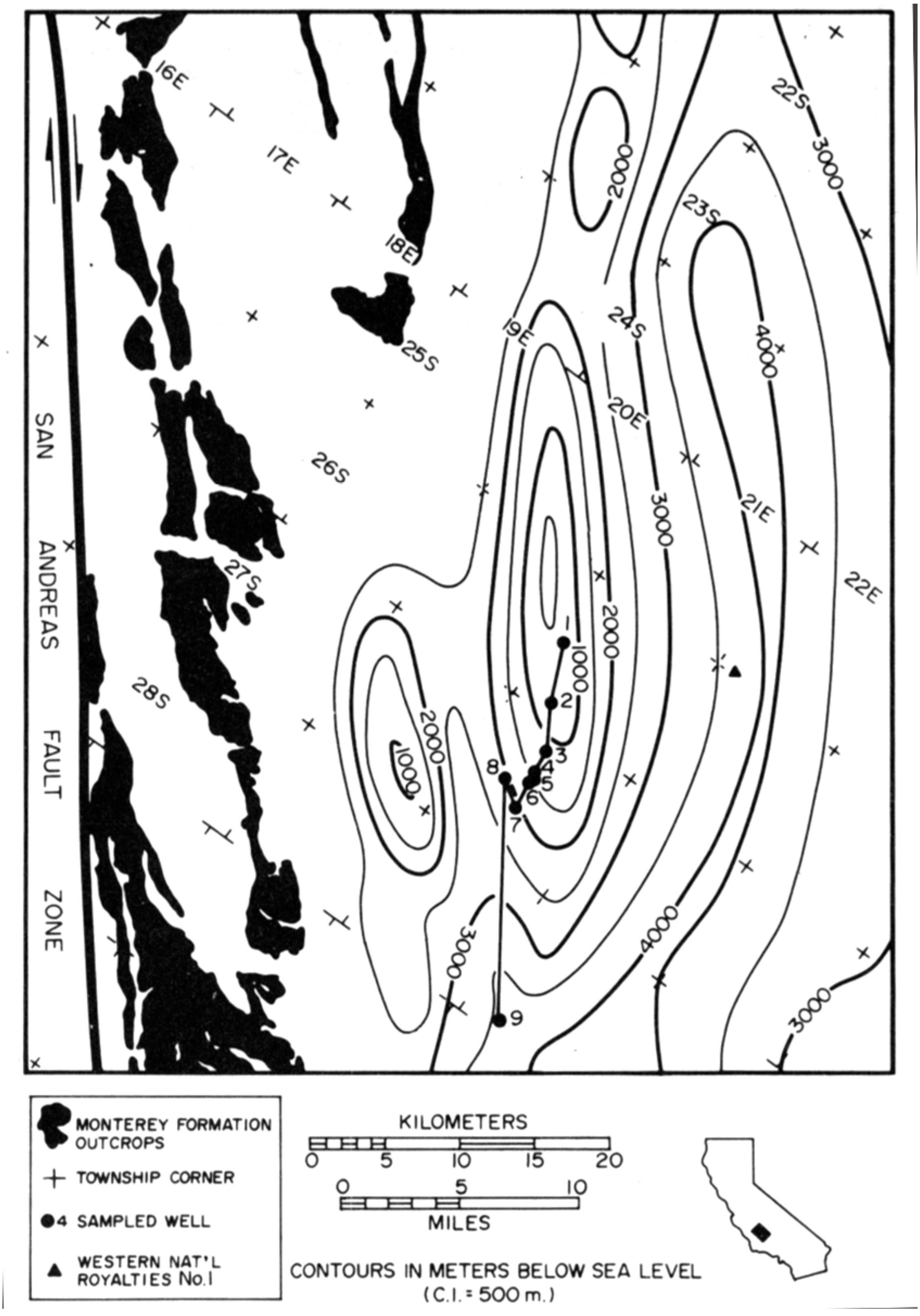
The Miocene Monterey Formation of California has come under increased scrutiny lately as it contains some of California's most important petroleum source and reservoir rocks. However, there have been relatively few published investigations of Monterey organic diagenesis until very recently. In an early study, Philippi (1965) documented changes as a function of burial depth in the distribution of hydrocarbons extracted from shales of the Monterey and younger formations in the Ventura and Los Angeles Basins. He found that for Monterey shales (upper Miocene), only those which had been subjected to geothermal temperatures of 120-140°C or greater yielded extracts resembling crude oils. In other studies, Giger and Schaffner (1979, 1981) found that a gradual loss of unsaturation in steroids and loss of stereospecificity in isoprenoids correlated with advancing diagenesis in rocks from the southern Santa Barbara County coast. Kvenvolden (1970) found high carbon preference indices for both normal fatty acids and alkanes in a sample from the same area, indicating that it is of low diagenetic grade. Isaacs (1980) performed elemental analysis (C, H, 0) on kerogens separated from Monterey rocks, also collected along the coast near Santa Barbara, finding that the O/C ratio decreased with advancing diagenesis.

Seifert (1978) and Seifert and Moldowan (1978, 1979) used Monterey rock and oil samples in developing biomarker techniques for maturity determination and oil-source rock correlation. Claypool et al. (1979) analyzed the organic matter in samples from the Point Conception stratigraphic test well, which penetrated the Monterey Formation. They found that a large portion of the organic matter in the Monterey samples was solvent extractable, suggesting either the presence of non-indigenous hydrocarbons or the generation of hydrocarbons at relatively low thermal maturity levels. A follow-up study (King and Claypool, 1983) applied biomarker techniques to the same samples. The extract-rich samples were shown to contain bitumens of higher maturity than in surrounding rocks, lending credence to the migration hypothesis. Surdam and Stanley (1981) compared the diagenesis of silica and organic matter in Monterey rocks from the Pismo Syncline in San Luis Obispo County. They report an association between hydrocarbon occurrence and the completion of the opal-CT to quartz diagenetic conversion. This may be the result of either the development of fracture porosity in the more brittle quartz, with subsequent filling by non-indigenous hydrocarbons, or of early hydrocarbon generation. Kablanow and Surdam (1983) present evidence suggesting predominantly heavy oil generation in the Monterey Formation of the Huasna Basin at depths of 3-4 km. This implies generation temperatures > 130 °C in this relatively warm basin. Curiale et al. (1985) argue that Monterey oils from the San Joaquin, Los Angeles, Ventura and Santa Maria Basins originated from clastic-poor source beds early in the maturation sequence. Graham and Williams (1985) conclude that petroleum generation in the Monterey Formation of the San Joaquin basin is restricted to the very deep synclinal areas.

In several California oil fields, notably Lost Hills, petroleum is produced directly from fractured Monterey shales. Thus, the Monterey Formation in these fields has been cored extensively for reservoir evaluation. Lost Hills was chosen for the present study in part because of this availability of material. Conveniently, due to the geologic structure, the Monterey in the subsurface near Lost Hills in the San Joaquin Basin (Fig. l) forms a natural laboratory for the study of diagenesis. Rocks of similar age and lithology are buried to depths ranging between 500 and 3500 m, and are thus exposed to a temperature range of 45-l30 °C.

<Figure 1>

Fig. 1. Generalized structure of the west central San Joaquin Basin , showing locations of sampled wells. See Table 1 for well identification. Contoured on an upper Miocene horizon (see Kruge, 1985). Subsurface geology after Graham and Williams (1985). Surface geology after Jennings (1958) and Smith (1964). Note inset map of California.



METHODS

Sample preparation

Full procedural details are presented in Kruge (1985). Briefly, representative conventional core samples were chosen from the suite of Lost Hills area Monterey rocks (Fig. 2 and Table 1) previously screened by pyrolysis-FID (Rock- Eval) (Kruge, 1983; 1985). After powdering, the rock was extracted by repeated sonication, in either 50:50 toluene: methanol or 50:50 CH_2Cl_2:methanol. After removal of asphaltenes, the non-aromatic hydrocarbon fraction was isolated with preparative TLC (hexane developer).

<Figure 2>

<Table 1>

GC and GC-MS conditions

A Varian 3700 gas chromatograph was employed with a 0.25 mm x 25 m OV-1 fused silica capillary column (He carrier gas, T_{inj} = 270 °C, T_{det} = 300 °C). Column temperature was held at ~ 30 °C until solvent elution was complete, then the temperature was reset to 100 °C and the program was begun (100-310 °C at 4 °C min^{-1}, then isothermal at 310 °C for 10 min).

Gas chromatography - mass spectrometry was performed on a Varian 3700 gas chromatograph (0.25 mm x 30 m column, SE-52) connected to a Kratos MS-25 mass spectrometer with modified Logos Spectratech software for data collection and processing. GC conditions were the same as above. The mass spectrometer was set to a scan time of 1.3 sec and an ionizing voltage of 70 eV.

Chromatogram peaks were identified by elution order and, in the case of mass chromatograms, also by reference to molecular ions and key fragment ions (Kruge, 1985). Peak areas form the basis for the ratios used in the text. They were determined by manual quantitation on the following mass chromatograms: m/z 191 (terpanes) and m/z 217 (steranes).

Pyrolysis - gas chromatography

Pyrolysis-GC of extracted, powdered whole-rock samples was done on a proprietary apparatus similar to that described by Dembicki et al. (1983).

Shorthand notation

Although a large number of polycyclic compounds are recognized in this study, most can be grouped in several homologous series. A shorthand system will be used in the text, as follows:

Compound class	*Configuration*	*Shorthand*
Steranes	5β(H),14α(H),17α(H)	$\beta\alpha\alpha$
	5α(H),14α(H),17α(H)	$\alpha\alpha\alpha$
	5α(H),14β(H),17β(H)	$\alpha\beta\beta$
Diasteranes	13α(H),17β(H)	$\alpha\beta$
	13β(H),17α(H)	$\beta\alpha$
Hopanes	17α(H),21β(H)	$\alpha\beta$
	17β(H),21α(H)	$\beta\alpha$ ("moretane")

Fig. 2. Correlation section showing locations of GC samples. Datum is ground level. For location, see Fig. l. The Antelope unit of the McClure Member of the Monterey Formation is upper Miocene. For sample identification, see Table 1.

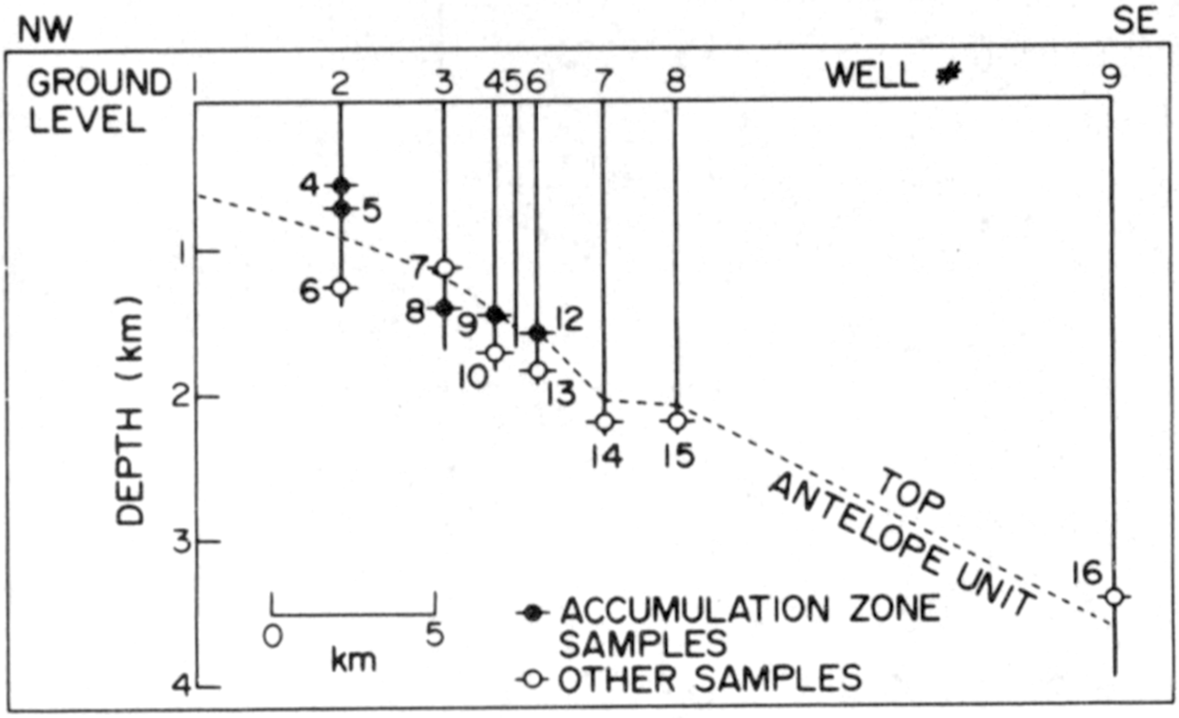


Table 1. Sample identification.

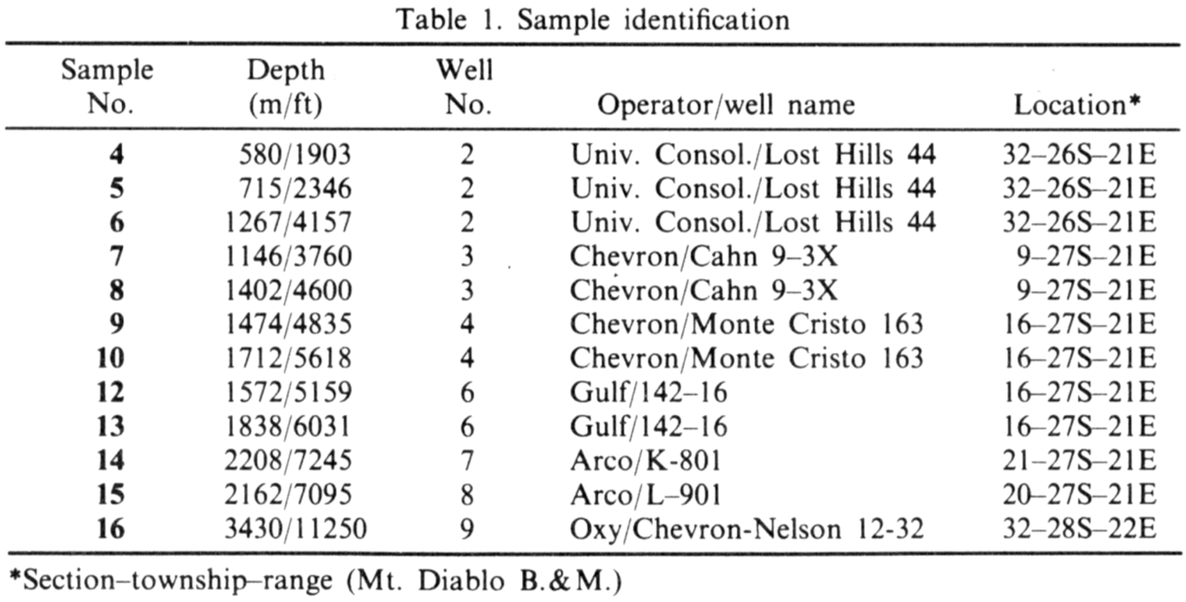


Table 1. Sample identification

Sample No.	Depth (m/ft)	Well No.	Operator/well name	Location*
4	580/1903	2	Univ. Consol./Lost Hills 44	32–26S–21E
5	715/2346	2	Univ. Consol./Lost Hills 44	32–26S–21E
6	1267/4157	2	Univ. Consol./Lost Hills 44	32–26S–21E
7	1146/3760	3	Chevron/Cahn 9–3X	9–27S–21E
8	1402/4600	3	Chevron/Cahn 9–3X	9–27S–21E
9	1474/4835	4	Chevron/Monte Cristo 163	16–27S–21E
10	1712/5618	4	Chevron/Monte Cristo 163	16–27S–21E
12	1572/5159	6	Gulf/142–16	16–27S–21E
13	1838/6031	6	Gulf/142–16	16–27S–21E
14	2208/7245	7	Arco/K-801	21–27S–21E
15	2162/7095	8	Arco/L–901	20–27S–21E
16	3430/11250	9	Oxy/Chevron-Nelson 12-32	32–28S–22E

*Section–township–range (Mt. Diablo B.&M.)

COMPARISON OF DIAGENETIC INDICATORS

A suite of 86 Lost Hills samples was previously analyzed for mineral composition and silica phases by XRD and for organic richness, type and maturity by pyrolysis-FID (Kruge, 1983). XRD showed that the great majority of samples were mineralogically very similar, with biogenic silica and detrital quartz, clays and feldspars as most common. Diatomaceous silica progresses from the original amorphous opal-A to opal-CT and ultimately to microquartz with diagenesis. Silica phase changes in the Monterey Formation are widely used to establish diagenetic zones (e.g. Pisciotto, 1981; Isaacs, 1980). However, the final transformation to quartz occurs in relatively early diagenesis. For example, at Lost Hills, no opal-CT was detectable by XRD below a depth of only 1500 m. Thus, unfortunately, no further diagenetic zonation by silica phases is possible below this depth, even though the sample collection contains core material from as deep as 3430 m. Although silica phase determination is an important diagenetic tool in the Monterey Formation, it must be supplemented by other parameters.

Vitrinite reflectance is the most commonly employed organic maturity indicator. It works well if care is taken not to misidentify as vitrinite other similar macerals. This problem may arise in Monterey samples where low-reflectivity solid bitumen particles are mistaken for vitrinite, giving an overall average reflectance which is too low. A more serious problem in the Monterey is the simple lack of vitrinite. For this study, out of 24 samples submitted for analysis, only 6 had any measurable vitrinite, of which 4 samples had only a few particles (Kruge, 1985). These successful results (Fig. 3), although limited, should help in calibrating other diagenetic indicators.

<Figure 3>

Vitrinite reflectance measurements show the section to be immature. A tentative best fit line is given for the 4 deepest samples, which are remarkable for their low R_o values, even at depths greater than 3 km. Samples from wells 1 and 2 sit at the crest of the anticline, which has been uplifted and partly unroofed. Their relatively higher R_o values are the result of their previous deeper burial and cannot be included in the present-day trend. Similarly, uplifting caused tilting of the opal-CT /quartz diagenetic boundary (Kruge, 1983, 1985). Conventional onset of oil generation ($R_o \sim 0.6 \pm 0.05\%$) is roughly projected to occur at a depth of 4-4.5 km, in accord with vitrinite data from the very deep Miocene rocks of the Paloma oil field, 65 km southeast of Lost Hills (Hood and Castano, 1974). This is well below the depth of complete opal-CT/quartz conversion (< 1500 m), which suggests that the silica phase change has no relation to oil generation, contrary to previous hypotheses (e.g. Surdam and Stanley, 1981; McGuire et al., 1983).

SAMPLE CLASSIFICATION BY GAS CHROMATOGRAPHY

The transformation ratios (pyrolysis $S_1/S_1 + S_2$) calculated on Lost Hills Monterey rocks show a gradual increase with depth (Fig. 4a), but the most prominent features on this figure are the two peaks , at ~600 m and at ~1500 m, which represent the "accumulation zones" . These correspond to the two hydrocarbon production zones in the Lost Hills oil field: the shallow diatomaceous interval and the deeper fractured quartzose zone, termed the "Cahn Pool" of the McClure Member. In the most straightforward interpretation, the accumulation zones would have to be fed by deeper source rock at some distance away.

<Figure 4>

Fig. 3. Vitrinite reflectance data for Lost Hills area samples. Wells 1 and 2 are close to the crest of the anticline, where Miocene rocks have been uplifted. Best fit line applies to samples currently at maximum burial depth.

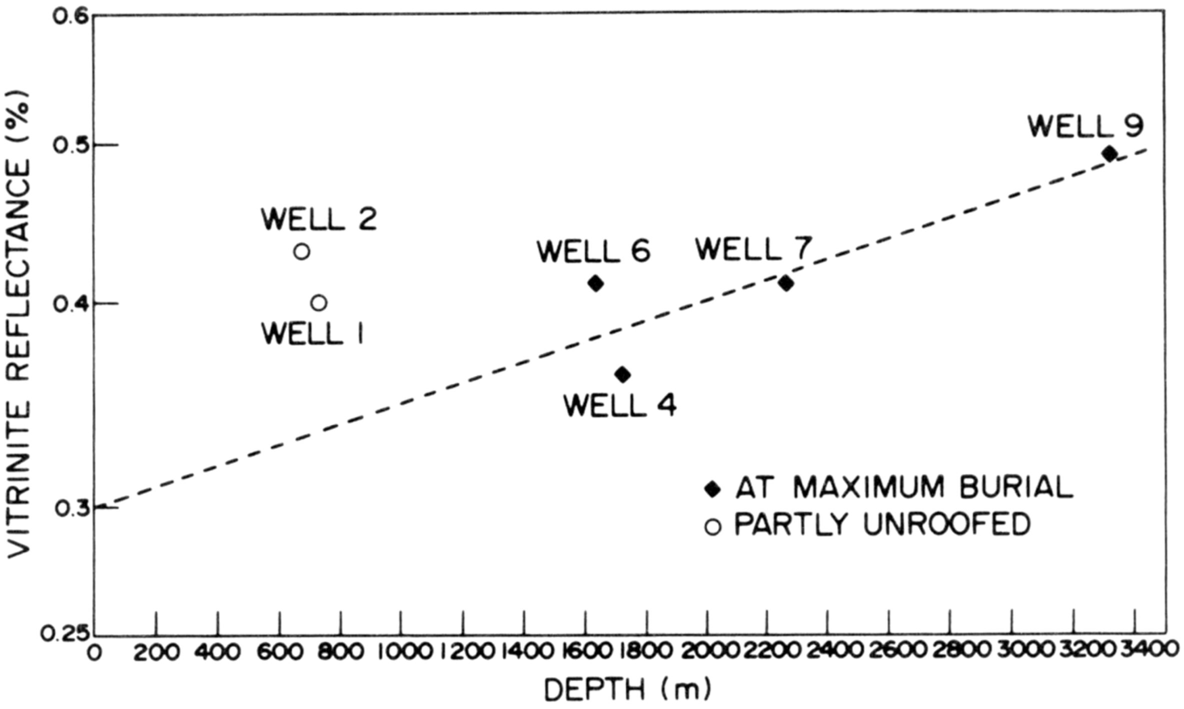
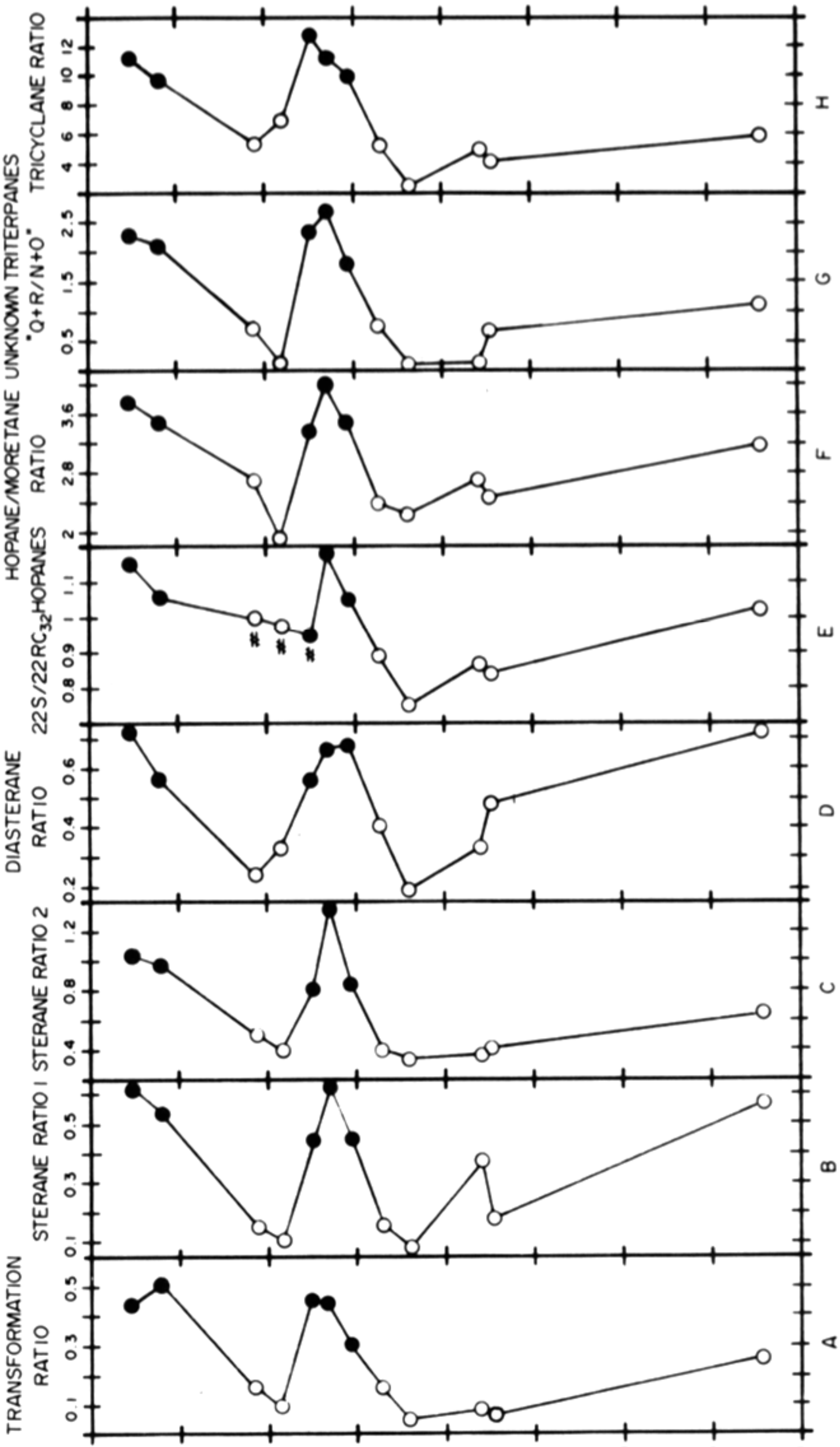


Fig. 4. Lost Hills biomarker ratios in depth context. See text for exact definition of each ratio. Accumulation zone samples marked with solid circles. Other samples marked with open circles. For 4c, m/z 191 mass chromatograms of samples marked with a "#" are noisy or have rising baselines and are thus less reliable.



One would expect the nature of the bitumens in the accumulation zones to differ from bitumens in "normal" (non-accumulation zone) rocks, in maturity and/or source imprint. Gas chromatography (GC) and combined gas chromatography - mass spectrometry (GS-MS) are effective tools for such a determination .

Gas chromatography of the saturate fraction shows that the samples form three distinct groups, each with characteristic, similar chromatograms (Kruge, 1985). These groupings correspond precisely to the subdivisions established by the transformation ratio: (1) the normal or "background" samples, (2) the deep accumulation zone and (3) the shallow accumulation zone. Figure 5 shows representative examples of chromatograms from each of these groups.

<Figure 5>

Chromatograms from the background samples are typical for immature bitumens. They show a strong dominance of the acyclic isoprenoid alkanes pristane and phytane over the *n*-alkanes with similar elution times, *n*-heptadecane and *n*-octadecane, (Fig. 5: samples 7, 14). In addition, the complex cluster of peaks on the right side of each chromatogram, corresponding to the steranes and triterpanes, is clearly visible above the baseline. These features are commonly seen in immature extracts from other basins (e.g. Connan and Cassou, 1980; Douglas and Williams, 1981).

The deep accumulation zone samples, exemplified by sample 9, resemble the alkane fraction of crude oils (see for example, Tissot and Welte, 1984). *n*-Alkanes clearly predominate in these chromatograms, overwhelming the steranes and triterpanes, which are hardly discernible above the baseline. Pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios are approximately unity, compared to values of 2-3 typical for the background sample group. These features all indicate that the deep accumulation zone bitumens are more mature than the background samples.

The shallow accumulation zone samples, represented by sample 4, appear to completely lack *n*- alkanes and isoprenoids. This is the characteristic result of biodegradation (Philippi, 1977; Connan et al., 1980). Since the *n*-alkanes and isoprenoids have been stripped away, it is impossible to use the maturity criteria applied to the previous two sample groups. However, because their transformation ratio values are so high, these samples must remain classified as accumulation zone samples, while further evidence is sought.

BIOMARKER INDICATORS OF MATURITY

Gas chromatography - mass spectrometry was used to characterize the assemblages of three classes of polycyclic biomarker compounds in the alkane fraction: the steranes, the hopanes and the tricyclic terpanes. The GC-MS results reinforce the initial grouping into accumulation zone and background samples. No distinction between shallow (No. 4) and deep (No. 9) accumulation zone samples is apparent (Figs 6 and 7), indicating that the biodegradation of the shallow samples had not been great enough to affect the steranes and terpanes. The biomarker ratios of the background samples show minor increases in maturity below 2000 m. More significantly, the same ratios show that the accumulation zone samples are as mature or more mature than the deepest background sample (sample 16: 3430 m), even though they are up to 3 km shallower, implying migration.

<Figure 6>

<Figure 7>

Fig. 5. Representative Lost Hills gas chromatograms. 4: shallow accumulation zone. 7 and 14: non-accumulation. 9: deep accumulation. For stratigraphic context see Fig. 2. For sample identification see Table 1.

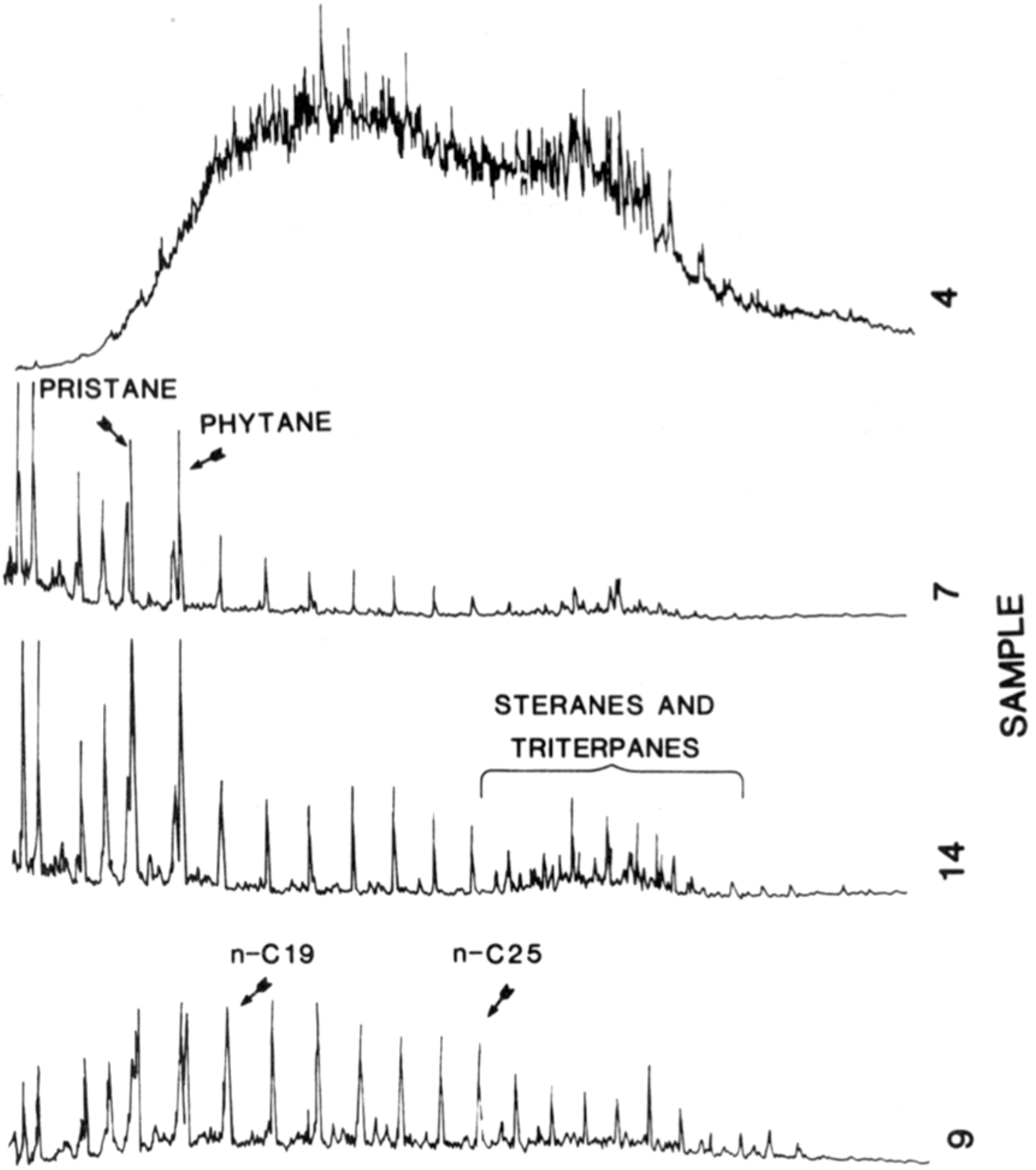


Fig. 6. Representative sterane mass chromatograms (m /z 217), with 2 accumulation zone samples (4, 9) and 2 non-accumulation (7, 14). Compare corresponding gas chromatograms (Fig. 5). Non-accumulation samples appear very immature i.e., dominated by $\alpha\alpha\alpha$ steranes (VII, XII, XV) and lacking $\alpha\beta\beta$ steranes (VI, VII, IX, XI, XIV).

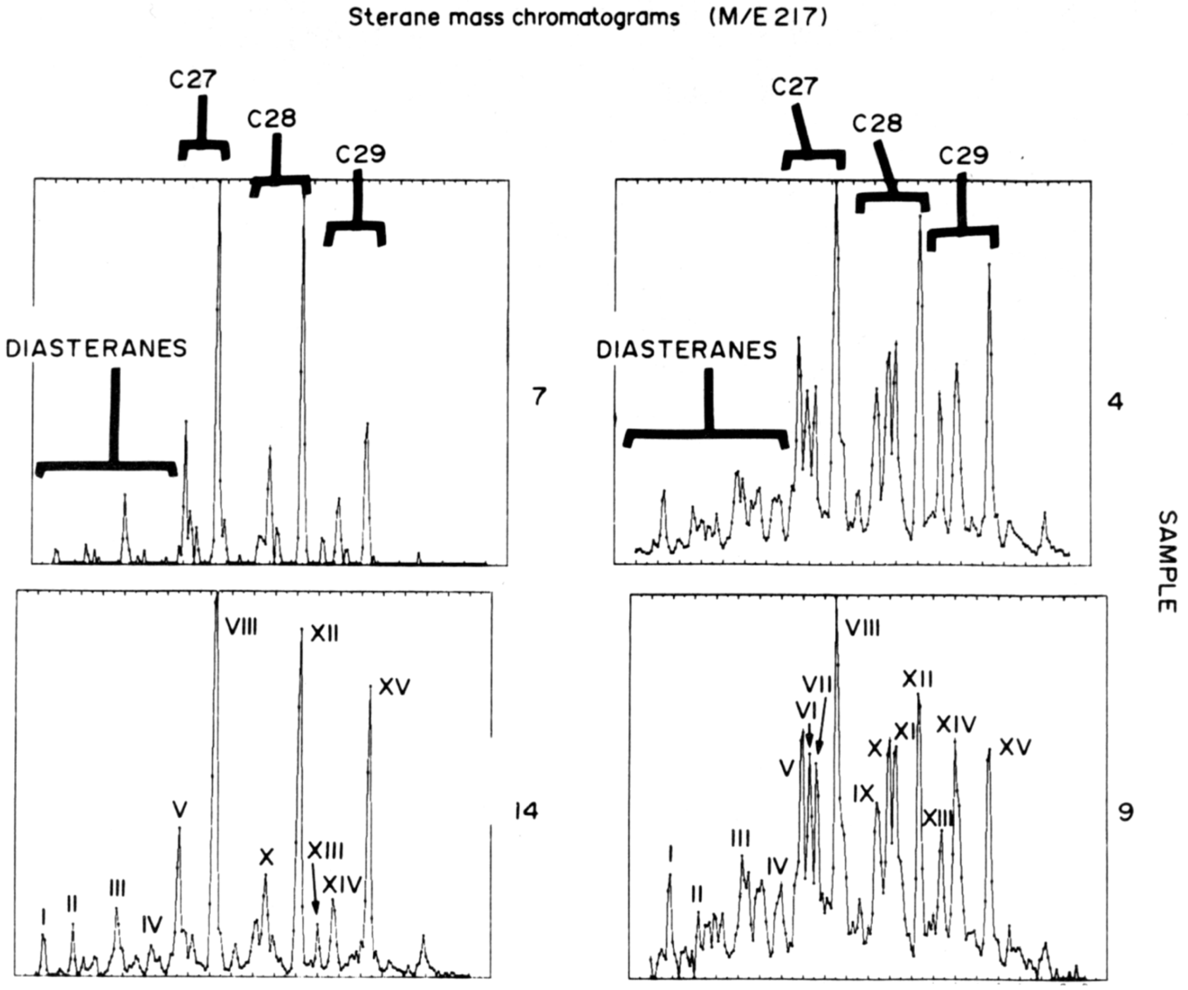
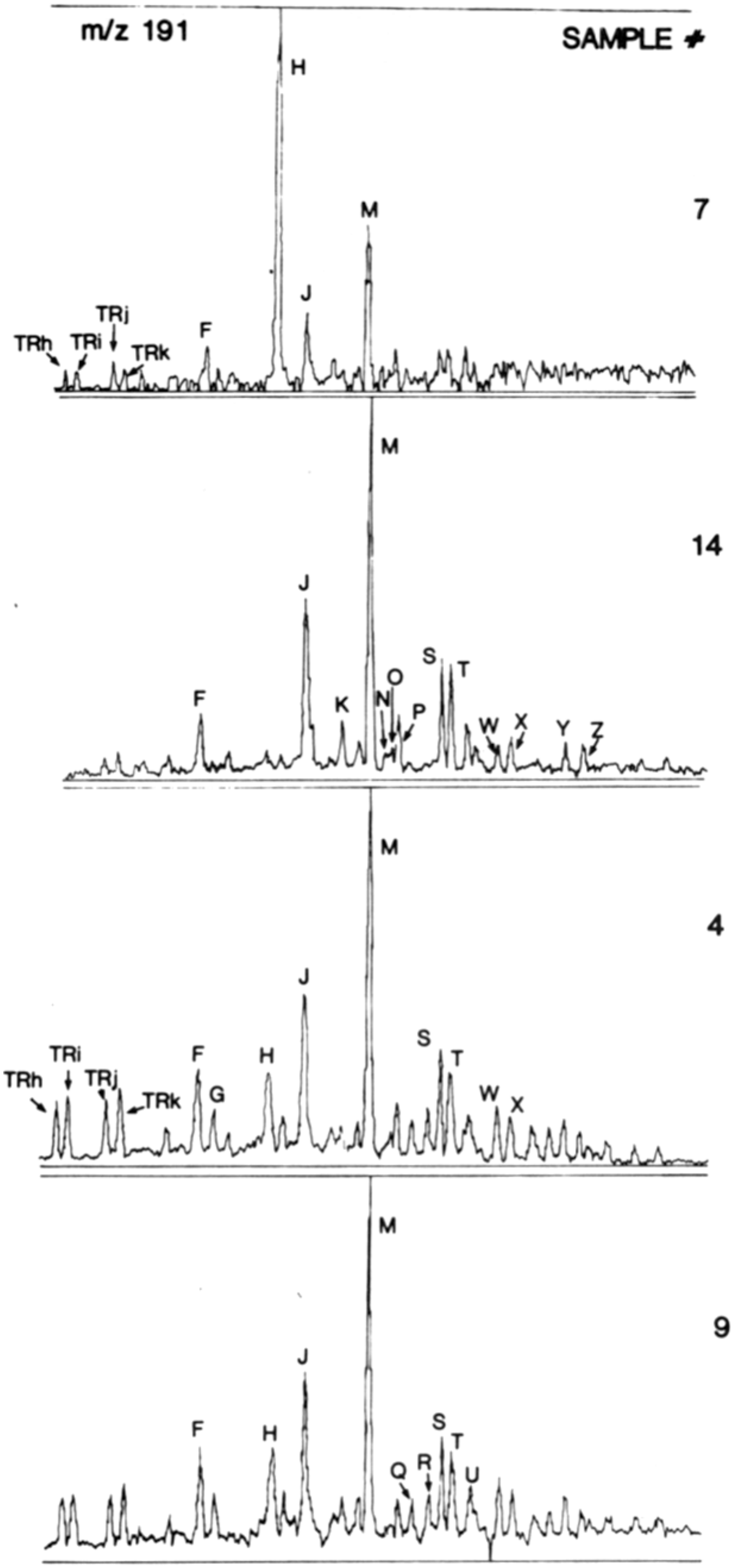


Fig. 7. Representative hopane mass chromatograms (m z 191) with 2 accumulation zone samples (4, 9) and 2 non-accumulation (7, 14). Note variable 28,30-bisnorhopane content (peak H) . Note higher tricyclane content (peaks labelled TR_) in accumulation zone samples.



Sterane maturity parameters

M/z 217 mass chromatograms best depict the sterane components. Figure 6 shows representative chromatograms for the Lost Hills samples. [Sec Kruge (1985) for the full set of chromatograms].

C_{29} regular steranes. Ratios of 24-ethylcholestane isomers are widely used maturity parameters (e.g. Seifert and Moldowan, 1978; Mackenzie et al., 1982). Sterane ratio I ($\alpha\alpha\alpha$ 20S/$\alpha\alpha\alpha$ 20R or peaks XIII/XV as in Fig. 6) and sterane ratio 2 ($\alpha\beta\beta$ 20S + R/$\alpha\alpha\alpha$ 20R or peaks XIV /XV) are plotted against depth (Figs 4b,c). In the depth context, they show a remarkable parallelism with the transformation ratio (Fig. 4a). Therefore, in the accumulation zone samples, where the transformation ratio shows sudden increases in the proportion of extractable organic matter, there is also a sudden increase in maturity of the extract. This is logical if the affected samples are in receipt of migrated bitumen, sourced from deeper, more mature strata. If the accumulation were the result of *in situ* generation in exceptionally rich, but shallowly buried immature rocks, there would be significant increases in extractables, yet maturation sensitive sterane ratios should be the same as those in unaffected strata of similar burial depth. In the case of Lost Hills, accumulation zone samples show sterane ratios much higher than even those from deeper background samples. The accumulation zone samples are in fact not exceptionally rich in kerogen. The initial pyrolysis-FID work showed them to have very high S_2 values of up to 40 mg/g, but repeating the pyrolysis after solvent extraction of the rock showed much lower values (~ 10 mg/g), indicating that most of the "kerogen" was actually heavy bitumen (Kruge, 1983; 1985).

There is nothing to distinguish pyrolysis gas chromatograms of accumulation zone samples from the others. For example, sample 9 is virtually identical with the somewhat shallower sample 7 and the deeper sample 10 (Fig. 8). The pyrograms show no reason why the generation capabilities of rocks represented by accumulation zone sample 9 should be any different from non-accumulation samples 7 or 10. This is an additional argument against major *in situ* oil generation in accumulation zone samples.

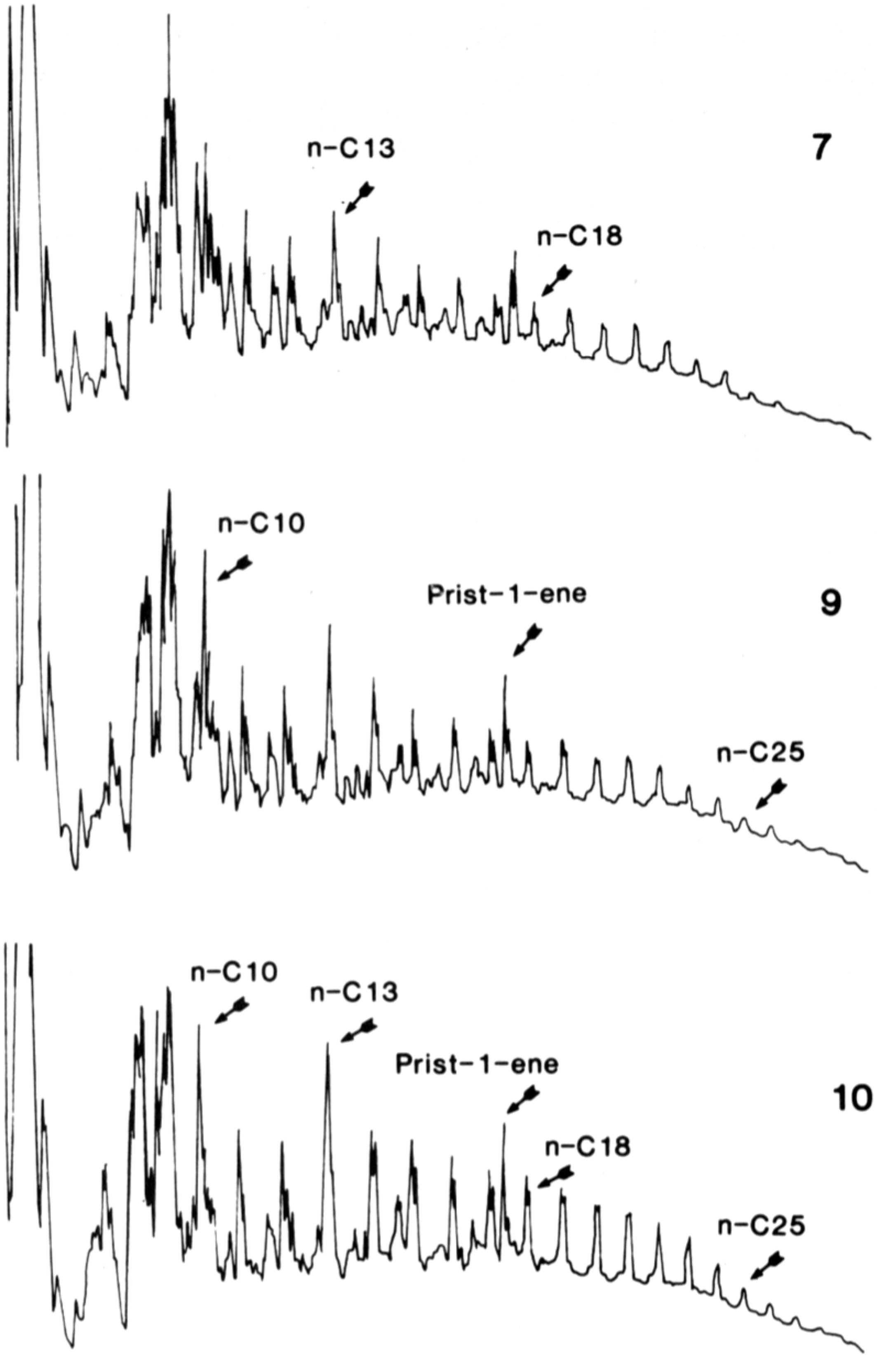
<Figure 8>

Considering the background samples alone, sterane ratio 1 increases from 0.09 to 0.56 over the depth range involved (Fig. 4b). The highest value among the background samples is from the deepest (sample 16: 3430 m), whose value of 0.56 is in the range of the accumulation zone samples (0.45-0.64). The increase seen in background samples in sterane ratio 2 is from 0.31 to 0.64 (Fig. 4c), putting the most mature of these (again sample 16) at a lower value than any accumulation zone sample (0.78-1.35).

Diasteranes. Diasterane trends with depth for the Lost Hills samples are shown in Fig. 4d, which uses the peak area sum of the four most prominent diasteranes (C_{27} and C_{28} 13β(H),17α(H), 20R and 20S) divided by the peak area of the C_{27} $\alpha\alpha\alpha$ (20R) regular sterane. Using the labeling code of Fig. 6, this is expressed as (I + II + III + IV)/VIII. One of the C_{29} $\beta\alpha$ diasterane isomers coelutes on peak VIII, which dampens somewhat the sensitivity of the ratio, but it still is effective. The trend in Fig. 4d is remarkably parallel to that seen in the transformation ratio (Fig. 4a) and in sterane ratios 1 and 2 (Figs 4b, c). This suggests that the relative diasterane content increases with maturity, in a formation such as this with essentially a single source rock facies.

Hydrogenation of diasterenes apparently occurs at a more advanced stage of diagenesis than does the regular sterene to sterane conversion, owing to the steric hindrance at the double bond in diasterenes (Brassell et al., 1980). Diasterenes themselves first appear at DSDP Site 467 in a claystone section with a vitrinite reflectance of ~ 0.4 % (Kruge, 1985 and references therein). Therefore, their hydrogenation to diasteranes must occur at somewhat

Fig. 8. Pyrolysis- gas chromatograms showing similarities of the kerogens of accumulation samples (represented by sample 9) and non-accumulation (7, 10). *n*-C_n notation identifies *n*-alkene /*n*-alkane couplets .



higher maturity levels. Yet diasteranes neoformed from regular steranes or kerogen are unlikely, since kerogen pyrolysis experiments fail to produce them (Seifert and Moldowan, 1983). Diasterane formation thus appears to occur predominantly in latest diagenesis, prior to the onset of kerogen breakdown.

The diasterane ratio may also be increased by migration (Seifert and Moldowan, 1978; Seifert et al., 1979). Chromatography may provide an analogy, as diasteranes elute faster on a capillary column than regular steranes of equivalent molecular weight.

The values of the diasterane ratio for Lost Hills samples (Fig. 4d) are not intended for comparison with those from other basins. The significance stressed here is in their relative increases. This technique should be applied with caution to basins with multiple source rock units. Source rocks rich in Al-bearing clays would produce larger proportions of diasteranes in their sterane fraction than calcareous or siliceous source beds (Rubenstein et al., 1975; Sieskind et al., 1979), masking any maturity differences. For example, extracts from the clay-rich post-Neocomian shales of the North Slope of Alaska have high diasterane contents, even when at low maturity levels (Seifert et al., 1979). Indeed, the apparent maturation effect at Lost Hills might be traceable to a higher clay content in the deep source rocks generating the accumulation zone bitumens . This is supported by the west San Joaquin depositional model, by which fine-grained terrigenous clastics , entrained in bottom-seeking turbidites, diluted biogenic deposits in basinal areas (Graham and Williams, 1985).

Whether they are sensitive to maturation, migration or source facies, diasterane ratios support the conclusion that accumulation zone bitumens at Lost Hills are not indigenous.

Pentacyclic terpane maturity parameters

Isomerization at C-22. The classic pentacyclic triterpane maturity parameter is the isomerization at C-22, which is a chiral center in hopanes with a carbon number of 31 or higher . The isomeric pairs are seen as peaks S and T (C_{31}), W and X (C_{32}) and Y and Z (C_{33}) on Fig . 7. These ratios show their largest increase prior to the conventional onset of oil generation (Mackenzie and Maxwell, 1981). They should thus adequately demonstrate the relative maturity of the Monterey samples from Lost Hills, all of which are conventionally immature.

The C_{32} 22S/22R ratio best shows the maturation trend and is plotted against depth in Fig . 4e. Maxima, as expected, are seen in the shallow accumulation zone, samples 9 and 12 of the deep accumulation zone and the deepest sample (16). Minima are observed in the background samples from 1700 to 2200 m. The m/z 191 chromatograms of three samples (6, 7 and 8) are noisy and/or have rising baselines, due to chromatographic column bleed in the region of interest. Their data are deemed less reliable and marked as such in Fig. 4c. However, the correlation with other maturity parameters is good, even including the questionable values . The C_{32} 22S/22R ratio is clearly representing the same maturity trends described by the other parameters.

Configuration at the D / E ring junction. The relative concentration of moretanes (17β(H),21α(H) configuration or rings D/E *trans*) should decrease with maturity as they are termed less stable than the 17α(H),21β(H) hopanes (Seifert and Moldowan, 1980). To test this, the ratio of the dominant hopane (C_{30}) to the sum of the most prominent moretanes (C_{29} and C_{30}), expressed as peaks M/(K + P) of Fig. 7, is plotted against depth (Fig. 4f). As with other biomarker maturity parameters applied to Lost Hills samples, there is an overall increase with burial depth among non-accumulation zone samples. Here also, the highest values are for the shallow and deep accumulation zones, with accumulation zone sample 9 again appearing the most mature. This is yet another case of a parameter showing sharp maturity increases for shallow bitumen-rich samples, implying the in-migration of mature hydrocarbons. Again, the non-indigenous bitumens seem more mature than the deepest indigenous extract (sample 16: 3430 m), so they must have originated in source rocks buried at an even greater depth.

M/z 191 peaks N, O, Q and R. A novel maturity parameter which is in excellent agreement with sterane ratios involves four as yet unidentified peaks on m/z 191 mass chromatograms, termed N, O, Q and R on Fig. 7. These compounds are in low concentration and give noisy or incomplete mass spectra (Kruge, 1985). Both compounds N and 0 have a prominent m/z 191 peak, which is the base peak for O and the strongest peak above m/z 90 for N. M/z 229 and 273 are also important. Molecular ions are apparently either m/z 412 or 414 for both N and O, which implies either a C_{30} pentacyclic or tetracyclic alkane structure . Tetracyclic terpanes should have a strong fragment at m/z 329, corresponding to the four-ring skeleton stripped of its extended side-chain (Aquino Neto *et al.*, 1983), yet this fragment is not present on the spectra of N and O. Therefore, a pentacyclic structure appears more likely. Serratane, a C_{30} pentacyclic triterpane, shows very similar mass spectral fragmentation patterns to peaks N and O (Kimble et al., 1974), except m/z 231 and 274 are prominent instead of m/z 229 and 273. Mass spectra from compounds Q and R are poor, but show a clear dominance of m/z 191. Compound P, eluting after O and before Q (Fig. 7), is the C_{30} moretane.

Compounds N and 0, while always in low concentrations in the Lost Hills samples, are stronger in the least mature bitumens. Compounds Q and R are stronger in the accumulation zone samples. Thus, ratios of (Q + R)/(N + 0), plotted against depth, vary sympathetically with the sterane ratios and transformation ratio (Fig. 4g).

Tricyclic terpane maturity parameters

Tricyclic terpanoids are as yet unknown in the biosphere, however their ubiquity in sediments implies a microbial or algal origin (Aquino Neto *et al.*, 1983). The homologous series of tricyclanes may derive from a common precursor, such as tricyclohexaprenol, by diagenetic or catagenic processes (Ourisson et al., 1982). Alternatively, by analogy to the full series of acyclic isoprenoid hydrocarbons found in some archaebacteria (Tornabene *et al.*, 1979), the distribution of tricyclic terpanes may in part be inherited directly from a bacterial source. The variations seen in assemblages of tricyclic compounds will remain somewhat equivocal, until more is known about the precursor/product relations, so that source input differences may be distinguished from maturity (or migration) effects.

For Lost Hills samples, tricyclane content appears to increase with maturity. This phenomenon has previously been seen elsewhere (Seifert and Moldowan, 1983). Among Lost Hills Monterey samples, relative concentrations of tricyclanes on m/z 191 mass chromatograms show distinct trends. The sum of the prominent C_{28} and C_{29} tricyclane peak couplets, labeled TRh , TRi , TRj and TRk (Fig . 7), is normalized to the sum of all measured m/z 191 peaks and plotted against depth (Fig. 4h). A pattern emerges parallel to maturity trends established by the transformation and sterane ratios (Figs. 4a-c). As with these latter ratios, values are sharply higher in the accumulation zones.

At Lost Hills, there is no marked increase in the tricyclic component simply with depth, even in the deepest sample (No. 16, 3430 m), yet significant enrichment occurs in all accumulation zone samples (Fig. 4h). This parallels the response of sterane ratio 2 (Fig. 4c). This may indicate that the maturity level of sample 16 ($R_o \sim 0.49\%$) is not sufficient to initiate the reactions measured by these ratios. It is interesting to note that sterane ratio 2 becomes active at significantly higher maturity than does sterane ratio 1 (Mackenzie *et al.*, 1982). At Lost Hills. sample 16 is clearly within the "reaction window" for ratio 1, but not 2, thereby bracketing the maturity level. The low tricyclane ratio of sample 16 suggests further that its maturity level of 0.49% R_o is insufficient to initiate significant release of tricyclane moieties bound in kerogens and asphaltenes. The higher tricyclane ratios of accumulation zone samples show that they likely originate in deeper, more mature strata, with perhaps some tricyclane enhancement by preferential migration. This may be analogous to the *n*-alkane enrichment observed in the deep (i.e. non-biodegraded) accumulation zone samples, as with sample 9 in Fig. 5.

DISCUSSION

Relative maturity of Lost Hills area samples: implications for petroleum generation

Petroleum production from kerogen-rich Monterey diatomites and fractured siliceous shales has created some confusion in the oil industry regarding the locus of petroleum generation. Some have proposed that the oil is the result of *in situ* generation in organic-rich, but very immature rocks (e.g. Earnest, 1981; Surdam and Stanley, 1981; McGuire et al. 1983). Biomarker ratios however, show these hydrocarbons to be distinctly more mature than the bitumens in surrounding rocks, which all should have undergone the same diagenetic-catagenetic processes. Richness differences cannot explain the oil accumulations, as background samples are often richer in kerogen than the reservoir rocks (Kruge, 1985). In-migration of more mature hydrocarbons originating deep in the basin is the logical explanation. Yet curiously, while the accumulation zone hydrocarbons are more mature than those in surrounding rocks, they often appear less mature than typical petroleums from other basins around the world. It would be interesting to make a regional assessment of the maturity levels observed in the San Joaquin Miocene section and compare them to those elsewhere.

Vitrinite reflectance is the standard for maturation measurements among petroleum geochemists. Unfortunately, R_o data for Monterey shales is typically sparse and of poor quality. The few reliable values obtained for this study are shown in Fig. 3, with a very tentative trend line fit to the four points deemed to be presently at their maximum burial depth. Yet these data agree very well with extensive vitrinite work done in the Paloma oil field, in the San Joaquin Basin 65 km southeast of Lost Hills (Hood and Castano, 1974). In both cases, for upper Miocene samples at about 3500 m, $R_o \sim 0.5\%$, which is expected since both sites are nearby and have similar geothermal gradients (~ 33 °C/km). Such low R_o values at such great depths are explained by the very short effective heating times of these young rocks, as can be shown by Lopatin modeling (Kruge, 1983; 1985).

Further evidence of deep, hot generation is from the Monterey shales of the Los Angeles and Ventura Basins, where generation is shown to commence at ~ 140 °C and to begin to peak at 160-170 °C (Philippi, 1965). These are purportedly reservoir temperatures measured in production wells and should be close to equilibrium values. If they are indeed correct, comparison of the Philippi and Hood and Castano studies suggests that oil generation in the Monterey could start at a maturity level corresponding to 0.5% R_o, with peak generation achieved by 0.60- 0.7% R_o. This contrasts with the usual assignment of 0.6% R_o for the onset of generation and 1.0% for peak (Waples, 1980), which suggests that Monterey kerogen depolymerizes more readily than average Type II kerogens from other basins. Alternatively, the extraordinary richness of Monterey source rocks (pyrolysis S_2 up to 54 mg/g at Lost Hills) may mean that early realization of only a fraction of the generation potential could still yield significant quantities, in other words, apparent early generation. It is important to note that great depths (> 3500 m) and high temperatures are still required since the rocks are so young (late Miocene) and have been deeply buried for only a few million years. What characteristics can be expected from immature petroleums and bitumens? High sulfur content, typical of Monterey petroleums (e.g. Magoon and Isaacs, 1983) is one indication, however, it is dependent in part on the variable sulfur content of the source rock. Low API gravity, due to high asphaltene content, may be another criterion (Tissot and Welte, 1984), but this can also be caused by biodegradation. In fact, the API gravity of non-biodegraded oils at Lost Hills is moderately high (25-35 °API, Cal. Div. Oil and Gas, 1973).

Maturity-sensitive biomarker ratios can be used as more precise indicators. The sterane ratios of most petroleums are at maximum (equilibrium) values, which are associated with peak catagenesis (Mackenzie et al., 1982). Sterane ratio 1 from even the most mature Lost Hills extract is only 0.64, far short of equilibrium, which should be 1.0-1.2. Similarly, sterane ratio 2 is never above 1.35, whereas the equilibrium value is ~ 6.0. This means that either: (1) the ratios do not always kinetically respond consistently in varied geologic settings, (2) the extracts are the result of mixing of mature in-migrating hydrocarbons with immature indigenous material, or (3) the Lost Hills accumulation zone bitumens are the product of relatively early generation.

To address the first possibility, Mackenzie and McKenzie (1983) consider sterane ratio 1 especially reliable and independent of catalysis effects. They in fact chose it to be the basis for their basin thermal history analysis procedure. As to the mixing question, this has almost certainly occurred to some extent. A proposed migration pathway is via fractures in the siliceous upper McLure Member of the Monterey, from a point of origin in the syncline at depths > 4 km. An exploration well located in the syncline, Western National Royalties No. 1 (Fig. 1), penetrated the upper McLure at such depths and its drilling log describes it as fractured. Fractures in the McLure are common on the Lost Hills anticline, therefore a fracture network can be envisioned as extending throughout the entire system. As the mature hydrocarbons travelled gradually updip, they would dissolve a portion of the bitumens indigenous to the organic-rich strata through which they passed. Since only the same member of the same formation is involved, these bitumens would all be very similar, except in maturity. What is the extent of mixing? There is variation in maturity even among Lost Hills accumulation zone samples. Samples 4 and 9 always arc slightly more mature than 5, 8 and 12, no matter which ratio is used. Since their hydrocarbons likely have the same source, perhaps their small but consistent differences could be due to the extent of mixing.

The apparent relative immaturity of Lost Hills accumulation zone extracts as compared to typical petroleums seen in other basins is certainly in part a function of mixing with indigenous immature bitumens. But is this the whole story? The accumulation zone extracts are representative of San Joaquin Basin petroleums (Seifert and Moldowan, 1978, 1979; Curiale et al., 1985), all showing sterane ratios below equilibrium values. To produce the vast quantities of oil in this prolific basin, the efficiency of high temperature generation is almost certainly a necessity. The admixed immature component is probably a minor one . Thus, it is not unreasonable to assume that volumetrically significant generation occurs in the Monterey somewhat earlier than is usual. Still, great depths are required: 4 km in the San Joaquin, even for "early" maturation.

CONCLUSIONS

(1) Monterey Formation core samples from the vicinity of the Lost Hills oil fields can be grouped according to their pyrolysis S_1 /S_1 + S_2 ratios and alkane gas chromatograms. Samples from petroleum accumulation zones have higher $S_1/S_1 + S_2$ values and *n*-alkane contents (when not biodegraded). One accumulation zone is in porous diatomaceous strata at ~ 600 m and the other is in fractured porcelanites, just below the opal-CT /quartz diagenetic boundary (~ 1500 m).

(2) A series of maturity-sensitive biomarker ratios corroborate this classification. The following ratios are all markedly higher in accumulation zone samples: $\alpha\alpha\alpha$ 20S/20R and $\alpha\beta\beta$ 20S + R/$\alpha\alpha\alpha$ 20R (C_{29} steranes), 22S/22R (C_{32} hopanes), C_{30} hopane / C_{29} + C_{30} moretanes, tricyclic/tricyclic + pentacyclic terpanes and unknown terpanes Q + R/N + 0. This

indicates that accumulation zone bitumens are anomalously mature for their shallow burial depths and are therefore largely in-migrated.

(3) In the accumulation zone samples, the relatively higher concentrations of *n*-alkanes (where not biodegraded), diasteranes, tricyclic terpanes and $\alpha\beta\beta$ steranes may in part be due to preferential migration. This further indicates that these bitumens are not indigenous.

(4) For each biomarker maturity ratio, values for accumulation zone bitumens are greater than or equal to those for the deepest non-accumulation zone sample, collected at a burial depth of 3430 m. Therefore, the source rock for the accumulations must be deeper than 3400 m, at vitrinite reflectance levels > 0.5%.

(5) Maturity ratio maxima, even in accumulation zones, are below equilibrium values. The 20S/20R and $\alpha\beta\beta/\alpha\alpha\alpha$ 20R (C_{29} steranes) and 22S/22R (C_{32} hopanes) conventionally all equilibrate during the phase of peak oil generation. Therefore at Lost Hills: (a) mature hydrocarbons, generated in the trough of the San Joaquin syncline, entrain enough immature bitumen during the course of their up-dip migration through fractured organic-rich Monterey shales to depress their biomarker maturity signatures and/or (b) the Lost Hills accumulations are the product of slightly early generation from rich Monterey kerogens.

(6) The diagenetic transformation of biogenic silica to quartz is complete in Lost Hills rocks at depths of 1500 m or less. It is estimated by biomarker maturity ratios that upper Miocene rocks would have to reach depths > 3400 m to begin the main phase of oil generation. Therefore, the conversion to quartz seems an unsuitable diagenetic event to associate with the onset of major petroleum formation . However, once converted to quartz, siliceous rocks, such as those in the upper McClure Members, are brittle. Under tectonic stress fractures form which may become filled with petroleum if it is available. In dealing with the Monterey Formation, it is important to separate the issue of hydrocarbon reservoir quality from that of hydrocarbon generation.

Acknowledgements - I would like to thank the following individuals for their help at various stages of this project: Alan Samoun (Rock- Eval pyrolysis), Ray Lukco and Joe Haykus (pyrolysis-GC), Gary Cole (vitrinite reflectance), Esther Roitman (advice concerning solvent extraction and thin layer and gas chromatography), and Roberto Renato (GC-MS). Jack Tucker, Robert Skillin, David Woltz, Lynn Schuetter and Jim Hill made samples and well information available.

This work was undertaken as part of my Ph.D. dissertation research. As such, I must thank the members of my advisory committee: Professors Rudy Wenk, Al Burlingame and Melvin Calvin. Further special thanks go to Professor Steve Graham and Dr. Lori Williams.

REFERENCES

Aquino Neto F. R., Trendel J. M., Restle A., Connan J. and Albrecht P. A. (1983) Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums. In *Advances in Organic Geochemistry 1981* (Edited by Bjorøy M. et al.), pp. 659-667. Wiley, Chichester.

Brassell S. C., Comet P. A., Eglinton G., McEvoy J., Maxwell J. R., Quirke J.M. E. and Volkman J. K. (1980) Preliminary lipid analysis of cores 14, 18 and 28 from Deep Sea Drilling Project Hole 416A. In *Initial Reports of the Deep Sea Drilling Project* (Edited by Lancelot Y., Winterer E. L. et al.), Vol. 50, pp. 647-670. U.S. Govt. Printing Office Washington.

California Division of Oil and Gas (1973) *California Oil and Gas Fields*, Vol. 1 (North and East Central California).

Claypool G. E., Baysinger J. P., Lubeck C. M. and Love A. H. (1979) Organic geochemistry. *In Geologic Studies of the Point Conception Deep Stratigraphic Test Well OCS-CAL 78-164 No. 1, Outer Continental Shelf, Southern California, United States* (Edited by Cook H. E.), U.S. Geol. Survey Open File Rept. 79-1218, pp. 109- 124.

Connan J. and Cassou A. M. (1980) Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. *Geochim. Cosmochim. Acta* **44**, 1- 23.

Connan J., Restle A. and Albrecht P. (1980) Biodegradation of crude oil in the Aquitaine basin. In *Advances in Organic Geochemistry 1979* (Edited by Douglas A. G. and Maxwell J. R.), pp. 1- 17. Pergamon Press, Oxford.

Curiale J. A., Cameron D. and Davis D. V. (1985) Biological marker distribution and significance in oils and rocks of the Monterey Formation, California. *Geochim. Cosmochim. Acta* **49**, 271- 288.

Dembicki H., Horsfield B. and Ho T. T. Y. (1983) Source rock evaluation by pyrolysis- gas chromatography. *Bull. Am. Assoc. Pet. Geol.* **67**, 1094-1103.

Douglas A. G. and Williams P. F. V. (1981) Kimmeridge oil shale--a study of organic maturation. In *Organic Maturation Studies and Fossil Fuel Exploration* (Edited by Brooks J.), pp. 255- 270. Academic Press, London. Earnest L. J. (1981) Diatomite may yield petroleum. *Geotimes*, Mar. 1981, pp. 17- 19.

Giger W. and Schaffner C. (1981) Unsaturated steroid hydrocarbons as indicators of diagenesis in immature Monterey shales. *Naturwissenschaften* **68**, 37- 39.

Giger W. and Schaffner C. (1979) Hydrocarbon indicators of diagenesis in Monterey shale, *California. Geol. Soc. Am. Abs. Programs*, 11, 432.

Graham S. A. and Williams L. A. (1985) Tectonic, depositional and diagenetic history of Monterey Formation (Miocene), Central San Joaquin Basin, California. *Bull. Am. Assoc. Pet. Geol.* **69**, 385-411.

Hood A. and Castano J. R. (1974) Organic metamorphism: its relationship to petroleum generation and application to studies of authigenic minerals. *CCOP Technical Bull.* 8, 85- 118. United Nations ESCAP.

Isaacs C. M. (1980) Diagenesis in the Monterey Formation examined laterally along the coast near Santa Barbara, California. Ph.D. thesis, Stanford Univ., Calif.

Jennings C. W. (1958) Geologic map of California, San Luis Obispo sheet, Calif. Div. Mines and Geology.

Kimble B. J., Maxwell J. R., Philp R. P. and Eglinton G. (1974) Identification of steranes and triterpanes in geolipid extracts by high-resolution gas chromatography and mass spectrometry. *Chem. Geol.* **14**, 173- 196.

King J. D. and Claypool G. E. (1983) Biological marker compounds and implications for generation and migration of petroleum in rocks of the Point Conception Deep Stratigraphic Test Well, OCS-CAL 78-164 No. 1, offshore California. In *Petroleum Generation and Occurrence in the Miocene Monterey Formation, California* (Edited by Isaacs C. M. and Garrison R. E.), pp. 191- 200. Soc. Econ. Paleon. Miner. Pacific Section.

Klabanow R. I. and Surdam R. C. (1983) Diagenesis and hydrocarbon generation in the Monterey Formation, Huasna Basin, California. In *Petroleum Generation and Occurrence in the Miocene Monterey Formation, California* (Edited by Isaacs C. M. and Garrison R. E.), pp. 53-68. Econ. Paleon. Miner. Pacific Section.

Kruge M. A. (1983) Diagenesis of Miocene biogenic sediments in Lost Hills oil field, San Joaquin Basin, California. In *Petroleum Generation and Occurrence in the Miocene Monterey Formation, California* (Edited by Isaacs C. M. and Garrison R. E.), pp. 39- 54. Soc. Econ. Paleon. Miner. Pacific Section.

Kruge M.A. (1985) Organic geochemistry and comparative diagenesis: Miocene Monterey Formation, Lost Hills oil field and vicinity, west San Joaquin Basin, California. Ph.D. thesis, University of California, Berkeley.

Kvenvolden K. A. (1970) Evidence for transformations of normal fatty acids in sediments. In *Advances in Organic Geochemistry 1966* (Edited by Hobson G. D. and Speers G. C.), pp. 335- 366. Pergamon Press, Oxford.

Mackenzie A. S. and Maxwell J. R. (1981) Assessment of thermal maturation in sedimentary rocks by molecular measurements . In *Organic Maturation Studies and Fossil Fuel Exploration* (Edited by Brooks J .), pp . 239-254. Academic Press, London .

Mackenzie A. S. and McKenzie D. (1983) Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. *Geol. Mag*. **120**, 417-470 .

Mackenzie A. S., Brassell S. C., Eglinton G. and Maxwell J. R. (1982) Chemical fossils: the geologic fate of steroids . *Science* **217**, 491-504.

Magoon L. B. and Isaacs C. M. (1983) Chemical characteristics of some crude oils from the Santa Maria Basin, California . In *Petroleum Generation and Occurrence in the Miocene Monterey Formation, California* (Edited by Isaacs C. M. and Garrison R. E.), pp. 201-212. Soc. Econ. Paleon. Miner. Pacific Section .

McGuire M. D., Bowersox J. R. and Earnest L. J. (1983) Diagenetically enhanced entrapment of hydrocarbons southeastern Lost Hills fractured shale pool, Kern County, California. In *Petroleum Generation and Occurrence in the Miocene Monterey Formation, California* (Edited by Isaacs C. M. and Garrison R. E.), pp. 171-184. Soc. Econ . Paleon. Miner . Pacific Section .

Philippi G. T. (1965) On the depth, time and mechanism of petroleum generation. *Geochim. Cosmochim. Acta* **29**, 1021-1049.

Philippi G. T. (1977) On the depth , time and mechanism of origin of the heavy to medium-gravity naphthenic crude oils. *Geochim. Cosmochim. Acta* **41**, 33-52 .

Pisciotto K. A. (1981) Diagenetic trends in the siliceous facies of the Monterey Shale in the Santa Maria region, California. *Sedimentology* **28**, 547-571.

Rubenstein I., Sieskind 0. and Albrecht P. (1975) Rearranged sterenes in a shale: occurrence and simulated formation. *J. Chem. Soc. Perkin Trans*. **1**, 1833-1836.

Seifert W. K. (1978) Steranes and triterpanes in kerogen pyrolysis for correlation of oils and source rocks. *Geochim. Cosmochim. Acta* **42**, 473-484.

Seifert W. K. and Moldowan J. M. (1978) Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta* **42**, 77-95.

Seifert W. K. and Moldowan J. M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. *Geochim. Cosmochim. Acta* **43**, 111-126.

Seifert W. K. and Moldowan J. M. (1980) The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. In *Advances in Organic Geochemistry 1979* (Edited by Douglas A. G. and Maxwell J. R.), pp. 229-237. Pergamon Press, Oxford.

Seifert W. K. and Moldowan J. M. (1981) Paleoreconstruction by biological markers. *Geochim. Cosmochim. Acta* **45**, 783-794.

Seifert W. K. and Moldowan J.M. (1983) Use of biological markers in petroleum exploration. In *Organic Geochemistry of Contemporaneous and Ancient Sediments* (short course notes), pp. 3-1 to 3-31. Soc. Econ. Paleon. Mineral. Great Lakes Section.

Seifert W. K., Moldowan J. M. and Jones R. W. (1979) Application of biological marker chemistry to petroleum exploration. In *Proc. 10th World Pet. Cong*., Vol. 2, pp. 425-440. Heyden, London.

Shi J.-Y., Mackenzie A. S., Alexander R., Eglinton G., Gowar A. P., Wolff G. A. and Maxwell J. R. (1982) A biological marker investigation of petroleums and shales from the Shengli oilfield, the People's Republic of China. *Chem. Geol*. **35**, 1-31.

Sieskind 0., Joly G. and Albrecht P. (1979) Simulation of the geochemical transformations of sterols: superacid effect of clay minerals. *Geochim. Cosmochim. Acta* **43**, 1675-1679.

Smith A. R. (1964) Geologic map of California, Bakersfield sheet, Calif. Div. Mines and Geology.

Surdam R. C. and Stanley K. O. (1981) Diagenesis and migration of hydrocarbons in the Monterey Formation, Pismo Syncline, California. In *The Monterey Formation and Related Siliceous Rocks of California* (Edited by Garrison R. E., Douglas R. G., Pisciotto K. E., Isaacs C. M. and Ingle J. C.), pp. 317-327. Soc. Econ. Paleon. Miner. Pacific Section.

Tissot B. P. and Welte D. II. (1984) *Petroleum Formation and Occurrence*, 2nd edn. Springer, Berlin.

Tornabene T. G., Langworthy T. A., Holzer G. and Oro J. (1979) Squalenes, phytanes and other isoprenoids as major neutral lipids of methanogenic and thermoacidophilic "archaebacteria". *J. Mol. Evol.* **13**, 73-83.

Waples D. W. (1980) Time and temperature in petroleum formation: Application of Lopatin's method to petroleum exploration. *Bull. Am. Assoc. Pet. Geol*. **64**, 919-926.