

Hydrous pyrolysis of crude oil in gold-plated reactors

J. A. CURIALE,¹ P. D. LUNDEGARD¹ and Y. K. KHARAKA²

¹Unocal, Inc., Brea, California and ²U.S. Geological Survey, Menlo Park, California, U.S.A.

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Abstract—Crude oils from Iraq and California have been pyrolyzed under hydrous conditions at 200 and 300°C for time periods up to 210 days, in gold-plated reactors. Elemental (vanadium, nickel), stable isotopic (carbon), and molecular (*n*-alkanes, acyclic isoprenoids, steranes, terpanes and aromatic steroid hydrocarbons) analyses were made on the original and pyrolyzed oils. Various conventional crude oil maturity parameters, including 20S/(20S + 20R)-24-ethylcholestane ratios and the side-chain-length distribution of aliphatic and aromatic steroidal hydrocarbons, were measured in an effort to assess the modification of molecular maturity parameters in clay-free settings, similar to those encountered in “clean” reservoirs.

Concentrations of vanadium and nickel in the Iraq oil decrease significantly and the V/(V + Ni) ratio decreases slightly, with increasing pyrolysis time/temperature. Whole oil carbon isotope ratios remain fairly constant during pyrolysis, as do hopane/sterane ratios and carbon number distribution of 5 α (H), 14 α (H), 17 α (H), 20R steranes. These latter three parameters are considered maturity-invariant.

The ratios of short side-chain components to long side-chain components of the regular steranes [$C_{21}/(C_{21} + C_{29}R)$] and the triaromatic steroid hydrocarbons [$C_{21}/(C_{21} + C_{28})$] vary systematically with increasing pyrolysis time, indicating that these parameters may be useful as molecular maturity parameters for crude oils in clay-free reservoir rocks. In addition, decreases in bisnorhopane/hopane ratio with increasing pyrolysis time, in a clay-free and kerogen-free environment, suggest that the distribution of these compounds is controlled by either differential thermal stabilities or preferential release from a higher-molecular weight portion of the oil.

Key words—hydrous pyrolysis of oil, biomarkers, California oil, Iraq oil, vanadium and nickel in oil, molecular maturity parameters, bisnorhopane, in-reservoir oil maturity, gold reactors

INTRODUCTION

Crude oil, while resident in sandstone and carbonate reservoirs, will undergo elemental, isotopic and molecular alteration with increased thermal stress. This alteration is often caused by molecular disproportionation. Because the rate, and often the effect, of this disproportionation can be altered by the presence of clays (e.g. Miloslavski *et al.*, 1991, and references therein), *in situ* experiments cannot distinguish effects that are solely thermal from those influenced by mineralogy. For this reason we turned to experimental pyrolysis as a means of understanding compositional modifications that are due only to increased maturity.

Molecular disproportionation is often investigated by monitoring changes in molecular ratios, which are considered to record the appearance or disappearance of a particular compound, relative to a second compound that is assumed to be conserved throughout the reaction. This rationale usually invokes compound destruction; the “production” of compounds (or compound types) is rarely cited. For example, where a decrease in the ratio of regular to rearranged steranes in an oil is often explained as a net loss of regular steranes (Goodwin *et al.*, 1983), the “production” of rearranged steranes during the process is never invoked. In the case of crude oils, such pro-

duction of particular compound types can occur either by *de novo* synthesis in the oil (unlikely), or by preferential release of compounds that have been “sequestered” (either weakly bonded or occluded) in non-hydrocarbon fractions (Montgomery, 1984; Sinninghe Damste *et al.*, 1990; Myhr *et al.*, 1990, and references therein). Thus the molecular changes evident in oil maturation could result from either differential thermal degradation or preferential release of compounds from higher molecular weight material.

In the present study, we have pyrolyzed two crude oils at 200 or 300°C in the presence of liquid water in gold-plated reactors, for periods of time up to 210 days, in an effort to understand the effects of thermal alteration on biological markers (steranes and hopanes), carbon isotope ratios and transition metal (vanadium and nickel) distributions (Curiale *et al.*, 1991). Our goal is to examine, in an oil/water, clay-free setting, the maturity-dependence and maturity-invariance of particular geochemical parameters used to evaluate source rock maturity and assess oil-source rock correlation possibilities.

Various experimental procedures are available to separate the influence of clays on thermally-induced alteration of oil. Hydrous pyrolysis, now commonly used to simulate the generation of petroleum from source rocks (Lewan, 1985), has also been used to

study thermal alteration of oil in the presence and absence of known inorganic catalysts (Chung *et al.*, 1988, 1991; Bjoroy *et al.*, 1988; Monin and Audibert, 1988). Results of such experiments may be applied to define the thermal effects on oils reservoirized in relatively inert reservoirs (e.g. quartz-rich sands), and to isolate the effects of water washing on crude oil (by creating a water-washed oil without the overprinting compositional effects caused by biodegradation; Palmer, 1984).

Many studies have suggested new (and/or improved) methods of thermal maturity measurement, leading to several popular and widely-used molecular maturity indicators (see Mackenzie and Maxwell, 1981; Brassell, 1985; Curiale *et al.*, 1989; van Graas, 1990). However, the literature is ambiguous as to the influence of either organic or inorganic catalysts on these parameters. Thermal alteration experiments involving extractable organic matter isolated from associated minerals and kerogen have, in certain instances, revealed little effect on hopane stereochemistry (Monthieux and Landais, 1989, and references therein). In contrast, Bjoroy *et al.* (1988) showed that steroid molecular maturity parameters are altered in oil pyrolyzates. Indeed, these authors also observed thermally-induced alteration of other parameters which are often considered maturity-invariant. Despite conflicting literature evidence, many workers continue to assume implicitly that catalytic effects during the thermal maturation of oil in porous rocks are minor. However, at least one worker has suggested that hydrocarbon distributions can be affected by *in situ* catalysis during petroleum generation (Mango, 1987, 1990a). Therefore, such assumptions could be unwarranted, particularly in instances where transition metal concentrations are high (Mango, 1990b).

Many workers have conducted clay-free experiments monitoring maturity increases in source rocks (Tannenbaum and Kaplan, 1985; Tannenbaum *et al.*, 1986) and oils (Orr, 1986; Bjoroy *et al.*, 1988; Chung *et al.*, 1988, 1991). The elimination of clay from the reaction vessel is straightforward. However, because a reactor must be used in thermal alteration experiments, the total elimination of catalytic influence is impossible. Various workers have cited problems with contamination, and have presumed that inorganic catalysis occurs during experiments in which sample material comes in contact with stainless steel. Nickel in 316 stainless steel commonly forms tiny nickel sulfide crystals (Ni_3S_2) on the interior surface of the reaction vessel (Monin and Audibert, 1985); presumably, finely-disseminated foreign nickel-containing compounds may then become incorporated in sample material. We have observed the formation of silver and iron sulfides during hydrous pyrolysis of petroleum source rocks in stainless steel reaction vessels (G. P. Ouellette and J. A. Curiale, unpublished results). Gold reactors were recently employed to minimize such problems (Kressmann *et al.*, 1989).

The use of gold surfaces minimizes problems associated with stainless steel catalytic effects, including the effect of organic acid destruction (Palmer and Drummond, 1986; Lundegard and Senftle, 1987; Kharaka and Lundegard, in prep.). Our use of reactors whose interiors are entirely gold or gold-plated provided us with reasonable certainty that reactor-induced inorganic catalysis was absent. No inorganic solids were observed to form within the reaction vessel during the experiments described here.

METHODS

We subjected oils to hydrous pyrolysis using one-liter gold-plated reactors. All interior parts of the reactor were gold-plated over 316 stainless steel. Iraq (Kirkuk Field) and California (Midway-Sunset Field, San Joaquin Basin) oils were pyrolyzed. The Iraq sample is a paraffinic oil having a sulfur content of 1.5 wt %, a pristane/phytane ratio of approximately 1.0, and no *n*-alkane carbon chain length preference. It exhibits no obvious signs of biodegradation. The California oil contains high relative concentrations of tetra- and pentacyclic hydrocarbons, and has virtually no *n*-alkanes or isoprenoids (both lost due to extensive biodegradation). Its sulfur concentration is 0.8 wt %.

In the 300°C experiments, 215 g of double-distilled, deionized water and either 195.6 g (Iraq) or 214.6 g (California) of oil were pyrolyzed in the gold-plated reactor. For the 200°C experiment, 214.2 g of water and 205.9 g of California oil were used. The reactor configuration and rotation apparatus are similar to those described by Seyfried *et al.* (1979, 1987), except that one-liter gold-plated reactors were used instead of gold-foil bags, and a dual sampling tube arrangement was employed. The reactor was purged with argon prior to sealing, and the oil/water mixture was pyrolyzed under a helium atmosphere at 200 or 300°C for various lengths of time. During the experiments, the reactors were continuously rotated through a 180 degree arc (as described in Seyfried *et al.*, 1979) to maintain a homogenous mixture.

Rotation of the reactors was stopped briefly to facilitate fluid sampling during the course of the experiment. Sampling of oil, water and gas was conducted at the experimental temperature through capillary sampling tubes (gas analyses are reported elsewhere; see Kharaka and Lundegard, in prep.). The main reactor chamber was connected to the sample exit port with gold capillary tubes (0.090 in o.d.) encased within 1/4 inch o.d. 316 stainless steel tubes. The first tube entered the reactor chamber only a short distance, and was used to sample gases when the reactor was upright, and water when the reactor was inverted. The second tube was used to sample the oil. It extended approximately halfway into the reactor chamber, to a point within the oil phase. Other details of the procedure, including reactor specifications, are in Seyfried *et al.* (1979, 1987).

Table 1. Reactor sampling conditions
(a) 300°C Experiment

Days	Iraq Oil		California Oil	
	Temp. (°C)	Press (bars)	Temp. (°C)	Press (bars)
2	302	106.3	282	72.5
8	302	111.6	297.5	90.7
19	305	111.4	301	96.3
30	305	110.2	302	100.1
58	302.6	109.4	293.8	93.5
85	302	110.3	300	104.3
98	299	105.1	302.2	107.8

(b) 200°C Experiment, California Oil

Days	Temp. (°C)	Press (bars)
1	202	14.7
60	204	17.0
210	207.4	18.0

Minor flaking of the gold coating was observed when the reactor was emptied after the 300°C experiment with Iraq oil. The time at which this flaking occurred, and the time during which the stainless steel reactor wall was exposed to the oil/water/gas during the experiment, are unknown. However, the effect of this exposure is considered minor because the area of exposure is small (estimated to be less than 0.1% of the entire interior reactor surface). Furthermore, the trends observed in the Iraq oil experiment are very similar to those observed in the California oil experiment, in which flaking did not occur.

Subsamples of oil/water were taken throughout each experiment, at experimental PT conditions. For example, in the 300°C experiments, samples were taken at pressures of 73–112 bars and temperatures of 288–303°C (PT details are listed in Table 1). Oils were allowed to cool to ambient conditions and placed in pre-cleaned glass vials and refrigerated until analysis. Water for organic acid analysis (results reported by Kharaka and Lundegard, 1992) was filtered through a 0.45 µm membrane, and stored in refrigerated glass vials until just prior to analysis. Mercuric chloride was added to the organic acid samples at the time of sampling, to inhibit bacterial growth. Water for inorganic solute determination was filtered through 0.2 µm membranes, acidified to pH 2 with ultrapure nitric acid, and stored in polyethylene vials. Full details and conclusions concerning the water analyses are presented by Kharaka and Lundegard (in prep.).

The Iraq and California oils were heated for 2–98 days at 300°C, and the California oil was heated in a separate experiment for 1–210 days at 200°C. In the 98 day experiments (300°C), approx. 5 ml of oil were removed after 2, 8, 19, 30, 58, 85 and 98 days, at the conditions described above. Two samples were taken after 98 days. The first (5 ml) was sampled at the temperature/pressure conditions of the reactor, whereas the second (the remaining oil in the reactor—approx. 150 ml) was sampled after the reactor cooled to ambient conditions and was opened. In the 210 day experiment (200°C), approx. 5 ml of oil were removed

after 1, 60 and 210 days. Specific sample identifications and pyrolysis times are given in Tables 1 (pressure/temperature data), 2 (elemental and isotopic data), and 3 (molecular data).

Whole original and pyrolyzed oils were analyzed by inductively-coupled plasma emission spectrometry (ICP-AES; vanadium, nickel), isotope ratio mass spectrometry ($\delta^{13}\text{C}$), capillary gas chromatography (*n*-alkanes and isoprenoids), and capillary gas chromatography-mass spectrometry (GCMS; steranes and selected terpanes). ICP-AES measurements were made on whole oil ash dissolved in an aqueous medium, as outlined by Odermatt and Curiale (1989, 1991) and Curiale (1992a). $\delta^{13}\text{C}$ values were obtained using whole oil, closed-tube combustion methods. Oils were combusted as received, without removal of light ends; experimental details are reported elsewhere (Curiale, 1989, 1992a). Carbon isotope ratios are reported relative to the PDB standard.

Biomarker analyses were completed on whole oils using selected ion recording techniques at approx. 5000 resolving power (RP) on a VG 70-250SE instrument. Compound identities were confirmed *via* full scan analysis at approx. 1000 RP on the same instrument. Full details of the gas chromatographic and gas chromatographic-mass spectrometric analyses are in Curiale (1991, 1992a). All biomarker ratios are computed based on peak heights, using customized chromatographic algorithms for baseline assignments (VG 11-250 peak processing software; see Curiale, 1991, 1992a). The specific compound ratios involved are listed in the footnotes to Table 3 and discussed in a later section.

Analytical precision was determined from several previous studies in this laboratory (Curiale *et al.*,

Table 2. Elemental and isotopic data

Days	Ni (ppm)	V (ppm)	V/(V + Ni)	$\delta^{13}\text{C}$ (‰)
<i>IRAQ/300°C</i>				
orig.	12.0	25.0	0.68	-27.14
orig.	13.0	29.0	0.69	-26.44
2	14.0	28.0	0.67	-26.48
8	13.0	27.0	0.68	-26.43
19	12.0	24.0	0.67	-26.80
30	10.0	20.0	0.67	-26.71
58	9.4	17.0	0.64	-26.22
85	†	†	†	-26.36
98	6.0	9.8	0.62	-26.03
98*	4.7	7.9	0.63	-26.10
<i>CALIFORNIA/300°C</i>				
orig.	†	†	†	-23.46
2	†	†	†	-23.18
8	†	†	†	-23.48
19	69.0	22.0	0.24	-23.32
30	74.0	24.0	0.24	-23.48
58	77.0	24.0	0.24	-23.24
85	†	†	†	-23.33
98	†	†	†	-23.24
98*	†	†	†	-23.75
<i>CALIFORNIA/200°C</i>				
1	73	20	0.22	-23.49
60	78	21	0.21	-23.49
210	93	22	0.19	-23.50

*Sampled after reactor cooled to ambient temperatures.

†Sample size too small for reliable analysis.

Table 3. Molecular data

Days	1	2	3	4	5	6	7	8	9
IRAQ/300°C									
orig.	0.64	0.39	0.41	0.42	*	8.8	11.13	0.23	47/20/33
orig.	0.67	0.45	0.38	0.40	*	9.2	13.06	0.27	47/20/32
2	0.67	0.41	0.42	0.35	*	8.7	9.44	0.21	42/22/36
8	0.74	0.42	0.64	0.47	*	11.7	6.43	0.39	49/19/31
19	0.71	0.46	0.64	0.42	*	9.8	11.26	0.27	54/15/31
30	0.80	0.50	0.73	0.42	*	23.7	9.91	0.32	47/22/31
58	0.87	0.47	0.95	0.69	*	12.9	9.95	0.42	54/20/26
98	0.84	0.49	0.95	0.44	*	7.9	24.64	0.26	46/21/33
98	0.82	0.48	0.95	0.53	*	8.9	17.13	0.27	53/17/29
CALIFORNIA/300°C									
orig.	0.26	0.32	0.15	0.64	0.49	†	4.71	0.25	38/36/25
2	0.42	0.35	0.28	0.85	0.48	†	5.14	0.41	39/36/25
8	0.29	0.34	0.17	0.68	0.50	†	4.55	0.31	37/37/26
19	0.38	0.36	0.28	0.91	0.47	†	7.97	0.38	45/35/20
30	0.40	0.39	0.25	0.68	0.43	†	6.23	0.23	38/39/23
58	0.50	0.43	0.41	1.24	0.40	†	6.59	0.28	39/39/23
85	0.53	0.47	0.95	1.18	0.35	†	8.86	0.16	44/34/22
98	0.65	0.42	0.81	0.88	0.36	†	7.53	0.36	42/36/22
98	0.67	0.41	0.80	0.82	0.33	†	10.00	0.31	39/38/22
CALIFORNIA/200°C									
0	0.26	0.32	0.15	0.64	0.49	†	4.71	0.25	38/36/25
1	0.25	0.37	0.20	0.77	0.41	†	4.56	0.15	38/37/25
60	0.26	0.36	0.22	0.77	0.44	†	4.20	0.17	38/37/25
210	0.27	0.36	0.20	0.80	0.44	†	4.57	0.17	38/37/25

1. $C_{21}/(C_{21} + C_{29R})$ -5 α (H),14 α (H),17 α (H)-sterane (m/z 217).2. $20S/(20S + 20R)$ -5 α (H),14 α (H),17 α (H)-ethylcholesterane (m/z 217).3. $C_{21}/(C_{21} + C_{28})$ -tri-aromatic steroid hydrocarbons (m/z 231).4. 13 β (H),17 α (H),20R/5 α (H),14 α (H),17 α (H),20R - C_{27} -sterane (m/z 217).5. 17 α (H),18 α (H),21 β (H)-28,30-bisnorhopane/hopane (m/z 191).6. $n - C_{12}/n - C_{29}$ alkane (peak height; computed from whole oil gas chromatograms).7. Hopane/5 α (H),14 α (H),17 α (H),20R-ethylcholesterane (m/z 191 and m/z 217).8. C_{23} -tricyclic terpane/hopane (m/z 191).9. Normalized distribution of 5 α (H),14 α (H),17 α (H),20R-cholestanes having 27/28/29 carbon atoms.

*Bisnorhopane not present.

† n -Alkanes absent in original oil due to biodegradation, and in low concentration in pyrolyzates.

1985; Curiale, 1989, 1991, 1992a; Curiale and Lin, 1991). In addition, duplicate samples of the original Iraq oil were analyzed as a precision check. Metal concentrations are precise to within 6% relative (Ni) and 9% relative (V); V/(V + Ni) ratios are ± 0.02 , absolute. Carbon isotope ratios in whole oils are precise to within $\pm 0.1\%$ (absolute). The reason for the wide variance in carbon isotope ratios of the original Iraq oil (Table 2) is unknown. All "closed" molecular ratios (i.e. those that can range from 0 to 1) have relative standard deviations (based on repetitive GCMS experiments, $n > 5$) between 2 and 6%, except for the sterane/hopane ratio, discussed below (12%).

RESULTS AND DISCUSSION—ELEMENTAL AND ISOTOPIC DATA

Elemental and isotopic data for the original oils (designated as 'orig' in Tables 2 and 3) and pyrolyzates are listed in Table 2. In some cases, pyrolyzed oils recovered from the California/300°C experiment were used for other experiments not described here. In these instances, the amounts of sample left for ICP-AES analysis were too low for reliable metal determinations.

In the Iraq/300°C experiment, both vanadium and nickel concentrations in the oils decrease significantly with increasing pyrolysis time. The V/(V + Ni)

ratio also falls slightly. These metal data are plotted against pyrolysis time in Fig. 1. The decreasing trend observed in the Iraq/300°C experiment is not evident in the California/300°C experiment, or in the California/200°C experiment (Table 2). Although the V/(V + Ni) ratio does appear to decrease in the

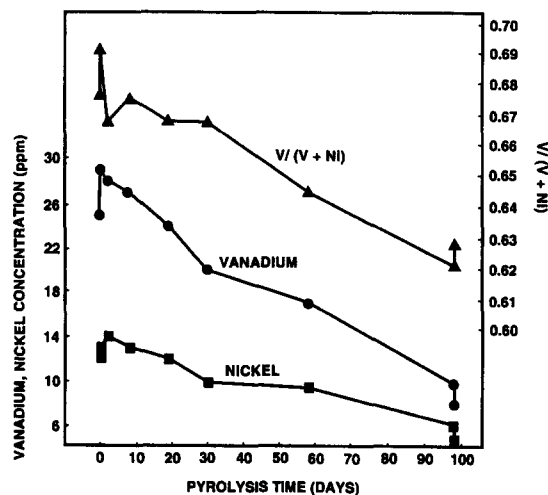


Fig. 1. Variation of vanadium and nickel concentrations (left axis; ppm) and V/(V + Ni) ratio (right axis) with pyrolysis time, for the Iraq oil pyrolyzed at 300°C. Note preferential loss of vanadium with increased heating time.

Data are listed in Table 2.

California/200°C experiment, the decline (a) is at the margin of our analytical precision and (b) is accompanied by an increase in Ni concentration in the 210-day sample. A minor increase in Ni concentration is also observed with increasing pyrolysis time in the California/300°C experiment, although again this increase is at the limit of our precision.

The data in Fig. 1 indicate that vanadium and nickel are depleted in the Iraq oil during hydrous pyrolysis. Previous studies have documented similar results in anhydrously pyrolyzed crude oil (Hodgson and Baker, 1957). This may be due to the thermal destruction of tetrapyrroles (including metalloporphyrins) which are the sites of much, if not all, of the vanadium and nickel in the oil (Baker and Louda, 1983, 1986; Mackenzie *et al.*, 1980). Because the absolute concentration of these elements in the oils is decreasing with increasing pyrolysis time, both elements must pass into the water phase either as divalent cations (Kharaka and Lundegard, in prep.), or as organometallic complexes formed by reaction with the interior surface of the reactor. Alternatively, vanadium and nickel may become part of a solid phase residue during the experiment. Although formation of such a residue was not evident during our experiments, a char was formed during similar (but anhydrous) experiments by Hodgson and Baker (1957).

The data in Table 2 may be used to calculate degradation rate constants for the elimination of vanadium and nickel from oil under the experimental conditions described (hydrous, 300°C). Our results suggest that metal loss in our experiments was a first order process. The values obtained for vanadium and nickel are $12.4 \times 10^{-8} \text{ s}^{-1}$ ($y_{\text{int}} = 29.1 \text{ ppm}$; $r^2 = 0.99$) and $9.3 \times 10^{-8} \text{ s}^{-1}$ ($y_{\text{int}} = 13.7 \text{ ppm}$; $r^2 = 0.96$), respectively, and compare favorably with values extrapolated to 300°C from Hodgson and Baker's (1957) sealed tube anhydrous oil pyrolysis experiments (e.g. $13.9 \times 10^{-8} \text{ s}^{-1}$ for vanadium). The similarity in rate constants for metal depletion during hydrous and anhydrous experiments is surprising, and suggests that the presence of water is not a controlling parameter in the destruction of organometallic complexes in oils during maturation (Kharaka and Lundegard, in prep.).

Our results suggest that individual metal concentrations are of limited utility as oil-oil correlation parameters. This is consistent with previous studies (Branthaver and Filby, 1987, and references therein). Furthermore, because vanadium is lost from the oil at a greater rate than nickel, it is clear that the $V/(V + \text{Ni})$ ratio is not maturity-invariant in this experiment (Fig. 1). The decrease in this ratio with time, although minor (from 0.69 to 0.62), is experimentally significant (see below). This finding is in agreement with results of Hodgson and Baker (1957) but in contrast to some previous investigations. Several workers have found the V/Ni ratio to be invariant with most non-source effects (Costan-

tinides *et al.*, 1959; see also the review by Branthaver and Filby, 1987), whereas Baker and Louda (1986) observed increasing V/Ni ratios with increasing maturity of petroleum porphyrins. It is noted that these previous studies were often conducted without significant controls on any of the four processes responsible for changes in metal concentrations in oils (i.e. original source input, thermal maturity, migration, and in-reservoir alteration—see Curiale, 1992b). In contrast, the experimental design of our work eliminates non-maturity effects as possible causes of variance. In any event, it is noted that, even though analytically significant $V/(V + \text{Ni})$ ratio decreases were observed, the total drop [6% of the 0–1 $V/(V + \text{Ni})$ scale] is quite minor. This indicates that the ratio may still be useful as an oil-oil and oil-source rock correlation tool throughout much of the oil window, when $V/(V + \text{Ni})$ ratio differences between oil families are greater than about 0.1 (Bonham, 1956; Lewan, 1984).

Carbon isotopic data for all three experiments are listed in Table 2 and plotted in Fig. 2. Systematic variations in $\delta^{13}\text{C}_{\text{oil}}$ were not observed in the California/300°C and California/200°C experiments, in contrast with minor changes in $\delta^{13}\text{C}_{\text{oil}}$ (about 2‰) observed by Chung *et al.* (1991) during anhydrous pyrolysis of a Monterey crude. Minor increases in carbon isotope ratios are apparent in the Iraq/300°C experiment. The slight change in $\delta^{13}\text{C}$ with pyrolysis time in the Iraq oil (Fig. 2) may result from increased thermal destruction (and conversion to gas) of the isotopically light *n*-alkanes with increased pyrolysis time, whereas these *n*-alkanes are in low starting concentrations in the California oil due to biodegradation (compare upper chromatograms in Figs 3 and 4). In general, our data support the conclusion that, in terms of whole oil $\delta^{13}\text{C}$ values, isotope ratios provide a valuable, and largely maturity-invariant, oil-oil rock correlation tool in the case of these particular oils. However, carbon isotope ratios of oil will, in general, change with maturity because of (a) changes in the isotope ratio of compound classes (Schoell, 1984) and (b) differences in

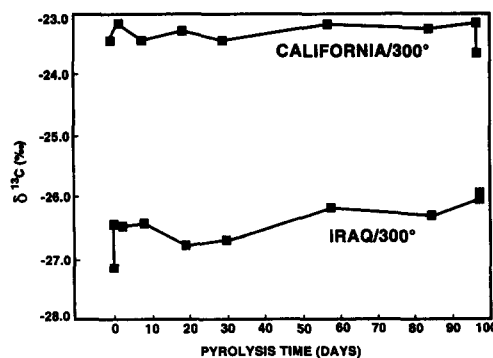


Fig. 2. Variation of carbon isotope ratio (whole, untapped oil) with time of hydrous pyrolysis, for the California and Iraq oils pyrolyzed at 300°C. Data are listed in Table 2.

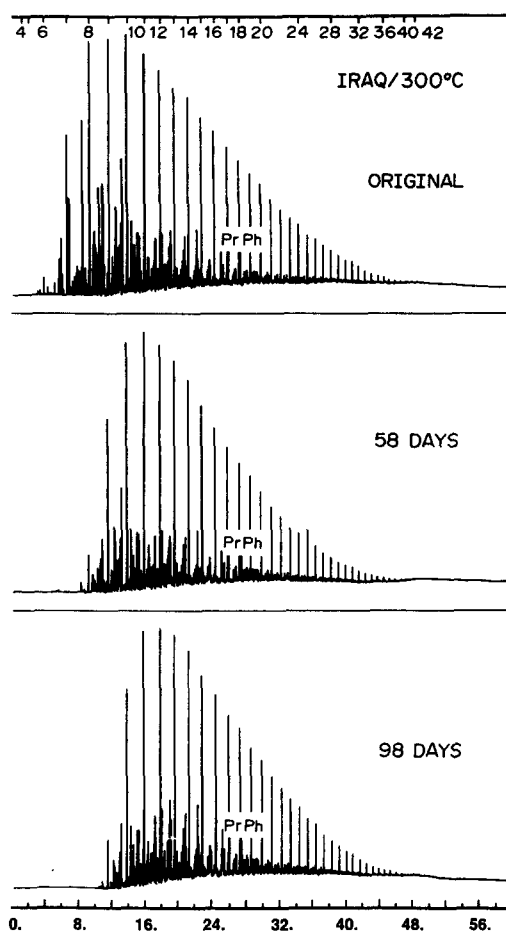


Fig. 3. Whole oil gas chromatograms of the original Iraq oil (top) and the Iraq oil after pyrolysis at 300°C for 58 days (middle) and 98 days (bottom). The top scale indicates the approximate elution location of the *n*-alkane of given carbon number.

the isotope ratio of each individual compound in the oil, particularly the *n*-alkanes (Sofer *et al.*, 1991). Therefore one must be cautious in applying these results to other crude oils.

RESULTS AND DISCUSSION—MOLECULAR DATA

Whole oil gas chromatograms for the original oil and the 58 and 98 day pyrolyzates are presented in Figs 3 (Iraq) and 4 (California). Aside from the differing extent of light-end loss in the oils, no consistent alteration pattern is evident in the *n*-alkane and isoprenoid distributions of the Iraq oil (Fig. 3). This observation contrasts with the changes apparent in the California oil: a shift to lower-boiling point constituents occurs as pyrolysis time increases. The intensity of the peaks in the "biomarker region" of the chromatogram (including the tetra- and pentacyclic hydrocarbons) is reduced considerably after 98 days of pyrolysis, relative to the peaks eluting early in the chromatogram. As noted earlier, this shift in distribution can result

from either a cracking phenomenon (i.e. higher molecular weight components are cracked to small molecules) or a dilution effect (i.e. preferential release of smaller molecules from asphaltenes and soluble high-molecular weight polymers in the oil, neither of which elute from the column at the conditions used). Internal standards are necessary to make this distinction; we will return to these two possibilities in a later section.

It is possible that, with respect to the chromatograms in Figs 3 and 4, the differential effects of pyrolysis on the overall hydrocarbon distributions of these two oils may be attributed to different initial extents of maturity and biodegradation. The non-altered, thermally mature Iraq oil shows no obvious variation as maturity is artificially increased. In contrast, the biodegraded, marginally mature (Curiale *et al.*, 1985) California oil alters considerably as maturity increases.

That molecular distributions do indeed change with increasing hydrous pyrolysis is evident from examination of the biomarker ratios in Table 3 (measured on a peak height basis). As expected,

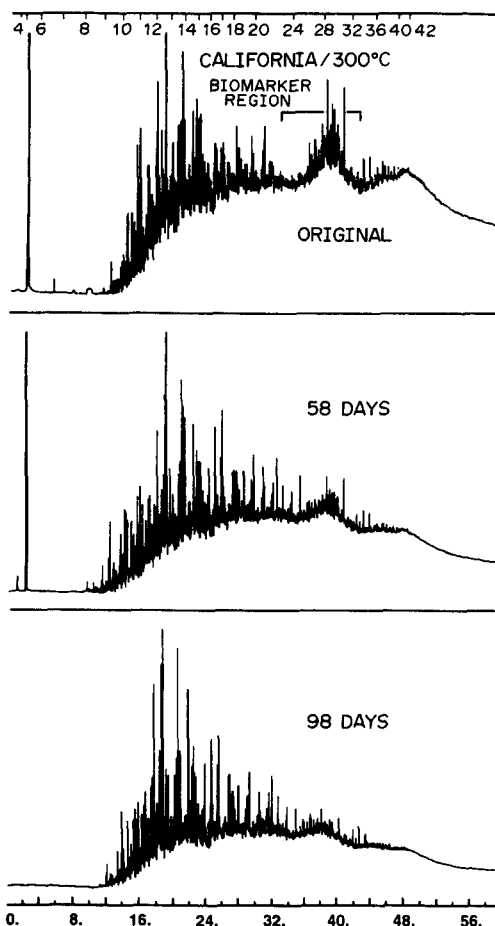


Fig. 4. Whole oil gas chromatograms of the original California oil (top) and the California oil after pyrolysis at 300°C for 58 days (middle) and 98 days (bottom). The top scale indicates the approximate elution location of the *n*-alkane of given carbon number.

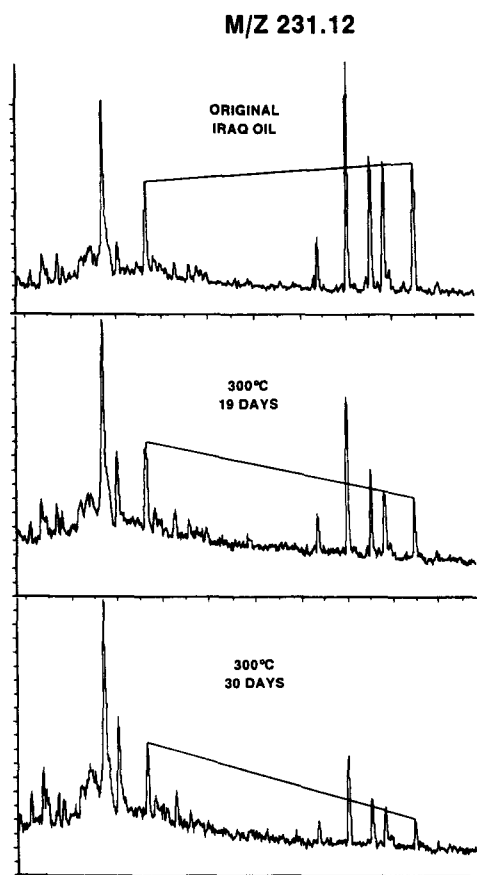


Fig. 5. M/z 231.12 mass chromatograms for original Iraq oil (top) and 19-day (middle) and 30-day (bottom) pyrolyzates. Sloping lines connect a C_{21} -triaromatic steroid hydrocarbon (left; becoming progressively enriched with increasing pyrolysis time) with a $20R$ - C_{28} triaromatic steroid hydrocarbon (right).

several of the accepted biomarker maturity parameters alter systematically with increasing pyrolysis time for both oils in the 300°C experiments. These include the $C_{21}/(C_{21} + C_{28})$ -triaromatic steroid hydrocarbon ratio (Fig. 5; data in Table 3, Column 3), the $C_{21}/(C_{21} + C_{29R})$ -sterane ratio (Column 1), and the diasterane/regular sterane ratio (Column 4).

The $20S/(20S + 20R)$ - $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$ -24-ethylcholestane ratio (Table 3, Column 2) increases slightly through the first 19 days of heating for the Iraq oil, then remains relatively constant. In the case of the California oil, the ratio increases to 0.40–0.45, with a high of 0.47 at 85 days of heating (e.g. Fig. 6; data in Table 3). A reversal appears to be evident (Curiale *et al.*, 1991), an observation similar to that made by other workers for this maturity ratio (Lewan *et al.*, 1986; Strachan *et al.*, 1988; Curiale and Odermatt, 1989; Abbott *et al.*, 1990, and references therein). However, the importance of this reversal is questionable, inasmuch as it is determined by only one data point. Furthermore, the usual equilibrium value of 0.50–0.55 is not reached for the California oil experiment prior to the “reversal” (Abbott *et al.*,

1990). Finally, it is relevant to note that no such reversal is evident in the Iraqi oil at the same temperature/time conditions.

It is of particular interest that the hopane/sterane ratio (Table 3, Column 7) shows no major systematic behaviour in the two oils. Values are quite variable for the Iraq pyrolyzates, whereas a slight increase may be evident in the California oil. Previous studies (van Graas, 1990; Curiale, 1992a) intimate that this ratio is not maturity-invariant, although work by Hoffman *et al.* (1984) and Isaken (1991) indicates that much of the natural variance is due to original source depositional setting. Our data suggest that, when source organic facies is controlled experimentally, and the catalytic effects of clays and kerogen are eliminated, the hopane/sterane ratio in oil does not show a systematic variation with increasing thermal stress.

The distribution of $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H}), 20R$ -steranes by carbon number (measured from the m/z 217 mass chromatogram—see Table 3 and Fig. 7) remains relatively constant as pyrolysis time increases for each oil. While consistent with implicit conclusions of maturity-invariance by many authors, this result contrasts with that of Bjoroy *et al.* (1988), who observed (non-systematic) variability in this distribution during similar crude oil pyrolysis experiments. This discrepancy may result from the higher temperatures used by Bjoroy *et al.* (1988), or by reactions of oil components with the 316 stainless steel (Palmer and Drummond, 1986; Lundegard and Senftle, 1987). Alternatively, it is noted that there is some support in the literature for variation of this carbon number distribution with thermal maturity (Mackenzie, 1984, p. 191; Curiale, 1986, 1992a; Horstad *et al.*, 1990; van Graas, 1990).

It is presumed that pyrolysis of these oils in gold-lined reactors has minimized catalytic effects in general, and eliminated clay-catalytic effects entirely. Further, the use of a single oil in each set of experiments allows us to interpret our results in a source-invariant manner. This indicates that those molecular parameters that vary systematically are “pure” maturity indicators, uninfluenced by either *in situ* clay catalysis or source variability. From this standpoint, data in Table 3 indicate that the most reliable molecular maturity parameters in crude oils are those that monitor the side-chain length distribution of steroid hydrocarbons, including steranes and triaromatic steroid hydrocarbons (Fig. 8; Table 3, Columns 1 and 3).

It is critical to recognize that, although side-chain length distributions in steroids may be useful as “pure” maturity indicators, this does not imply that side chain cracking is occurring. It may simply be that triaromatic steroids present as bound structures in asphaltenes or high-molecular weight hexane-soluble polymers are released preferentially with increasing maturity. As discussed in the introduction, this concern is valid for all molecular

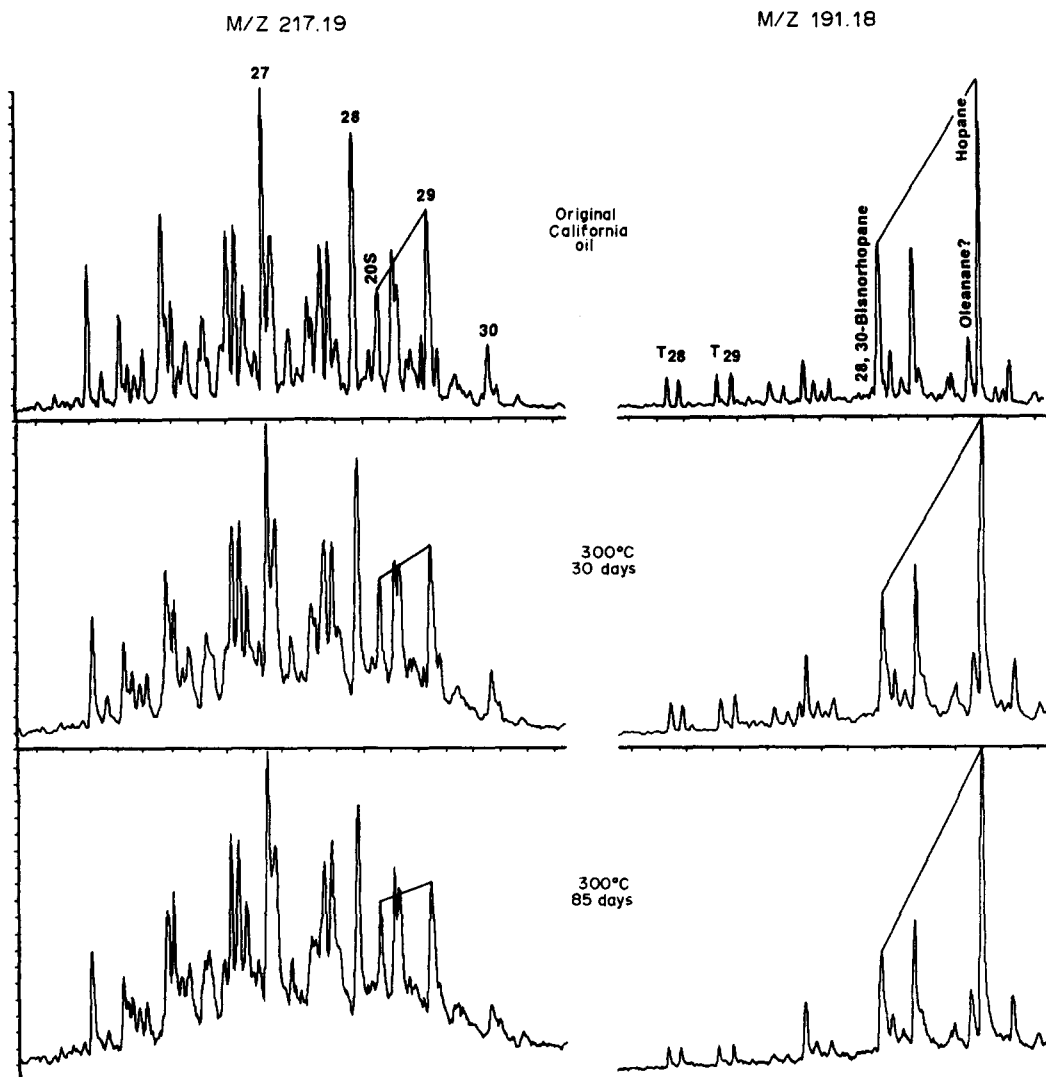


Fig. 6. M/z 217.19 (left) and 191.18 (right) mass chromatograms for original California oil (top) and 30-day (middle) and 85-day (bottom) pyrolyzates. Numbered sterane peaks (left) are $5\alpha,14\alpha,17\alpha,20R$ -steranes, according to number of carbon atoms. Peak labeled '20S' is $5\alpha,14\alpha,17\alpha,20S$ -24-ethylcholestane. T_{28} and T_{29} in the m/z 191.18 traces are tricyclic terpene epimer pairs. Presence of oleanane in 191.18 traces has not been confirmed by co-injection (cf. Moldowan *et al.*, 1991).

maturity interpretations made in this study, as well as interpretations of empirically validated maturity interpretations made in less controlled conditions (van Graas, 1990; Curiale, 1992a).

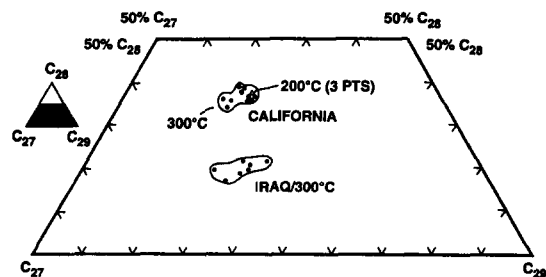


Fig. 7. The distribution of $5\alpha,14\alpha,17\alpha,20R$ steranes by carbon number (C_{27-29}) for Iraq and California oils before and after hydrous pyrolysis. Data are listed in Table 3.

The fact that the California oil used in these experiments is of low maturity and contains bisnorhopane suggests that these hydrous pyrolysis results may also have some bearing on the uncertainties concerning the origin of 28,30-bisnorhopane in California oils and source rocks (e.g. Noble *et al.*, 1985). Relatively high concentrations of this triterpane are present in this oil (Table 3, Column 5). As indicated in Fig. 9, the bisnorhopane/hopane ratio (± 0.02 , absolute; based on peak height) decreases systematically with increasing pyrolysis time. Data in Table 3, although unclear, may also indicate a minor decrease in this ratio over 210 days at 200°C . Variability in the bisnorhopane/hopane ratio in California Monterey Formation oils and extracts has been noted elsewhere (Curiale *et al.*, 1985), and has been attributed to the absence of bisnorhopane as an integral part of the kerogen structure (Noble *et al.*,

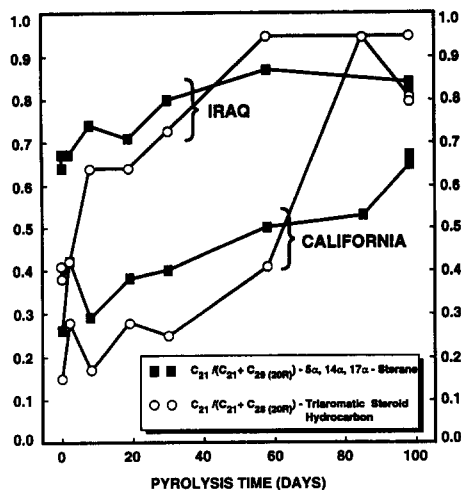


Fig. 8. Variation in ratio of short-side-chain steroids to long-side-chain steroids for aliphatic and aromatic steroids in Iraq (top) and California (bottom) whole oils. The vertical axes show the closed ratio values (i.e. from zero to one) for the regular steranes (■) and the triaromatic steroid hydrocarbons (○), as indicated in the key. The triaromatic steroid hydrocarbon ratio is the same as that defined in Curiale (1992a). The 'C₂₁' peak in the regular sterane ratio is actually a coeluted composite of the 14 α (H),17 α (H) compound (5 α -pregnane) and the 14 β (H),17 β (H) compound (diginane), as discussed by Wingert and Pomerantz (1986). All ratios are calculated from peak heights. Data used in the plot are listed in Table 3.

1985). Thus the decrease in bisnorhopane/hopane ratios in Monterey oils and rocks with increasing thermal maturity was assumed to result from an effective dilution of bisnorhopane concentration, due to the addition of hopane cracked from kerogen as maturity increases (Curiale and Odermatt, 1989; Philp and Gilbert, 1987; Noble *et al.*, 1985).

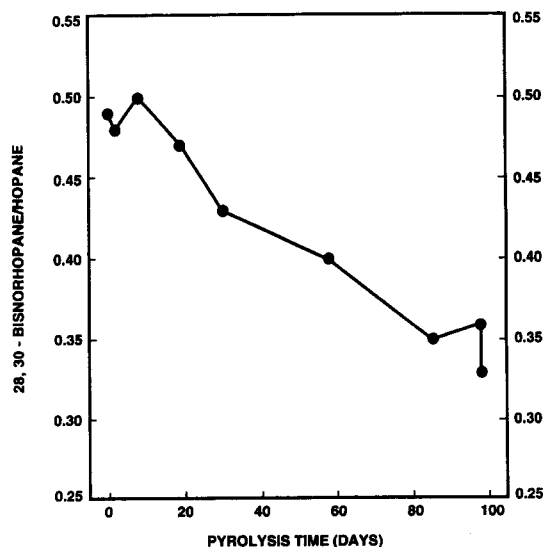


Fig. 9. Variation of 28,30-bisnorhopane/hopane ratio with increasing pyrolysis time, for the California oil subjected to 300°C hydrous pyrolysis. Data are listed in Table 3. Exact stereochemistry of the bisnorhopane has not been determined.

Because our experiments were conducted in the absence of kerogen and mineral matter, the decrease in bisnorhopane/hopane ratio shown in Figs 6 and 9 for the California oil cannot result from preferential release of hopane from kerogen. Based upon these data, we suggest that this ratio decrease is due to either (a) different thermal stabilities for both compounds or (b) preferential release of hopane (relative to bisnorhopane) from "sequestered" sites in the oil itself. Evidence exists for both possible causes. Molecular mechanics (MM2) derivations indicate that the enthalpies of hopane and bisnorhopane are different: calculations show that hopane has a lower heat of formation than 17 α (H),18 α (H),21 β (H)-28,30-bisnorhopane (Curiale, 1985, unpublished results). It is also clear that preferential release of hopane (relative to bisnorhopane) from asphaltenes must be considered. Sofer (1988) detected hopane but not bisnorhopane in California oil asphaltene pyrolyzates. Furthermore, recent evidence suggests that various hopanoids can be "sequestered" in asphaltenes and high-molecular weight soluble polymers of oils, due to the incorporation of sulfur in the molecular structure early in diagenesis (e.g. Sinninghe Damste *et al.*, 1990; Kohnen *et al.*, 1991). At this time we cannot assign a definitive explanation for the trend in Fig. 9.

CONCLUSIONS

Examination of elemental, isotopic and molecular compositions in oil hydrous pyrolyzates reveals systematic variations with increased time of heating in two oils. With increasing artificial maturity levels in the whole oil, (a) vanadium and nickel concentrations decrease by up to 60%, (b) V/(V + Ni) ratios decrease by approx. 0.06, and (c) carbon isotope ratios are invariant (or change only slightly). Changes in hopane/sterane ratios and carbon number distributions of 5 α (H),14 α (H),17 α (H),20R steranes with increasing artificial maturity level are not systematic, whereas 20S/(20S + 20R)-24-ethylcholestane ratios and ratios of short-side-chain to long-side-chain aliphatic and aromatic steroid hydrocarbons increase monotonically. Although side-chain cracking mechanisms could be proposed to explain the relative change in side-chain length that we observed, our data may also be explained by preferential release of these components from sequestered sites in higher molecular weight components of the oil. In a similar sense, the progressive decrease in bisnorhopane/hopane ratio in the California oil with increasing thermal stress, in a kerogen-free environment, indicates either differences in thermal stability or the preferential release of one compound from asphaltenes or resins in the oil.

Our data are useful in understanding the influence of thermal stress on crude oil in contact with water under reservoir conditions. For well-mixed oils reser-voired in sandstones or vuggy carbonates, petroleum

source input (i.e. organofacies) is effectively constant, and a high oil saturation level implies that inorganic catalysis (i.e. the effect of contact within the reservoir between mineral surfaces and petroleum) is minor. Petroleum compositional heterogeneities in such an environment have been attributed to inefficient mixing of oil charges having different source-inherited maturities (Leythaeuser and Ruckheim, 1989) and differential filling from geographically distinct parts of the basin (Horstad *et al.*, 1990). Our results have application in situations where maturity increases in an oil were unaccompanied by the effects of clay catalysis, such as within a reservoir interval or along a migration pathway. In such instances, the data suggest that ratios of selected transition metals and stable carbon isotopes will change only slightly, whereas average steroidal side chain length will decrease significantly. Deconvolution of molecular maturity parameters that require clay catalysis (e.g. hopane/sterane ratio?) from those that do not (e.g. steroid side chain scission) could eventually allow a distinction to be made between compositional changes due to maturity variations in the source and those in the reservoir. Studies of this nature will be most reliable when the source is of constant organic facies, reservoirs are "clean" (i.e. generally clay-free), and lateral in-reservoir maturity differences are present.

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