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PETROLEUM GENERATION AND OCCURRENCE IN THE MIOCENE MONTEREY FORMATION, CALIFORNIA

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DIAGENESIS OF MIOCENE BIOGENIC SEDIMENTS IN LOST HILLS OIL FIELD, SAN JOAQUIN BASIN, CALIFORNIA

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ABSTRACT

Major portions of the Miocene Monterey Formation of California were deposited under low oxygen conditions, with restricted clastic influx, beneath waters with high phytoplankton productivity. The resulting diatomaceous and organic-rich sediments underwent diagenetic modification as they were buried.

A suite of core samples was collected from eight wells in the Lost Hills oil field ranging in present depth of burial between 535 and 2285 meters. In one well, the entire Monterey section was sampled. Cores taken from the remaining wells sampled the Reef Ridge and Antelope Members of the Monterey Formation at various burial depths.

Silica mineralogy was studied using x-ray diffractometry and optical microscopy. Silica phases exhibit a clear diagenetic progression with depth from the opal-A of the diatom frustules to opal-CT and ultimately to microquartz. The $d_{(101)}$ spacing of opal-CT decreases from 4.088 to 4.044 Å with depth. No opal-CT was detected below 1470 meters.

Organic material was studied by bulk pyrolysis (Rock Eval) and optical methods. Organic carbon is abundant, comprising 1.4-10.2% of the rocks, mainly in the form of Type II kerogen (which reflects a dominantly marine origin) and soluble bitumens. A different organic facies is apparent in rocks sampled higher in the stratigraphic section, evidenced by admixed Type III kerogen.

Maturation parameters (maximum pyrolysis temperature, visual T.A.I. and vitrinite reflectance) indicate that none of the samples has yet reached the onset of the main phase of oil generation. Diagenetic transformation of biogenic silica to quartz is therefore complete before the kerogen begins to generate appreciable petroleum. Amounts of detectable free hydrocarbons (S_1) and hydrocarbons from kerogen pyrolysis (S_2) are consistently high. Heavy bitumens are common and in many cases inflate S_2 values. Where this occurs, pre-pyrolysis extraction is necessary to avoid misinterpretation of Rock Eval data. Oil is produced only in the limited intervals where $S_1/(S_1+S_2)$ is high (~0.4). This suggests that most of the oil migrated and accumulated rather than formed *in situ*, although some of the heavy bitumens may be indigenous.

INTRODUCTION

The surface waters of coastal regions with active upwelling are cool and nutrient rich. Such conditions are ideal for intensive productivity of siliceous plankton, especially diatoms (Heath, 1974). Sediments deposited below such a regime reflect the high biogenic input. This is especially true if dilution by terrigenous clastic influx is minimized by the basin configuration .

In addition to hard parts, some of the protoplasm of the phytoplankton may avoid degradation during transport and become incorporated into the sediment. Its chances of preservation are increased if it is deposited where bottom waters are oxygen-depleted and benthic scavenging is suppressed (Demaison and Moore, 1980). The siliceous and organic-rich facies of the Miocene Monterey Formation of California seem to fit this depositional model (Soutar and others, 1981; Pisciotto and Garrison, 1981).

Previous diagenetic investigations of the Monterey Formation have focused on biogenic silica. Murata and Larson (1975) clearly established the diagenetic sequence of this material. With burial, x-ray amorphous silica (opal-A), in the form of diatom frustules and siliceous microplankton tests, dissolves and reprecipitates *in situ* as poorly-ordered opal-CT (low cristobalite/low trydimite). The $d_{(101)}$ spacing of the opal-CT decreases with increased burial depth (Mizutani, 1977). With further burial, the opal-CT is in turn converted to cryptocrystalline/microcrystalline quartz. This diagenetic sequence has been well-documented in the Temblor Range (Murata and others, 1977; Murata and Larson, 1975; Murata and Randall, 1975), in the Santa Maria Basin (Pisciotto, 1978; 1981), along the coast near Santa Barbara (Isaacs, 1980; 1981a; 1982), and in the Lost Hills oil field (Kruge and Williams, 1982).

In contrast to the silica studies, few published organic geochemical investigations of the Monterey Formation exist. In one, 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 Formation 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) investigated steroid and acyclic isoprenoid diagenesis in rocks of known silica phase content from the southern Santa Barbara County coast. They found that a gradual loss of unsaturation in steroids and loss of stereospecificity in isoprenoids correlated with advancing silica diagenesis. Kvenvolden (1970) examined the distribution of normal fatty acids and alkanes in a sample from Gaviota Beach (near Santa Barbara), presumably bearing opal-CT as the dominant silica phase (Isaacs, 1981b). The relatively high carbon preference indices for both compound types indicates that they are of low diagenetic grade. Isaacs (1980) performed elemental analysis (C,H,O) on kerogens separated from Monterey Formation rocks, also collected along the coast near Santa Barbara. These kerogens were characterized as immature Type II. In addition, a decreasing O/C ratio correlated with increasing silica diagenesis. Claypool (reported in Taylor, 1976) analyzed six Monterey shales also from the Santa Barbara coast for the amounts of organic carbon and extractable organic matter. He found that the bitumens in these rocks contain mostly high molecular weight heterocompounds, as do typical crude oils produced from the Monterey Formation. Claypool and others (1979) analyzed the organic matter in samples from the Point Conception deep stratigraphic test well, which penetrated the Monterey Formation. They found that a large portion of the organic matter in the Monterey Formation samples was solvent extractable. This suggests either the presence of non-indigenous hydrocarbons or the generation of hydrocarbons at relatively low thermal maturity levels. Surdam and Stanley (1981) compared the diagenesis of silica and organic matter in Monterey Formation rocks from the Pismo syncline in San Luis Obispo County. They report an association between hydrocarbon occurence and the completion of the opal-CT to quartz conversion. This may be the result of either the development of fracture porosity, with subseqent filling by non-indigenous hydrocarbons, or of early hydrocarbon generation. Off the southern California coast, Miocene rocks similar to the onshore

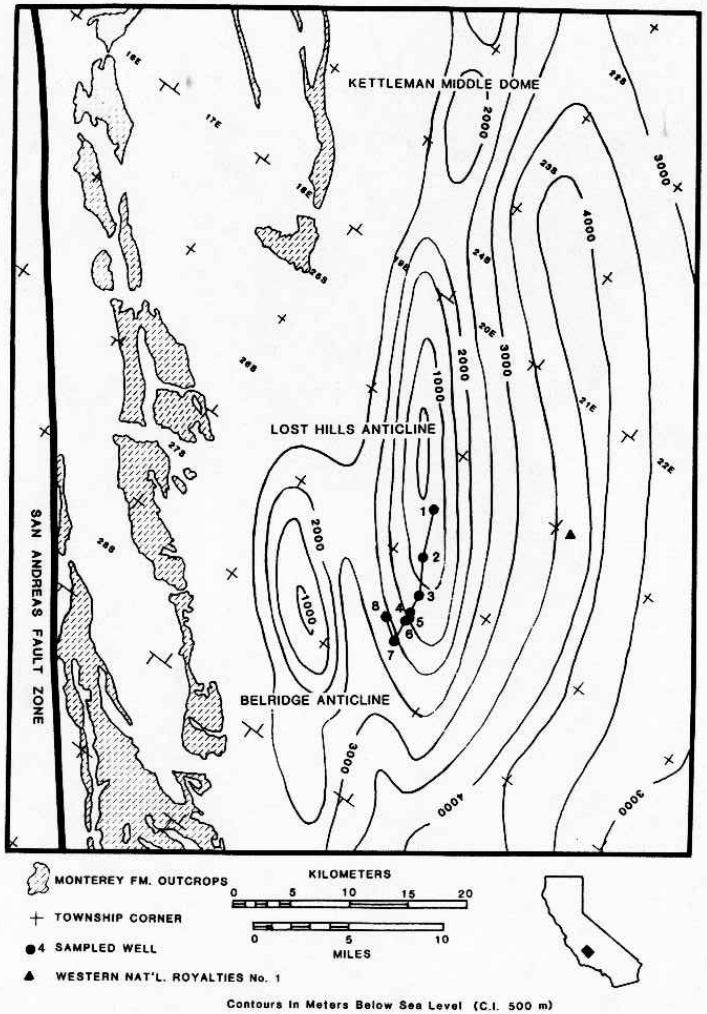

Figure 1- Generalized structure of the western central San Joaquin basin. Contoured approximately on correlation point "C" (upper Miocene) of figure 5. Subsurface geology after Graham and others, 1982. Surface geology after Jennings (1958) and Smith (1964).

SERIES	FORMATION / Member			CORREL. POINT
PLEIST.	TULARE			
PLIOCENE	ETCHEGOIN			— A
MIOCENE Upper	MONTEREY	Reef Ridge		— B
MIOCENE Upper	MONTEREY	Antelope	"Cahn Zone"	— C
MIOCENE Upper	MONTEREY	McDonald	"Cahn Zone"	
MIOCENE Middle	MONTEREY	Devilwater		
MIOCENE Middle	MONTEREY	Gould		
MIOCENE Lower	TEMBLOR			
OLIG.	TUMEY			
EOCENE	KREYENHAGEN			

Figure 2- Cenozoic stratigraphic nomenclature in the Temblor Range and western San Joaquin Valley (after Calif. Div. of Oil and Gas, 1973). Correlation points are based on electric logs.

Monterey Formation were collected and systematically analyzed on Leg 63 of the Deep Sea Drilling Project (Yeats and others,1981). A broad spectrum of studies documented parallel organic and inorganic diagenetic processes.

The Monterey Formation has come under increased scrutiny in recent years, as it contains some of California's most important petroleum source and reservoir rocks. Further understanding of this valuable natural resource requires more study of the original sediment type, depositional environment, and post-burial modification of the Monterey shales. Along these lines, the present investigation focuses on diagenetically sensitive biogenic components (silica and organic mattter) in order to delineate and predict zones of petroleum generation in the vicinity of the Lost Hills oil field (western San Joaquin basin). Lost Hills field is situated on a plunging anticline (fig. 1), one of a series of folds associated with the San Andreas fault (Harding, 1976). The structure is probably pre-upper Miocene in age, with major additional growth caused by post-Miocene intensification of activity along the San Andreas fault (S. Graham, pers. comm.). In several California oil fields, notably Lost Hills, petroleum is produced directly from fractured Monterey shales (Hardoin, 1963). Thus, the Monterey Formation in these fields has been cored extensively for reservoir evaluation. Lost Hills field was chosen for the present diagenesis study because of this availability of material.

A suite of core samples was collected from 8 wells (fig. 1), ranging in present depth of burial between 535 and 2285 m. In well 2, the entire Monterey section was sampled (see figure 2 for stratigraphic nomenclature). Cores taken from the remaining wells sampled the Reef Ridge and Antelope Members of the Monterey Formation at various burial depths.

MINERALOGY

Methods

Major mineralogy was determined by x-ray diffractometry (XRD), supplemented by light microscopy. For XRD, each sample was powdered, packed into an aluminum holder and scanned between 5 and 50° 2ϑ (Cu k_α radiation) at 1°/min. on a Phillips diffractometer.

The opal-CT $d_{(101)}$ spacings were measured by reference to the (111) peak of the silicon standard (at 28.467° 2ϑ) on diffractograms run at ½°/min. In each case the average of two determinations is presented.

Composition

Biogenic silica and organic matter are principal components of these rocks. In the shallowest samples, fragments of diatom frustules are still preserved. In addition, clay minerals (chiefly montmorillonite, illite and kaolinite) are ubiquitous. Clay-rich laminae interleave with bands of silica and organic matter of varying thicknesses. The clay shows preferred orientation, as is typical in compacted shales. In a few samples, there is minor admixing of coarser sediment. Calcite is common, often high magnesian, mostly as foraminiferal tests. Dolomite is present in some samples as microcrystalline rhombs, either scattered throughout the rock matrix or concentrated, forming megascopic nodules. Blebs of authigenic phosphate (poorly-ordered apatite) are locally common. Clusters of pyrite framboids fill voids in diatoms or foraminifera and may be disseminated in the matrix.

In general, samples from the Reef Ridge Member are more clastic-rich than those from the subjacent Antelope Member. In addition, samples from wells 1 and 2 appear overall more clastic-rich than do samples from equivalent strata in deeper wells.

Silica Phase Transformations

As reported earlier (Kruge and Williams,1982), biogenic silica deposited at the Lost Hills site was converted from opal-A to opal-CT to microquartz with increasing burial depth (fig. 3). The shallowest example (fig. 3a) shows a broad hump centered around 21° 2ϑ, corresponding to opal-A. Figure 3b shows the emergence of a diffuse peak at about 21.7° 2ϑ, which corresponds to disordered opal-CT. The shoulder at 21.5° 2ϑ is interpreted to indicate trydimitic layers interstratified in the dominantly cristobalitic structure (Flörke and others, 1976). A diagenetic decrease in the $d_{(101)}$ spacing of opal-CT corresponds to an increase in crystallographic order (Mizutani, 1977). Figures 3c and 3d show this with a sharpening and a slight shift (+0.24° 2ϑ) of the opal-CT (101) peak. In the deepest samples, as in figure 3e, all biogenic silica is in the form of quartz.

Figure 4 charts the silica phases in their structural and stratigraphic context. Datum was chosen as ground level in order to show the effects of the present depth of burial (and consequently temperature) on diagenesis. In this study all samples were found to contain biogenic silica or its diagenetic products. Three diagenetic zones are recognized:

(1) *The opal-A zone*- containing recognizable diatoms, but no XRD-detectable opal-CT.

(2) *The opal-CT zone*- containing detectable opal-CT.

(3) *The quartz zone*- containing authigenic quartz, but no detectable opal-CT.

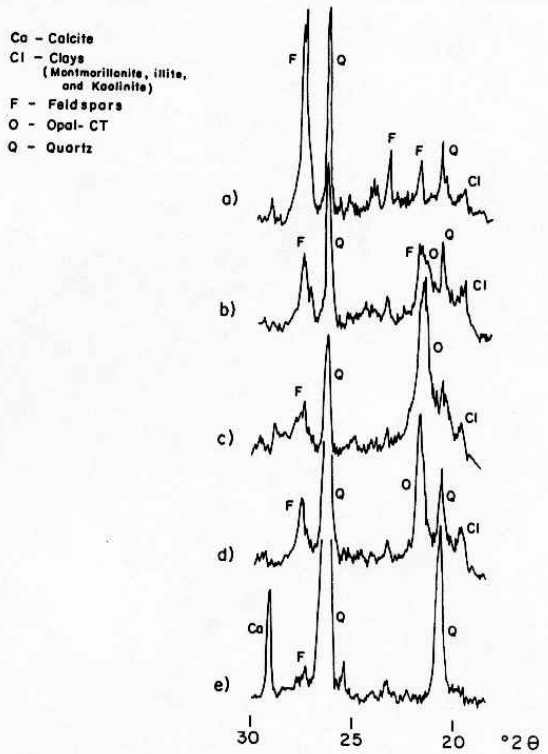

Figure 3- X-ray diffractograms for representative samples. Diagenetic grades increase from 3a to 3e. Note appearance, strengthening and disappearance of the opal-CT (101) peak near 21.7° 2ϑ. 3a: well 2, 580 m; 3b: well 2, 652 m; 3c: well 2, 989 m; 3d: well 3, 1302 m; 3e: well 5, 1474 m.

The opal-CT/quartz zonal boundary is recognized in wells 2, 3 and 4. This horizon is found progressively deeper moving down-dip from well 2 to 4, suggesting tilting of the diagenetic front during post-Miocene uplift of the Lost Hills anticline (Kruge and Williams, 1982). This disposition may also be in part a lithologic effect. The metastability range of opal-CT is apparently reduced in clay-rich rocks. Here, the conversion of opal-A to opal-CT requires a higher temperature and that of opal-CT to quartz a lower temperature than that required for more purely siliceous rocks (Isaacs, 1982). The Lost Hills samples, while similar in many respects, do vary lithologically, chiefly in detrital mineral (especially clay) content. These variations could have caused silica phase transformations at variable depths. Such a situation exists in well 4, at correlation point C, which marks the most siliceous portion of the Antelope Member. Here one porcelanite sample has a very strong opal-CT XRD signature, yet super- and subjacent samples show only quartz. Lack of additional (shallower) samples precludes better definition of the opal-CT zone in well 4.

Opal-CT $d_{(101)}$ Spacing

With increasing depth of burial (*i.e.*, increasing temperature), the $d_{(101)}$ spacing of opal-CT decreases (Murata and Larson, 1975; Mizutani, 1977). The d-spacing decrease can record small changes in diagenetic grade within the opal-CT zone. Figure 5 shows a clear overall decrease in d-spacing with depth for the Lost Hills samples in individual wells, as well as for all samples taken together. Over a depth range of 650-1470 m, opal-CT d-spacing drops from 4.088 to 4.044 Å. However, the decrease is not linear and the scatter may be due in part to the effects of lithologic differences (Isaacs, 1982).

A particularly interesting way to view the depth-related d-spacing decrease is to observe down-dip variations in rocks in the same stratigraphic interval. The best example of this is near stratigraphic marker "C" in wells 1-4. D-spacing values for the closest sample to marker "C" in each well are posted on figure 4. In wells 1 and 2, the samples show almost identical d-spacings of 4.076 and 4.078 Å. This is reasonable since they are at nearly the same depth. The sample from well 3 shows a marked reduction to 4.055 Å and that from well 4 drops further to 4.049 Å. The sample from well 4 is particularly interesting as it is the lone deep opal-CT rock within a quartzose zone. It seems likely therefore that the effect of the ongoing diagenesis of the opal-CT is imprinted upon the tilted "fossil" diagenetic front (Kruge and Williams, 1982), since the temperatures of the uplifted opal-CT bearing strata remained high.

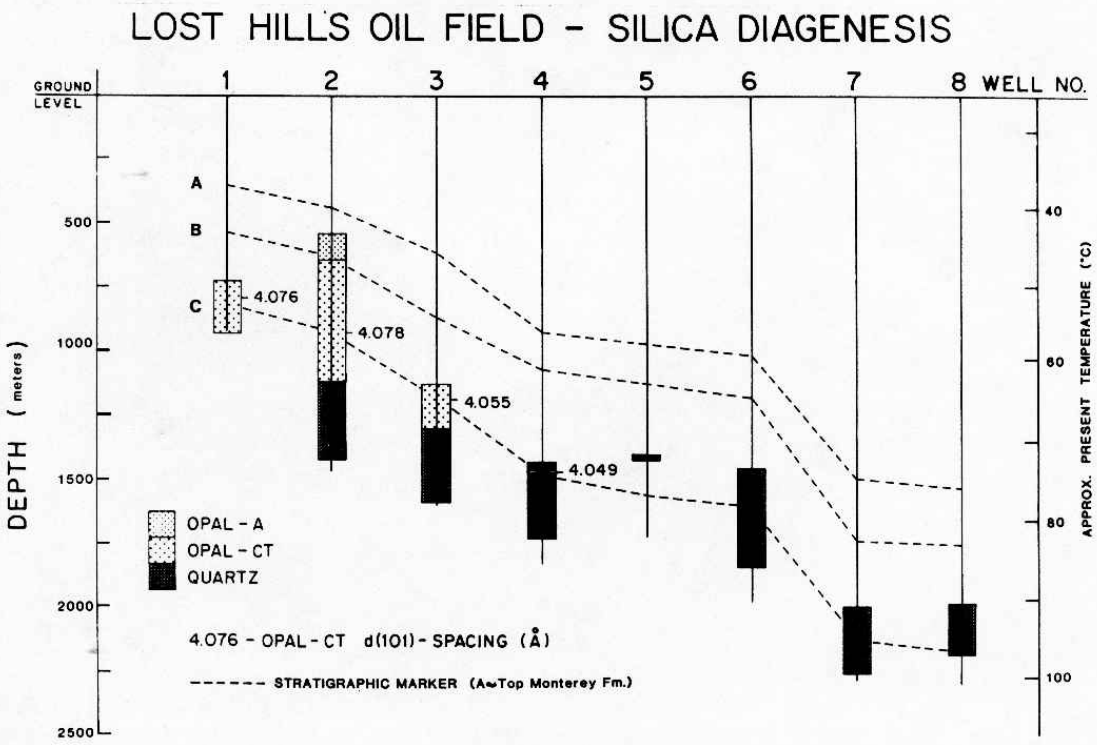

Figure 4- Cross-section across the south plunge of Lost Hills oil field (see fig. 1 for location). Stratigraphic control points are from electric log correlations. Present temperatures are from measurements made in well 6, corrected by the method of Dowdle and Cobb (1975).

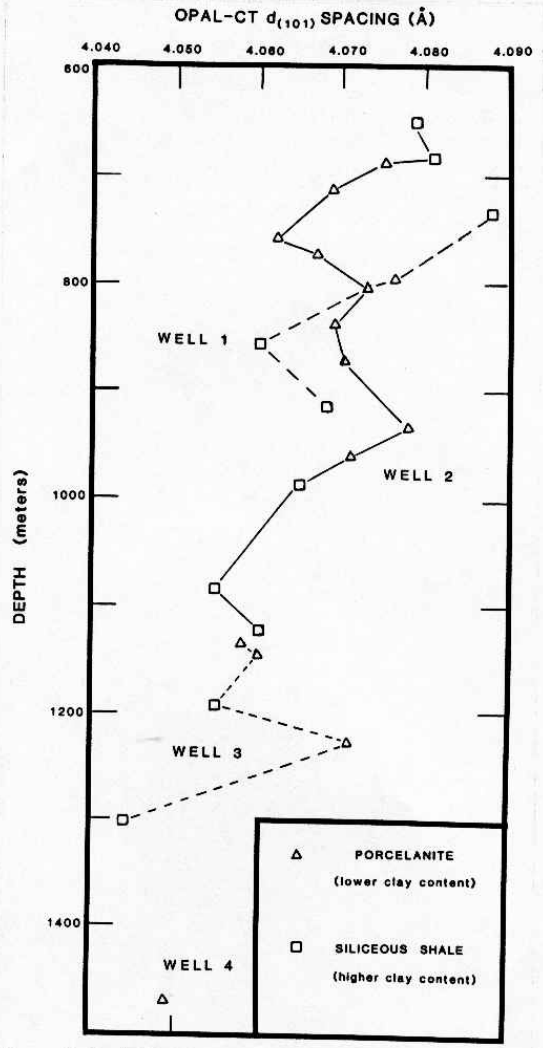

Figure 5- Opal-CT $d_{(101)}$ spacings as a function of present burial depth in Lost Hills oil field.

ORGANIC MATTER

The Monterey Formation is characteristically rich in organic matter. Monterey shales in the Lost Hills oil field are no exception. Organic matter is also highly sensitive to thermal stress and can be used to asses the extent of diagenesis. Parallels can be drawn between organic diagenetic indicators and inorganic ones such as silica phase transformations.

Methods

One of the best ways to access the geologic information held in sedimentary organic matter is to do detailed biomarker compound analysis. As a prelude to this, the present study screened a suite of 77 Lost Hills subsurface samples using bulk pyrolysis and combustion techniques.

Pyrolysis was performed using an automated Girdel "New Version Rock Eval" system. Espitalié and others (1977) and Tissot and Welte (1978) describe this technique in detail. Briefly, in this method, 100 mg of powdered rock are placed in a crucible and introduced into the pyrolysis oven. The oven remains at 300° C for three minutes and any free hydrocarbons are vaporized, measured and recorded as the "S_1" peak. The oven temperature then increases to 500° C at a rate of 25°/min. As appropriate temperatures are reached, kerogens begin to pyrolyze, releasing hydrocarbons. These are detected and recorded as the "S_2" peak. The temperature at which there is maximum pyrolysis yield is recorded as "T_{max}".

During pyrolysis, organic CO_2 also evolves and is trapped and measured as the "S_3" peak. The trap is closed at 390° C to avoid contamination with inorganic CO_2, since carbonates begin to decompose at ~500° C under these conditions. Some contamination possibly still occurs in carbonate-rich rocks and this remains a controversial point (Katz, 1981).

A combustion analyzer is associated with the Rock Eval device. After pyrolysis the sample crucible is automatically transfered to a furnace where any carbon residue is oxydized at 600° C. The CO_2 produced is collected and measured as the "S_4" peak. The areas under peaks S_1-S_4 are calculated by digital integration. Results are expressed in parts per thousand (mg of hydrocarbons or CO_2 per gram of rock), by comparison with standards, after adjusting for sample weight. Total organic carbon values (TOC) (in percent of whole rock) are computed:

$$TOC=(S_1+S_2)(0.1)(0.82) + (S_3+S_4)(0.1)(0.27)$$

The hydrocarbons comprising S_1 and S_2 are about 82% carbon by weight. S_3 and S_4 measure CO_2, which is 27% carbon.

Unfortunately, a TOC device was only available during Rock Eval analysis for 14 of the Lost Hills samples. As an alternative, 24 samples were processed using a Perkin-Elmer C-H-N analyzer, which employs a high temperature combustion oven (~950° C). Prior to this analysis, the samples were powdered, weighed, treated with hot 10% HCl to remove carbonates, washed, dried and reweighed. After analysis, values were adjusted to account for any lost carbonate. As a cross-check, four samples were analyzed by both techniques. The results are very similar (Table I).

For solvent extractions, the method of Clementz (1979) was used. 100 mg of powdered rock were agitated in 15-20 ml of a 50:50 acetone:dichloromethane mixture for 1 minute. After decanting the process was repeated 2-3 times, until the solvent was clear. After air-drying, the sample was ready for pyrolysis.

SAMPLE		TOC (%)	
Well Number	Depth(m)	Rock Eval	C-H-N
2	1267	7.52	7.73
4	1501	4.05	3.97
6	1572	3.80	3.87
8	2162	2.24	2.05

Table I- Comparison of alternate methods of total organic carbon determination.

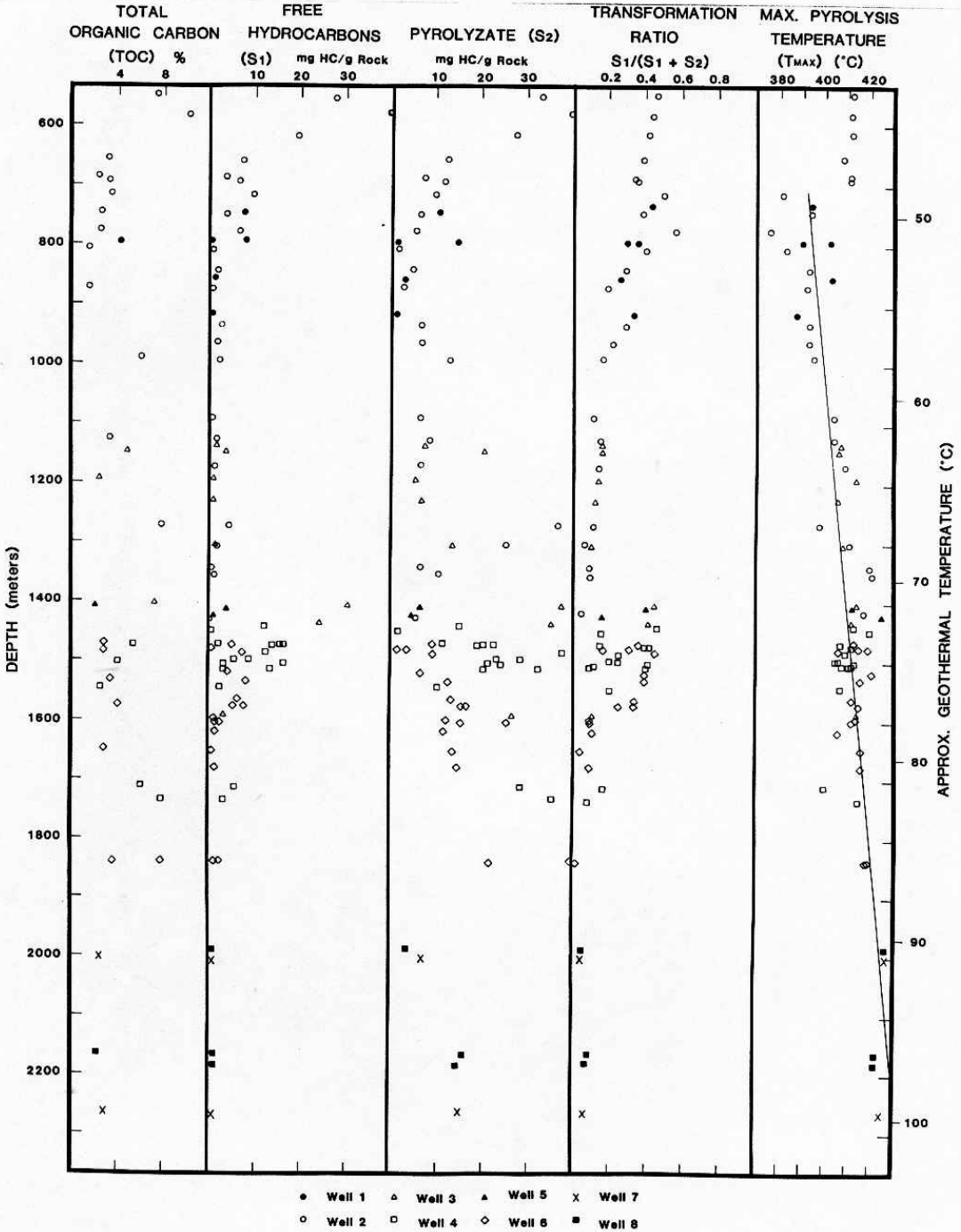

Figure 6- Lost Hills Monterey Formation Rock Eval pyrolysis results plotted as a function of depth. No solvent extraction. Not all samples were measured for TOC. Present temperatures as in figure 4. In T_{max} column, best fit line is calculated for all samples deeper than 700 m. For further explanation, see text.

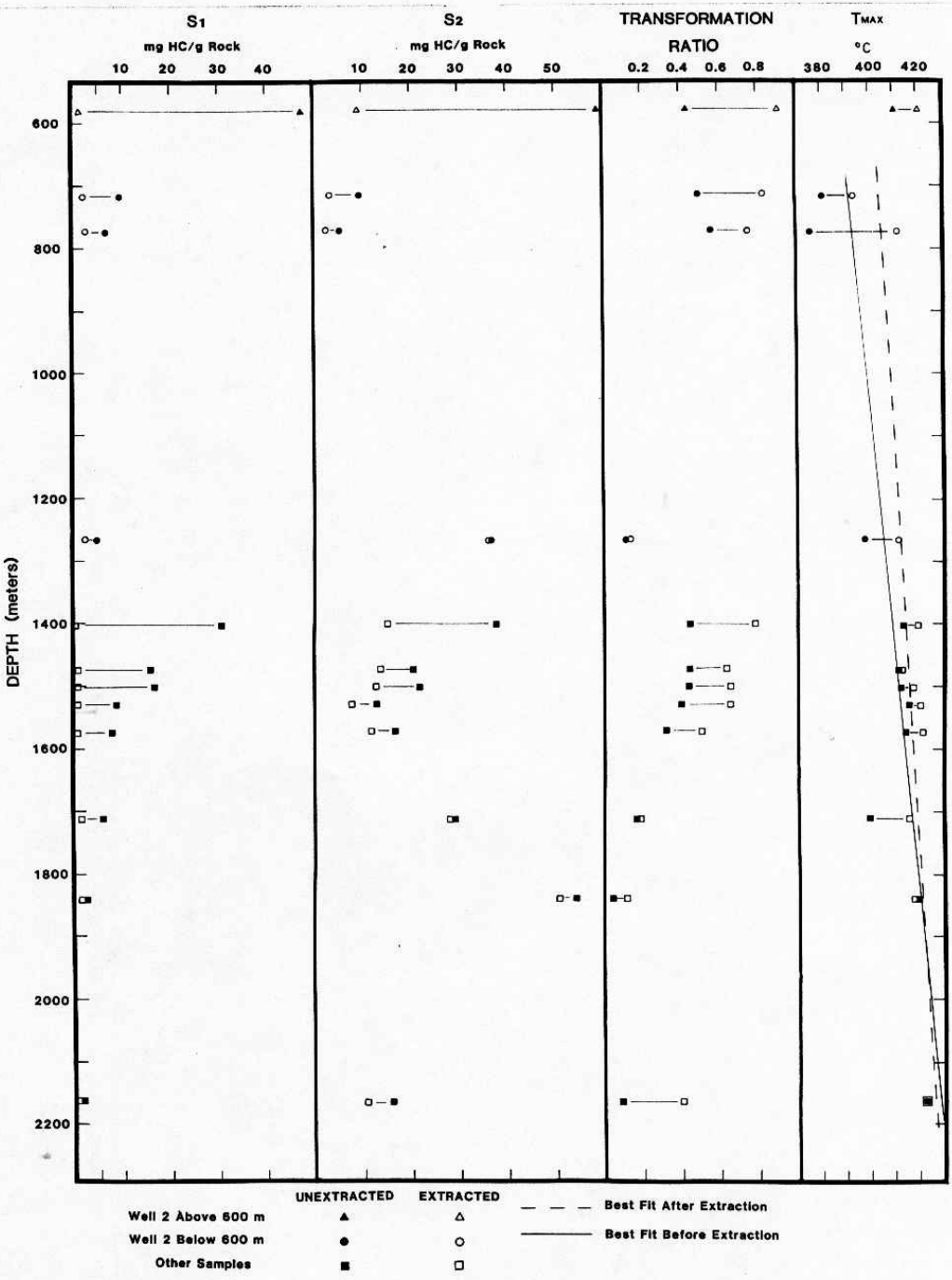

Figure 7- Rock Eval pyrolysis results for selected Lost Hills samples before and after solvent extraction. See text.

Results

Organic matter content

Rock Eval analysis reveals a consistent, extraordinary organic richness in the Monterey shales from the Lost Hills field. TOC values range between 1.43 and 10.23%, with a mean of 4.06%. For comparison, the world-wide average for shales is between 0.9 and 1.65% and for shale petroleum source rocks it is 2.16% (Tissot and Welte, 1978). Figure 6 shows persistently high values with no depth-dependent trends.

The S_1 peak corresponds roughly to the amount of extractable bitumen in a rock. An S_1 value >1 mg/g is considered "significantly" high (G. Demaison, pers. comm.). Lost Hills samples have values between 0.5 and 4 mg/g for most of the depth range (fig. 6), with two notable exceptions. One occurs in the 500-800 m depth range, where samples from wells 1 and 2 reach 47.49 mg/g and gradually decrease with depth to background level. The second increase occurs between 1400 and 1600 m, where S_1 ranges up to 30.63 mg/g. Wells 3-6 intersect the oil-producing "Cahn zone" at these depths.

The S_2 Rock Eval peak measures the pyrolyzable kerogen content. This is considered to represent the hydrocarbon generation potential of the rock (Tissot and Welte, 1978). Values above 5 mg/g indicate good potential (G. Demaison, pers. comm.). The Lost Hills samples show consistently high values for S_2. Values range from 1.07 to 61.16 mg/g, with only 9 out of the 77 samples <5 mg/g. Depth-dependent trends (fig. 6) essentially parallel those for S_1:

(1) Very high but decreasing in the 500-800 m range (wells 1 and 2)

(2) A broad increase in the 1300-1700 m range (wells 3-6).

In addition there is an increase below 2000 m (wells 7 and 8) for which there is no corresponding rise in S_1.

A standard means of comparison of S_1 and S_2 is the "transformation ratio" ($S_1/(S_1+S_2)$) (Tissot and Welte, 1978). In general, a kerogen-rich rock will become enriched in S_1 with increased maturity, as kerogen is converted to bitumen. Thus, a gradual increase in the transformation ratio with depth is expected (Tissot and Welte, 1978). This may be interrupted by a lithology change or by a zone of acculmulation of migrated hydrocarbons. In the latter case, the ratio will show a sharp increase: free hydrocarbon content will overshadow that pyrolyzed from indigenous kerogen. In the Lost Hills field, the transformation ratio shows a depth-dependent trend parallel to that of S_1 (fig. 6). This corresponds to hydrocarbon accumulations at 500-800 m in wells 1 and 2, where primary porosity is preserved in diatomaceous rocks, and at 1400-1600 m in wells 3-6, where fractured quartzose rocks provide secondary porosity.

Solvent Extraction

In rocks with high S_1 values (>1 or 2 mg/g), there may be associated heavy bitumens, especially asphaltenes. These would boil or decompose at temperatures above 300° C and be recorded as part of the S_2 peak instead of the S_1. This would inflate the estimate of pyrolyzable kerogen content (Clementz, 1979). Since the great majority of the Lost Hills samples showed S_1 values >1 mg/g, it was necessary to choose representative samples and reevaluate S_2 after solvent extraction.

Figure 7 illustrates the effectiveness of this process. S_1 should approach zero in thoroughly extracted samples. Overall the extraction was satisfactory, except in samples from well 2. They seem to show a residue of intractable bitumen. Since the well was drilled in 1925, this may be a function of degradation during the 57 years between sample collection and analysis.

Figure 7 clearly shows heavy bitumen contamination of S_2 in most of the samples, especially in the shallow diatomaceous mudstone just above 600 m in well 2. Clearly, S_2 values after extraction more accurately represent the pyrolyzable kerogen content. So the unextracted data must be interpreted with caution, since solvent extraction was not performed on all samples. Rock Eval parameters described below are presented in terms of both the unextracted and extracted values. One can thereby judge which parameters are significantly affected.

If the transformation ratio ($S_1/(S_1+S_2)$) represents the ratio of soluble to total organic matter, one should transfer the heavy soluble bitumen to the numerator. Figure 7 shows the effect of this modification. The transformation ratio now becomes:

$$(S_1 + S_2 - S_{2\,ex}) / (S_1 + S_2)$$

where $S_{2\,ex}$ is the S_2 value after solvent extraction. The boundaries for the zones of hydrocarbon accumulations suggested by the original transformation ratio do not significantly change. But the magnitude of the ratios appears greater, as "heavy oil" and tar are now included. One additional accumulation is apparent, at ~2150 m. Comparison of figures 6 and 7 suggests that this zone should contain only heavy oil. The rocks indeed have tar-stained fractures.

Organic Matter Type

Rock Eval data permit classification of samples according to generalized organic matter types. These reflect the quality of the original organic sediment and its depositional environment. This is based on the assumption that a kerogen rich in hydrogen was largely derived from aquatic organic matter deposited in a reducing environment (Demaison and Moore, 1980). An oxygen-rich kerogen reflects terrigenous plant input and/or a more oxic depositional environment. This can be represented on a Van Krevelen diagram, which plots H/C versus O/C atomic ratios, derived by chemical analysis of demineralized kerogen. Van Krevelen diagrams modified to use Rock Eval data give reasonably similar results (Espitalié and others, 1977; Tissot and Welte, 1978). The "hydrogen index" ((S_2 X 100)/TOC) and "oxygen index" ((S_3 X 100)/TOC) are calculated to substitute for H/C and O/C.

When plotted on such a diagram (fig. 8), the Lost Hills Monterey Formation data cluster into two fields. Field "a" encompasses the upper Type I and Type II branches (aquatic/anoxic). Field "b" lies between Type III (terrigenous/sub-oxic) and Type II. Field "a" points are from stratigraphically lower positions in their respective wells, with the exception of the shallow diatomaceous mudstone from well 2. Figure 9 illustrates this, plotting the hydrogen index as a function of drilled depth above or below stratigraphic correlation point C (late Miocene). From ~150 m above point C to about 300 m below it, the hydrogen index increases. This may indicate a subtle change in organic facies. A progressive increase in ocean bottom water aeration during the late Miocene may have caused this. If so, then one might expect fewer laminated rocks among the younger (field "b") samples, as burrowing infauna would have been more active. However, the distribution of laminated rocks in fields "a" and "b" is about equal. An alternative explanation for an organic facies change may be increased input of terrestrial organic matter. This seems to correlate in part with the transition from the siliceous Antelope Member to the more detrital-rich Reef Ridge Member, the base of which is picked at ~50 m above point "C".

Samples from the oldest well (well 2) show unusually depressed hydrogen index and high oxygen index values. This may be partly due to degradation (including oxidation) suffered during decades of exposure of the core material to air prior to analysis.

Only samples from well 2 represent the section >150 m above correlation point C. These show a trend opposite to the one below: the hydrogen index starts high and decreases with depth. The shallowest two samples are porous silty diatomaceous mudstones, rich in both light and

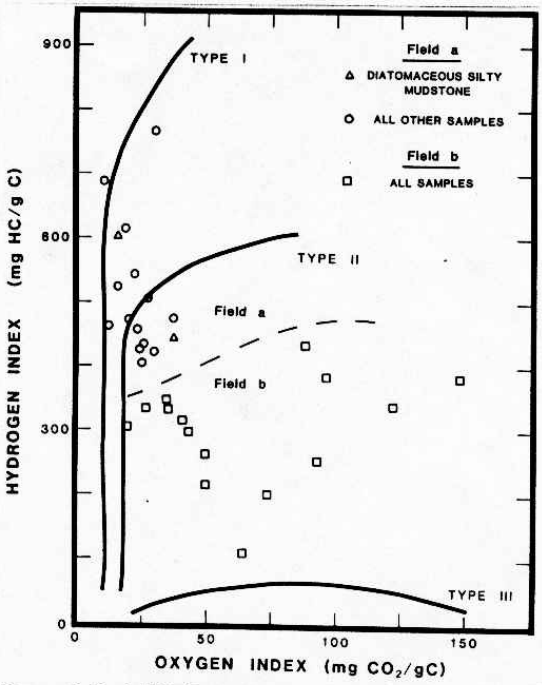

Figure 8- Lost Hills Rock Eval data plotted on a modified Van Krevelen diagram. Placement of kerogen type branches according to Tissot and Welte (1978).

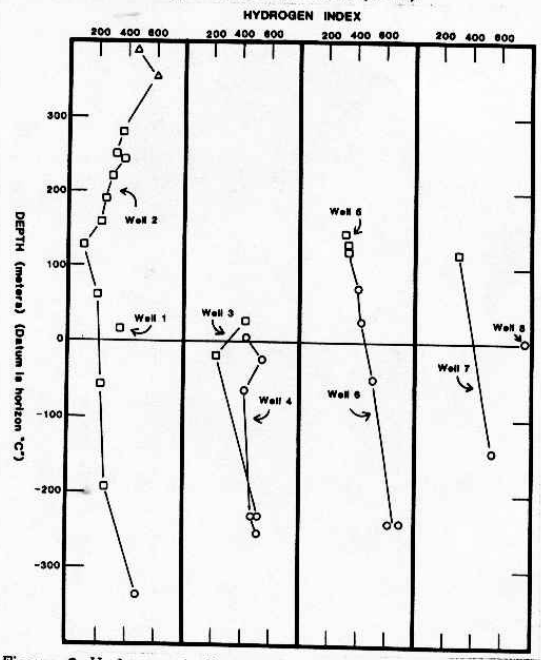

Figure 9- Hydrogen indices of Lost Hills samples as a function of drilled depth above and below correlation point "C". For position of point "C", refer to figure 4. Symbols as in figure 8. Wells plotted separately for clarity.

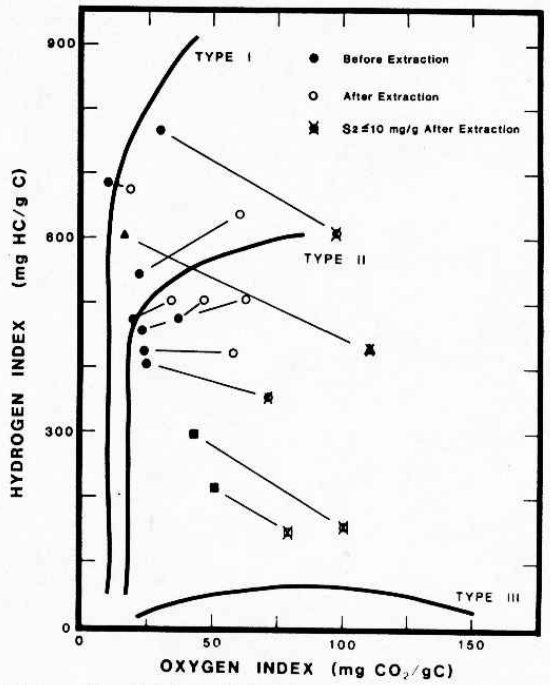

Figure 10- Modified Van Krevelen diagram depicting selected Lost Hills samples before and after solvent extraction. Symbol shapes as in figure 8.

heavy bitumen (figs. 6 and 7). Their high hydrogen indices probably represent these accumulated hydrocarbons, not indigenous kerogen. This suggests that heavy bitumen contamination of the S_2 (pyrolyzable kerogen) peak and hence of the hydrogen index could lead to misinterpretation of Van Krevelen diagrams, which are intended for *kerogen* classification. Proper application with bitumen-rich rocks such as these requires pre-pyrolysis solvent extraction. Figure 10 shows hydrogen and oxygen indices of 11 representative samples before and after extraction. Rocks leaner in kerogen (S_2 ≤10 mg/g after extraction) show significant drops in the hydrogen index and increases in the oxygen index. Most of the rocks richer in kerogen show increases in both parameters, but overall there is less change. Therefore rocks with higher bitumen to kerogen ratios are more likely to give misleading results. Bitumen contamination explains the anomalous situation of a shallow sample plotting in high-hydrogen field "a". However overall, data from extracted samples does not contradict the basic conclusions drawn from the unextracted: rocks lower in the stratigraphic section essentially contain Type II kerogen. Rocks higher in the section have a mixture of Types II and III.

Organic Diagenesis (Maturity)

In this study, several independent means of evaluating diagenetic grade were employed. Determinations of biogenic silica phases and maximum pyrolysis temperatures provide the bulk of the data. Thermal alteration index (TAI) and vitrinite reflectance (R_o) are more universally accepted diagenetic indicators. These were employed on a supplementary basis to standardize the interpretation.

The Rock Eval device plots the quantity of hydrocarbons evolved (S_2) as a function of pyrolysis temperature. The temperature at which this curve peaks is recorded as T_{max} (Espitalié and others, 1977). This is a function of the refractoriness of the material and hence, its diagenetic grade. A mature kerogen has already partially broken down as a result of being heated, leaving intact only the stronger inter-molecular linkages (Tissot and Welte, 1978). Severance of these surviving bonds requires higher energies. It must be remembered that T_{max} is *not* the maximum geothermal temperature a rock experienced. It may be proportional to such a temperature, but is usually much higher.

Figure 6 presents the maximum pyrolysis temperatures in a depth context. Shallow samples in well 2 (above 700 m) all show T_{max} values of ~410° C. Below this point, the data shows a collective trend increasing from 376 to 427° C with depth. A T_{max} of 430-435° is considered to be equivalent to an R_o of 0.5-0.6% and this marks the onset of the main phase of oil generation (G. Demaison, pers. comm.). On this basis, the entire section is immature.

The large drop in S_2 after solvent extraction in some samples raises the suspicion that T_{max} values may also have been affected. In the unextracted cases, heavy bitumen may skew the S_2 curve and possibly shift the peak. To visualize the extent of this effect, figure 7 plots T_{max} before and after extraction as a function of depth. The amount of increase in T_{max} after extraction varies between 0 and 16°. The largest increases are in samples that have very low pre-extraction T_{max} values. The amount of decrease in S_2 after extraction (fig. 7) seems to bear no relation to the magnitude of the T_{max} change. The same trends seen in figure 6 (unextracted) are still apparent in figure 7 (extracted):

(1) The sample representative of the zone in well 2 above 700 m is still anomalously high.

(2) Below 700 m, the collective trend still increases with depth, but over a narrower range.

Therefore the lowest values of T_{max} (<410° C) must be interpreted with caution in unextracted samples. However, in this case, there is no effect on the overall perception of the diagenetic trend.

Vitrinite reflectance and thermal alteration index measurements also show the section to be immature. Hemipelagic rocks such as these may lack sufficient vitrinite for reliable measurements. Out of the ten samples submitted for analysis, only two had statistically significant populations of autochthonous vitrinite. In well 6, at 1641 m, there is a mean R_o value of 0.30% (σ=0.06, N=34). In well 7, at 2263 m, mean R_o is also 0.30% (σ=0.05, N=23).

Thermal alteration index measurements are based on the color of organic debris using transmitted light microscopy. In this case the organic matter was mostly amorphous (probably algal), with some pollen and spores. TAI measurements on the same ten samples corroborate the low R_o values. They range between 1.5 and 2.3, with no depth-dependent trends. A TAI value of 2.0 corresponds to a vitrinite reflectance of 0.3% (Waples,1980).

DISCUSSION: IMPLICATIONS FOR PETROLEUM GENERATION

A series of parallel diagenetic indicators has been presented. Vitrinite reflectance, thermal alteration index and maximum pyrolysis temperature values are all substantially below levels conventionally associated with the onset of the main phase of petroleum generation. This is true even for the deepest samples, whose present burial temperatures are close to 100° C. Yet the transformation of biogenic silica to quartz is complete at moderate depths, at present temperatures <80° C. Therefore, energy requirements for silica diagenesis must be considerably less than those needed for ***substantial*** petroleum generation from kerogen.

Lopatin models of the effects of time and temperature on organic diagenesis are useful for predicting depths to mature petroleum source rocks (Waples, 1980). This technique is applied to two Lost Hills wells (2 and 8) and to a very deep exploratory well in the syncline 12 km northeast of Lost Hills (Western National Royalties No. 1, located on figure 1). The burial history of stratigraphic horizon "C" in the Antelope Member is reconstructed at each well site (fig. 11). The age of the horizon is estimated to be ~10 m.y., based on diatom and foraminiferal dating (L.Williams, pers. comm.; Bandy and Arnal, 1969, table 5). To account for growth of the Lost Hills anticline, 600 meters of uplift-related erosion are estimated as a maximum for well 2, by examination of figure 4. Using the method of Waples (1980), an extremely low time-temperture index (TTI) of 0.4 is calculated at well 2. If there were less than 600 m of erosion at well 2, this value would be even lower. Well 8, of the 8 wells studied at Lost Hills, penetrates the most deeply buried Monterey shales. However the calculated TTI value at 2200 m is still only 1.1. This agrees with the low vitrinite reflectance (0.3%) measured at about this depth (TTI converted to the equivalent R_o by the method of Waples, 1980). Interestingly, a TTI value of only ~0.7 represents the time-temperature conditions for complete conversion of opal-CT to quartz. The third well was not sampled in this study, but it can be correlated to the others by electric logs (Graham and others, 1982). A TTI value of 22 is calculated at 3700 m, barely past the onset of oil generation (TTI of 15). Therefore it is likely that petroleum generated to date from upper Miocene source rocks in the syncline should be only marginally mature, *e.g.*, characterized by high asphaltene content (Tissot and Welte, 1978). Indeed there are considerable amounts of heavy bitumen in Lost Hills samples. This is evidenced by the marked drop in the S_2 pyrolysis peak after solvent extraction (fig. 7). However, where they exist, the fractured shale reservoirs at Lost Hills do produce medium weight crude oil (A.P.I. gravity of 25-35, Cal. Div. Oil and Gas, 1973). This may be the result of:

(1) Fractionation during migration of initially heavy oil (Powell and others, 1975).

(2) A contribution of more mature oil from deeper, older strata, such as the lower Miocene or upper Eocene (Philippi,1973).

The preceding was a conventional interpretation of the origin of petroleum at Lost Hills. However, the Monterey shales may not be conventional source rocks. Powell and others (1975) note that phosphorites of low diagenetic grade have high concentrations of soluble organic matter, especially asphaltenes, relative to average shales with similar organic carbon contents. Thus oil rich in heterocompounds may become available for migration when a phosphatic source rock is still "immature" in conventional terms. Pelletal authigenic phosphates are common in the Monterey Formation, specifically in the Antelope and McDonald Members at Lost Hills. The dysaerobic environment favorable for phosphorite formation may somehow ensure creation and preservation of complex heterocompounds. Recent sediments off the coast of Peru may represent a partial depositional analog to the Monterey Formation (Soutar and others, 1981). There, phosphates are forming in sediments where the fringes of the oxygen minimum zone (O_2<0.2 ml/l) intersect the continental slope (Garrison and others,1979). These mildly reducing conditions are favorable for sulfur-oxidizing bacteria such as *Beggiatoa*. They grow in colonial clusters in the top few centimeters of sediment (Jørgensen, 1977). Reimers (1982) has observed such bacteria off the Peru coast forming quasi-stromatolitic mats. These serve to bind sediments shortly after deposition. The cohesiveness may survive as sediments are buried and enter the sulfate-reducing zone. This would decrease permeability, limiting further bacterial access to nutrients in these deeper zones. This could partially suppress consumption of labile organic fractions,

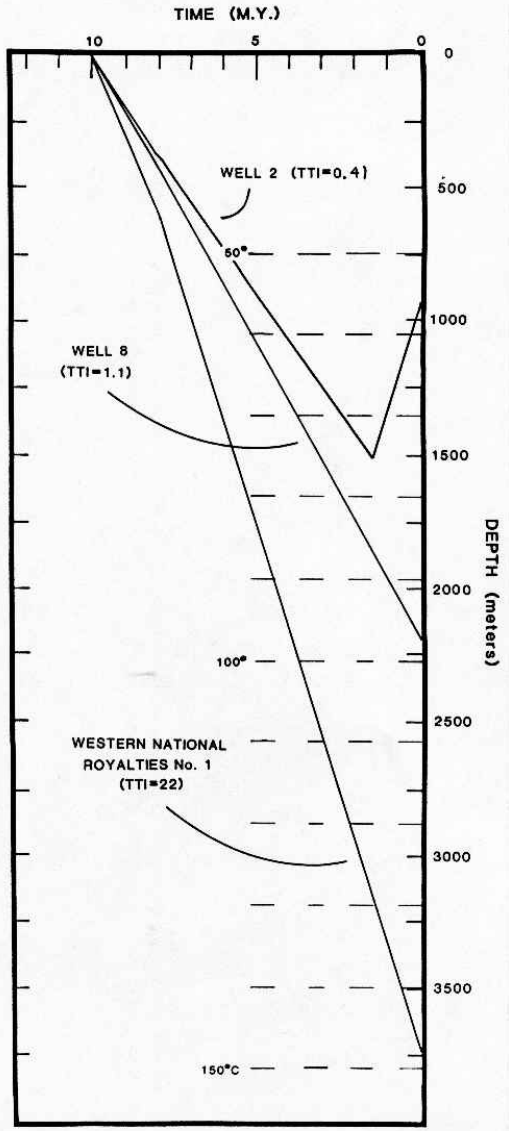

Figure 11- Lopatin reconstruction of the time/temperature history of an upper Miocene horizon (at correlation point "C") from 3 Lost Hills area wells. Present geothermal gradient (from figure 4) assumed constant for the last 5 m.y. See text.

already at low levels in anoxic pore waters. Lipids from *Beggiatoa* and other bacteria may also contribute to the sedimentary organic matter (Williams and Reimers, 1982).

Bacterial mats may not be required to explain these immature bituminous phosphatic rocks. The high concentrations of PO_4^{3-} in bottom and interstitial waters necessary to precipitate apatite are the result of an intense rain of organic debris down from a highly productive photic zone (Garrison and others, 1979). The decay of such vast amounts of organic material may simply overwhelm the system, favoring preservation of lipids.

The question remains why kerogen formation in phosphatic rocks would be incomplete. Kerogens may be thought of as complex polymers formed of biogenic molecules cross-linked by heteroatomic bonds. Their large size renders them insoluble. Asphaltenes are similar in structure, but much smaller and therefore soluble (Tissot and Welte, 1978). In theory, kerogens begin to coalesce in earliest diagenesis, as intermolecular linkages are formed (Philp and Calvin, 1976; Simoneit and Burlingame, 1974). During late diagenesis, the weaker linkages are broken, releasing large fragments (asphaltenes). During catagenesis, the stronger linkages binding the fragments may break, yielding hydrocarbons (Tissot and Welte, 1978). Powell and co-workers (1975) suggest that phosphatic sediments contain primary asphaltenes, with no kerogen precursors. Are these the products of chemically thwarted kerogen formation? Whatever their origin, there may be early hydrocarbon generation from these asphaltenes, if their intermolecular bond energies are favorably low. This process, though, should involve at least a minor increase in maturity. In this light,a peculiar situation exists at Lost Hills. There is a rich zone of bitumen (both light and heavy) between 1400 and 1570 m (wells 3-6). Their stratigraphic equivalent in well 8 is below 2100 m and contains only heavy bitumen. The zone in the deeper well is about 30° C hotter than it is the shallower wells. As expected, this deeper well also is at a slightly higher diagenetic grade, evidenced by the maximum pyrolysis temperatures. Can the lighter bitumens have been generated *in situ* in the cooler zone only? Perhaps instead the heavy bitumen is ubiquitous and indigenous, but the lighter has migrated from more mature strata down-dip. It could then accumulate locally where secondary porosity is well-developed, as in the siliceous Antelope Member after diagenetic conversion to quartz and tectonic fracturing, or where primary porosity is still available, as in the shallow silty diatomaceous mudstones. Alternatively, the lighter bitumen may have formed locally from the immature heavy bitumens. Due to its lower molecular weight, it could then preferentially migrate short distances and collect in high porosity zones.

A deep syncline which probably contains excellent source rock is present only 10 km east of the Lost Hills anticline. By conventional wisdom, one would need to look no farther for the source of the Lost Hills petroleum, assuming migration pathways are available. This is in accord with the conclusions of the San Joaquin Basin analysis of Zieglar and Spotts (1978). The locally high concentrations of light bitumens (S_1) may very well be the result of such migration. The more widespread heavy bitumens may either be indigenous or the residual fractions left behind during "geochromatographic" migration. Biomarker studies on samples representing a wide range of burial depths may serve to clarify the situation.

CONCLUSIONS

1) Monterey shales from the Lost Hills oil field are extremely rich in both soluble and insoluble organic matter, which is most likely derived from marine plankton and bacteria. There is evidence for a humic organic component in samples collected higher in the stratigraphic section.

2) Rock Eval pyrolysis of bitumen-rich rocks is best done twice on each sample: before and after solvent extraction.

Without extraction, one is able to delineate accurately zones of organic richness, but measurements of the magnitude of richness may be misleading. Heavy bitumen interference with measurements of pyrolyable kerogen (S_2) has little effect on maximum pyrolysis temperatures in the 410-430° C range. T_{max} values <410° may be low because of such contamination.

3) Silica diagenesis provides sensitve diagenetic indices, including opal-CT $d_{(101)}$ spacing. These can provide scales of comparison in studies of biomarker compound diagenesis.

4) Maximum pyrolysis temperatures, vitrinite reflectance and thermal alteration index measurements, and Lopatin time-temperature modeling all indicate that the Monterey Formation in the Lost Hills oil field is at low maturity levels. Due to this lack of thermal stress, it is likely that abundant biomarker compounds survive.

5) The diagenetic transformation of biogenic silica to quartz is complete in Lost Hills rocks at present temperatures of 80° C or less. It is estimated by time/temperature history modeling that upper Miocene rocks would have to reach temperatures of ~140° C 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 "Cahn Zone", 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.

6) Deeply buried, high quality source rock down-dip from the oil accumulation suggests that the San Joaquin Valley syncline is the main source of Lost Hills petroleum.

7) In addition to immature kerogen, the phosphatic Monterey shales at Lost Hills may also contain biogenic or early diagenetic bitumen. This may be the source of a portion of the Lost Hills petroleum. Biomarker studies are needed to clarify this point.

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