Effect of evaporation on C_7 light hydrocarbon parameters

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Abstract

Light hydrocarbons are commonly used to evaluate crude oils to determine oil families, in-reservoir alteration processes such as evaporative fractionation, water washing, incipient biodegradation, maturity, and temperatures at which oil is expelled from source rocks. Light hydrocarbons in the C_7 range will evaporate under ambient conditions, and losses can occur during sample collection, handling, or storage. However, the impact of partial evaporation on interpretation of light hydrocarbon data has not been reported previously. Laboratory evaporation experiments show that the rate of evaporation of each C_7 hydrocarbon is different, and these differential rates will affect the measured concentrations of these compounds, certain ratios, and other calculations or plots using these data. The paraffinicity/aromaticity ratio of Thompson [Marine Pet. Geol. 5 (1988) 237], parameters utilized in the transformation and correlation star diagrams of Halpern [AAPG Bull. 79 (1995) 801], and the oil typing ternary plot of Jarvie [The Mountain Geologist 38 (2001) 19] are affected by evaporation. Other interpretive schemes such as P2 versus N2/P3 and the invariant ratio [Science 273 (1987) 514; Geochim. Cosmoschim. Acta 54 (1990) 1315] are not grossly affected by partial evaporation because these parameters are primarily controlled by the concentration of methylhexanes or by offsetting rates of evaporation in certain compounds. By careful evaluation of these parameters and various interpretive plots, the extent of evaporation can be qualitatively assessed and discrimination of oil types, alteration effects, and evaporative artifacts can still be reasonably ascertained. This study demonstrates that preservation of crude oils from evaporation is essential for accurate application of all light hydrocarbon parameters, although some parameters may still be utilized when partial evaporation has occurred.

1. Introduction

Gasoline range hydrocarbons, especially the C_7 compounds, have been widely utilized in petroleum geochemistry studies for determining oil groups derived from the same source rock, prediction of maturity, alteration of the crude oils due to water washing, biodegradation or evaporative fractionation, and even

influence of source lithofacies (Thompson, 1983, 1988; Mango, 1990a,b, 1997; Halpern, 1995; Ten Haven, 1996; Odden et al., 1998; Magnier and Trindade, 1999; Lafargue and Le Thiez, 1996; Wever, 2000; Jarvie, 2001). Since condensates or light oils (> 50 API) have very low concentrations of the $C_{15}+$ fraction and, therefore, biological markers, correlation to source rocks can be problematic. In these cases utilization of light hydrocarbons from source rocks has been useful for correlating source rocks to condensates and condensates to black oils (Jarvie and Walker, 1997; Odden et al., 1998). The application of the entire range of

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hydrocarbons is essential when assessing a mixed or altered oil system since light hydrocarbons and biomarkers may yield different correlations and maturities. In these cases biomarker correlations and maturities will primarily reflect the input from the black oil or from the oil with the higher contribution of certain diagnostic biomarkers whether middle or high molecular weight range (C_{12}-C_{35}+), whereas the light hydrocarbons more accurately describe a condensate charge or oil alteration processes. Thus, the best practice for interpretation of oil geochemistry requires utilization of the entire range of hydrocarbons present in a crude oil from light to heavy molecular weight.

The oils analyzed in this study are found in marine carbonate reservoirs ranging in age from Kimmeridgian to Lower Cretaceous in the onshore Chiapas-Tabasco sub-province from the Mexican Gulf Coast Basin. Their bulk geochemical features include API gravities ranging from 33.41 to 38.77°, sulfur contents from 0.82 to 0.98%, and whole oil $\delta^{13}C$ values of −26.45 to −26.72‰ (Table 1). These geochemical characteristics are explained by a single source and expulsion over a very narrow maturity range.

Previous studies have interpreted these oils as related to shaly carbonate depositional environments (Guzmán-Vega and Mello, 1999). They have C_{30} steranes, an abundance of C_{29} relative to C_{27} steranes, abundant extended hopanes, C_{29}/C_{30} αβ-hopane ratios ⩾1, T_s/T_m ratios <1, low to medium abundance of tricyclic terpanes relative to pentacyclics, high C_{35}/C_{34} extended hopanes ratios, presence of hexahydrobenzohopanes, 17α(H) 29,30-bisnorhopane, and very low abundance of diasteranes. These characteristics have been considered diagnostic for marine carbonate environments (Peters and Moldowan, 1993). These oils correlate to organic-rich Tithonian shaly carbonates, which are considered the most important source rocks in Mexico.

Proper oil collection, sample handling, and storage are critical to obtain reliable analytical data that can be used for evaluation of the light hydrocarbons in crude oils (Mango, 1987, 1990b, 1997; Cooles et al., 1991; Lafargue and Le Thiez, 1996; and BeMent et al., 1994). Even so, virtually all crude oils received in a laboratory under atmospheric conditions in tightly sealed containers such as bottles or vials, will have undergone some measure of evaporation unless they are sealed in airtight containers. Despite this fact the effect of varying degrees of evaporation on light hydrocarbon ratios, calculations, and plots and more specifically, the impact on interpretation of these data, are unknown.

We report the effects of varying degrees of evaporation of C_7 compounds on various interpretive schemes used to evaluate light hydrocarbons. Included in this assessment is the impact, if any, of evaporation, on various light hydrocarbon parameters including the paraffinicity-aromaticity ratios of Thompson (1988), principal component analysis (PCA), star diagrams of Halpern (1995), ternary plots of Jarvie (2001) and Jarvie et al. (2001), invariant ratios (Mango, 1987), and calculated temperatures of oil expulsion (Ctemp) (BeMent et al., 1994; Mango, 1997).

2. Methodology

Crude oils were analyzed using a Hewlett-Packard 6890 gas chromatograph equipped with electronic mass flow controllers for constant flow programming throughout the oven heating program, an autosampler for reproducible injections, and a flame ionization detector (FID). The GC was operated using the following analytical materials and conditions: PONA column (50 m×200 μm I.D.×0.5 μm film thickness); injector temperature of 300 °C, split ratio set to 100:1, and FID temperature of 300 °C; the GC oven was programmed from 35 °C with a 5 min initial isotherm, then an initial heating rate program of 1.5 °C/min to 50 °C after which the rate was increased to 8 °C/min to a final temperature

Table 1
Bulk and molecular parameters of 9 light oils from southeast of México

Sample	Depth (m)	%S	$\delta^{13}C$ (‰)	API	%RoEq	%Rc	Pr/ C_{17}	Phy/ C_{18}	Pr/ Phy	Hop/ St	Tric/ Hop	Ts/ Ts +Tm	Hop29/ Hop30	Dia/ Reg. Col.
O1	5547–5570	0.98	−26.72	33.41	0.60	0.83	0.29	0.36	0.93	0.9	1.64	0.91	1.05	0.89
O2	5675–5705	0.94	−26.54	35.16	0.60	0.82	0.28	0.35	0.88	0.89	1.63	0.9	1.03	0.93
O3	5152–5164	0.89	−26.47	36.16	0.68	0.83	0.29	0.40	0.86	0.81	1.73	0.9	1.02	0.92
O4	5370–5378	0.87	−26.50	38.77	0.75	0.83	0.31	0.34	1.09	0.86	1.6	0.9	0.94	0.88
O5	5400–5453	0.90	−26.68	35.95	0.65	0.83	0.29	0.31	1.13	0.8	1.42	0.92	1.1	0.83
O6	5535–5560	0.87	−26.50	37.75	0.70	0.89	0.24	0.31	0.8	0.86	1.63	0.9	1.07	0.89
O7	5505–5535	0.88	−26.50	35.16	0.75	0.83	0.28	0.33	1.05	0.9	1.55	0.9	0.92	0.88
O8	5472–5492	0.90	−26.45	36.75	0.75	0.83	0.23	0.33	0.86	0.77	1.52	0.9	0.94	0.8
O9	5490–5520	0.82	−26.57	36.15	0.70	0.83	0.28	0.40	0.82	0.78	1.47	0.89	0.89	0.87

of 300 °C with a 20 min. hold time. Hydrogen carrier gas was used with a minimum purity of 99.998% with additional filters to remove any residual water, oxygen, and hydrocarbons. The injected sample volume was 0.5 µl with 1-hexene added as an internal standard to a known weight of oil for quantification (in weight percent); a response factor of 1 was utilized for all compounds. Carbon disulfide at 99.9 + % was used for clean-up and any dilution requirements. The assignment of the C_7 compounds was based on comparison to the reference chromatogram provided by the supplier of a commercial mixture of paraffins, naphthenes and aromatic hydrocarbons (Cat. HP 18900-60600).

To evaluate the effects of evaporation of the C_7 compounds over time, 38° and 54° API gravity crude oils were utilized for laboratory evaporation experiments. Both oils were carefully collected at the wellhead from wells with similar pressure conditions (12 and 16 kg/cm^2, respectively) and stored in 460 ml amber colored glass containers with a screw-on cap lined with Teflon. The oils were collected under ambient temperature conditions (30–35°C), but were immediately refrigerated at 4°C. Gas chromatographic analyses of the samples were completed over a three day period following collection. After the initial chromatogram was acquired, an aliquot of the 38 and 54° samples was allowed to evaporate for 26 h at 20°C and a new gas chromatographic acquisition on the partially evaporated aliquot was completed every hour. This procedure was used to evaluate evaporation of light hydrocarbons. The rate of evaporation of each compound was indirectly calculated in such a way that the compounds with the highest percentage of weight loss over a given period of time have the highest rates of evaporation. The calculation of the percentage of evaporation for each compound, $\%E_x$, was made with the following formula:

$$\%E_X = 100\frac{\%W_X - \%W_{Xi}}{\%W_X} \qquad (1)$$

where:

$\%W_x$ = wt.% of the compound X obtained from the initial chromatogram.

$\%W_{xi}$ = wt.% of the compound X obtained from the chromatogram obtained at the time i.

To evaluate how evaporation might affect interpretation of light hydrocarbon data, a set of 9 light oil samples (O1–O9) of similar origin and thermal maturity were fingerprinted. Again, to minimize the possibility of any pressure-induced variations in the light hydrocarbon composition, the 9 samples were taken from wells having similar wellhead pressure conditions (9–17 kg/cm^2). One of the oil samples (O6) was allowed to evaporate (i.e., topped) under controlled conditions in the laboratory at 20°C for 20 h. Chromatographic data were acquired every hour on the topped sample and

results from the 5, 10, 15, and 20 h analyses are reported with the results from the 9 original oils.

Using measured weight percents of each compound determined from the GC analysis on each of the 9 original oil samples and results from the 4 partially evaporated aliquots of oil sample O6, PCA analysis was performed on concentrations of C_7 compounds to evaluate statistically any differences among the oils. PCA is a statistical means for evaluating variance in data sets. SPSS software was used to perform PCA analysis; equal weight was given to each C_7 compound in the PCA.

3. Results and discussion

3.1. Evaluation of the chromatographic method

To evaluate effects of evaporation on light hydrocarbon data, a very precise and reproducible analytical methodology is required. Therefore, the reproducibility of the chromatographic method was evaluated by sextuple analyses of a commercial mixture of hydrocarbons (Fig. 1). Using the weight percent of each C_7 compound, the relative standard deviation or coefficient of variation in percent (CV%) of each compound in the mixture was calculated (Table 2). Values less than 1.5% CV were calculated, meeting the quality criteria established by analogous chromatographic methods (Cooles et. al., 1991). Utilizing these data to calculate the various light hydrocarbon parameters, we found that the CV% for each parameter was less than 1%, further confirming the quality of the chromatographic results. These results also meet the criteria reported by Halpern (1995) and ten Haven (1996) (CV < 5% and CV < 7%, respectively).

3.2. Evaluation of laboratory evaporation of the C_7 compounds

Gas chromatographic fingerprints of the 38 and 54 API gravity oil samples and their evaporated counterparts after 5, 10, 15, and 20 h are shown in Fig. 2. While certain ratios appear relatively consistent by visual inspection even after partial evaporation, e.g., n-C_7/MCH, detailed evaluation of quantitative yields and ratios does not support that casual observation. Analysis of the percentage of evaporation of each C_7 compound over time shows distinct differences (Table 3). Consistent with inherent structural differences among the C_7 isomers, 2,2-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2,2,3-trimethylbutane, and 1,1-dimethylcyclopentane evaporate more rapidly compared to n-heptane, methylcyclohexane, ethylcyclopentane, and toluene (Fig. 3). As expected there is an accelerated loss of the most volatile compounds (positive percentages of evaporation) and an apparent increase in the relative concentration of the least volatile
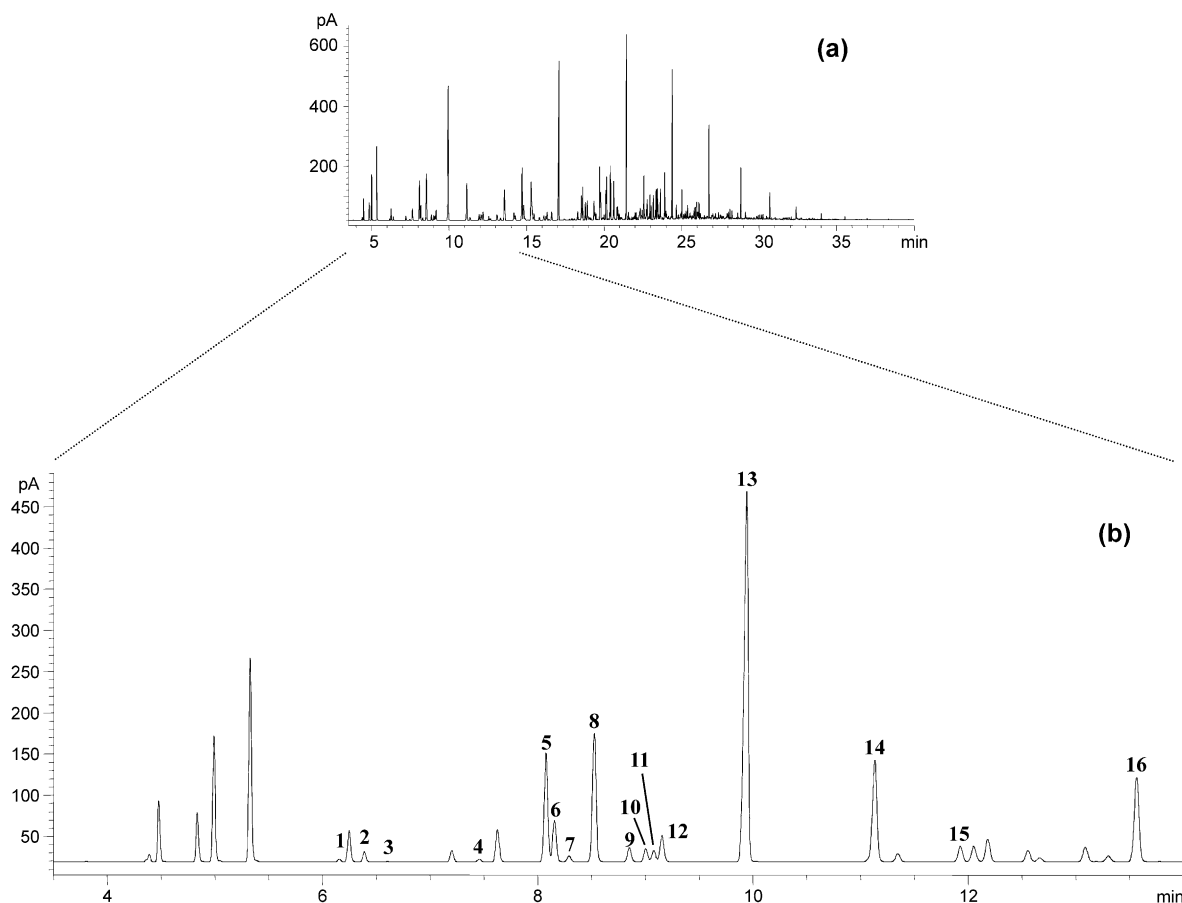
Fig. 1. (a) Gas chromatogram of a commercial hydrocarbon mixture. (b) Partial gasoline range gas chromatogram and assignment of peaks: 1 = 2,2-dimethylpentane (22DMP); 2 = 2,4-dimethylpentane (24DMP); 3 = 2,2,3-trimethylbutane (223TMB); 4 = 3,3-dimethyl-pentane (33DMP); 5 = 2-methylhexane (2MH); 6 = 2,3-dimethylpentane (23DMP); 7 = 1,1-dimethylcyclopentane (11DMCP); 8 = 3-methylhexane (3MH); 9 = c-1,3-dimethylcyclopentane (c13DMCP); 10 = t-1,3-dimethylcyclopentane (t13DMCP); 11 = 3-ethylpentane (3EP); 12 = t-1,2-dimethylcyclopentane (t12DMCP); 13 = n-heptane (nC7); 14 = methylcyclohexane (MCH); 15 = ethylcyclopentane (ECP); 16 = toluene (TOL).

compounds (negative percentage of evaporation). Diverse factors, such as molecular weight, isomeric structure, classification (linear, branched, cyclic, or aromatic compounds), and the overall bulk composition of the oil itself play a role in rates of evaporation among the various C_7 structural isomers (Thompson, 1988). Nevertheless, as expected these results suggest that the evaporation process is governed primarily by the individual volatility of each compound as shown by the relationship to compound boiling points (Fig. 3). More importantly, it is also obvious from these data that apparent enrichment of the less volatile C_7 hydrocarbons will occur following partial evaporation. Interpretive schemes using a wide range of C_7 compounds have to account for these differential rates of evaporation to be interpreted correctly.

3.3. The effect of evaporation on various interpretive schemes using C_7 hydrocarbons

The 9 oil samples from the Chiapas-Tabasco sub-province in Mexico were used to evaluate the effects of evaporation on various interpretive parameters and plots that have been reported in the literature to assess homologous oil groups (oils from the same source rock), alteration effects, maturity, and expulsion temperatures. These oil samples were chosen because interpretation of laboratory analyses such as biomarkers, carbon isotopes, $C_{15}+$ gas chromatography, and sulfur contents indicate that all the samples have the same source and level of thermal maturity (Table 1).

From PCA of the two main components obtained from the weight percent C_7 data matrix, it can be clearly

Table 2
C_7 wt.% of a standard hydrocarbon mixture

Replicate	Compound															
	22DMP	24DMP	33DMP	223TMB	2MH	23DMP	11DMCP	3MH	c13DMCP	t13DMCP	3EP	t12DMCP	nC7	MCH	ECP	TOL
1	0.0596	0.1575	0.0473	0.0124	1.4387	0.6704	0.2771	1.9168	0.6906	0.6506	0.1931	1.1419	4.8211	4.1570	0.4913	3.5545
2	0.0594	0.1562	0.0467	0.0120	1.4189	0.6609	0.2729	1.8896	0.6797	0.6404	0.1894	1.1235	4.7511	4.0902	0.4844	3.4967
3	0.0599	0.1580	0.0473	0.0124	1.4459	0.6740	0.2781	1.9276	0.6942	0.6539	0.1942	1.1481	4.8584	4.1890	0.4960	3.5874
4	0.0603	0.1585	0.0476	0.0124	1.4502	0.6759	0.2791	1.9337	0.6973	0.6571	0.1949	1.1525	4.8734	4.2123	0.4990	3.6179
5	0.0597	0.1580	0.0478	0.0123	1.4421	0.6727	0.2779	1.9231	0.6929	0.6527	0.1937	1.1460	4.8414	4.1810	0.4946	3.5852
6	0.0606	0.1587	0.0480	0.0125	1.4557	0.6790	0.2803	1.9419	0.7002	0.6598	0.1960	1.1578	4.9006	4.2388	0.5022	3.6454
Mean	0.0599	0.1578	0.0475	0.0123	1.4419	0.6721	0.2776	1.9221	0.6925	0.6524	0.1935	1.1450	4.8410	4.1781	0.4946	3.5812
S.D.	0.0004	0.0009	0.0004	0.0002	0.0128	0.0062	0.0025	0.0181	0.0071	0.0067	0.0023	0.0119	0.0517	0.0513	0.0062	0.0517
CV%	0.70	0.59	0.92	1.36	0.88	0.93	0.91	0.94	1.03	1.03	1.16	1.04	1.07	1.23	1.26	1.44

observed that the 9 oils form a single group suggesting a common genetic derivation based on C_7 data only (Table 4 and Fig. 4a). However, as a result of the laboratory evaporation of sample O6, this sample separates from the single group of the 9 original oils with increasing evaporation time. According to the loadings graph, the principal factors leading to the separation of the O6 oil from the 9 original oils are the reduced amounts of 2,2,3-trimethylbutane (223TMB), 2,2-dimethylpentane (22DMP), 3,3-dimethylpentane (33DMP), 1,1-dimethyl-cyclopentane (11DMCP), and 2,4-dimethylpentane (24DMP) (Fig. 4b). These compounds have higher volatility and evaporate faster resulting in an artificial enrichment of less volatile compounds such as toluene (TOL), methylcyclohexane (MCH), ethylcyclopentane (ECP), and *n*-heptane (n-C_7) (Fig. 3). While PCA is a particularly powerful statistical tool for evaluating large data sets, poor preservation of samples will affect the quality of results and interpretation derived from this analysis.

When the quantitative chromatographic results are utilized in the paraffinicity vs. aromaticity plot of Thompson (1988), the variably evaporated sample O6 (shown as "O6*") is displaced from its original placement and plots apart from the other oils as a result of varying degrees of evaporation (Fig. 5). This is due to the lower volatility of toluene and methylcyclohexane relative to *n*-heptane. If the original oils had ratios of these compounds that placed the original oils in area "D" of this plot, the inflated toluene/*n*-heptane ratio that might occur with evaporation could be confused with an alteration effect such as evaporative fractionation (Thompson, 1988) or as an oil from a different source rock. Biomarker data could likely be used to accurately classify an oil from a single source rock as in this case, but if the charge was purely a condensate or a mixed oil charge such as a retrograde condensate secondarily charged into a black oil, light hydrocarbons would be the only means to distinguish and infer the source type and maturity for the condensate charge. Certainly, having high quality, well preserved oil samples would be very useful to complete an accurate assessment on such a dual-charged reservoir. However, the impact of evaporation of the values for the O6* samples is reason for caution in interpreting the light hydrocarbon data.

The C_7 oil correlation star diagram reported by Halpern (1995) shows high correlation among the 9 original samples (Fig. 6a). However, the laboratory-evaporated sample, O6*, shows a significant decrease in the C1, C3 and C4 parameters, while the C2 and C5 parameters increase. The behavior of the C1 and C5 parameters agree with results presented above, which demonstrates the susceptibility of compounds used in these parameters to differential rates of evaporation (Halpern, 1995). Errors in classification could result from the evaporative effect observed in the C2, C3 and C4 parameters.
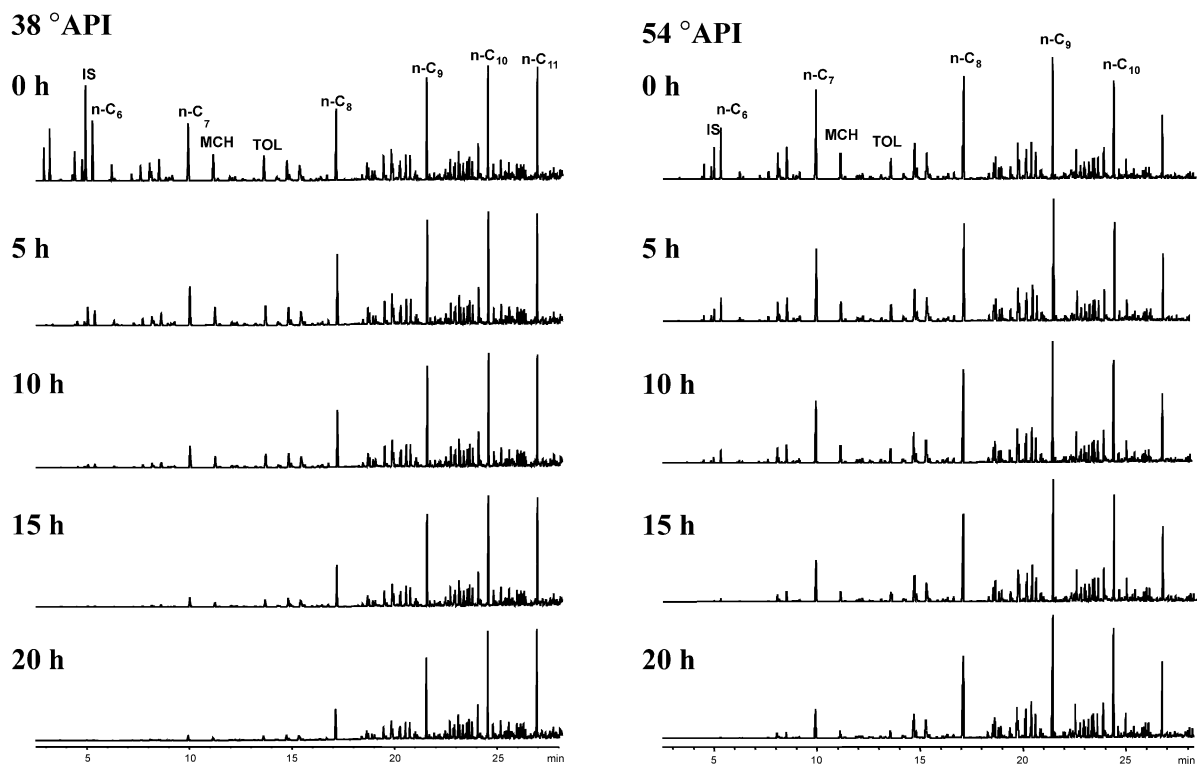
Fig. 2. Gas chromatograms acquired at 0, 5, 10, 15 and 20 h during the evaporation monitoring of a light oil (38° API) and a condensate (54° API).

Table 3
Boiling points and percentage of evaporation for the two light oils obtained during the monitoring of the process at 5, 10, 15 and 20 h

Compound	Boiling point (°C)	38°API				54°API			
		%E$_{5h}$	%E$_{10h}$	%E$_{15h}$	%E$_{20h}$	%E$_{5h}$	%E$_{10h}$	%E$_{15h}$	%E$_{20h}$
22DMP	79.2	42.06709	67.53419	100	100	23.1257	38.13188	65.32643	77.51697
24DMP	80.4	37.96403	63.30074	79.01743	100	20.255	35.17757	61.23868	74.71641
223TMB	80.8	33.03684	100	100	100	16.30685	38.18509	100	100
33DMP	86	26.42201	45.1968	100	100	12.76752	24.36137	46.103	57.2817
11DMCP	87.5	20.00467	35.13296	50.37545	100	10.68042	20.10236	38.77007	50.35651
23DMP	89.7	16.14523	31.43465	44.79697	50.89581	7.367704	14.46917	28.73275	39.78401
2MH	90	16.22366	32.79775	47.53612	53.39424	6.705239	12.49461	25.45253	35.59556
c13DMCP	90.8	13.07315	30.11213	40.19899	44.28502	7.343954	14.13382	27.56349	39.42438
t13DMCP	91.7	16.07523	25.16431	39.04102	43.91523	6.24963	12.30319	23.73136	34.28375
t12DMCP	91.9	9.47956	21.11224	37.32606	42.71634	5.497962	10.83646	20.85741	31.62854
3MH	92	11.83456	24.937	37.94731	44.0634	4.682923	8.917462	18.92634	27.1768
3EP	93.5	15.6012	24.41113	34.87165	36.91807	2.773426	5.190199	11.01812	17.92063
nC7	98.5	−3.51135	−4.06047	−2.09086	−0.71904	−2.92009	−5.7882	−11.1426	−15.0565
MCH	100.9	−6.60383	−13.6943	−19.3286	−18.7262	−2.95361	−5.29175	−10.2506	−14.3618
ECP	103.5	−12.1824	−26.6827	−33.8079	−36.2507	−6.01793	−11.1677	−23.5292	−34.5734
TOL	110.6	−19.8325	−43.9976	−74.8981	−94.356	−5.74694	−10.1272	−22.3977	−33.1778

Calculations were made with the formula indicated at methodology and the results were plotted in Fig. 3.
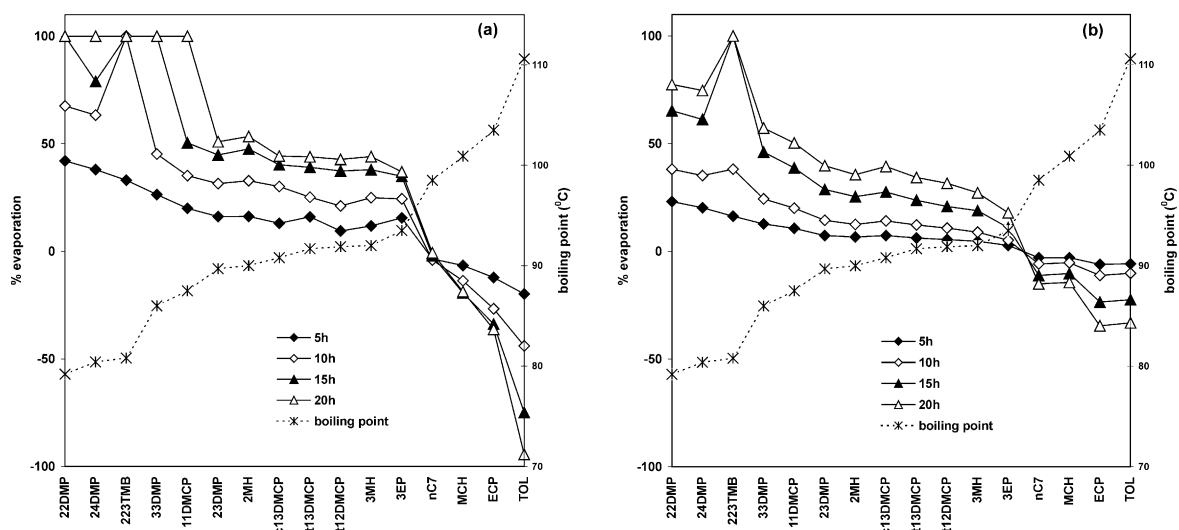
Fig. 3. Percentage evaporation for C_7 compounds at 5, 10, 15 and 20 h for (a) light oil (38° API) and (b) condensate (54° API).

A good correlation is shown among the 9 oils in the C_7 oil transformation star diagram (Halpern, 1995) (Fig. 6b). Changes in the Tr6 parameter were noted for the O6* samples suggesting that it is a useful parameter to evaluate the occurrence of evaporation in an oil sample; however, Halpern (1995) noted that it might also be an indication of migration or fractionation effects. Tr1 and Tr2 parameters are also affected by evaporation since the O6* sample also shows differences in those ratios. While lower Tr1 and Tr2 ratios may be caused by water washing processes or resultant low level biodegradation of an oil, changes in these ratios could also be an artifact of evaporation.

A ternary plot using all the isomers of C_7 hydrocarbons was utilized to classify oils in the Williston Basin (Jarvie, 2001), and to infer their source rock lithologies such as marine shales, carbonates, and lacustrine or *G. prisca*-sourced Ordovician oils (Jarvie et al., 2001). Plotting the 9 original oils in this same ternary plot, they group tightly together and would be inferred to be derived from the same source rock and also inferred to be from a shaly carbonate source facies (Fig. 7). These results correlate to thermal extraction fingerprints of the Tithonian Pimienta Formation marls (Morelos and Jarvie, unpublished data). However, the laboratory-evaporated oils fall into an undifferentiated region that might suggest mixing between oils from completely different source types. Thus, any inferred source lithofacies from the light hydrocarbons would be in error when substantial evaporation has occurred.

Using data from the original 9 oils in a source-specific plot of C_7 hydrocarbons (P3 vs. P2 + N2), a best fit line

shows excellent correlation ($r^2 = 0.999$), which is interpreted as a homologous oil set (Mango, 1990b) (Fig. 8). A homologous oil set is a group of oils derived from a single source rock with differences in concentrations within the set being due to differences in oil maturities (Mango, 1987). The effect of evaporation is demonstrated by data from the evaporated sample, O6*, where a subtle change is noted in the linear regression, although the correlation remains very high at $r^2 = 0.996$. The utility of these plots is quite dependent on the effects of evaporation and reiterates the need for extreme care in collecting oil samples and preserving high quality oil samples as advocated by Mango (1987). It is useful to note that near perfect correlation is seen on the original oils and, even after some alteration, the correlation remains excellent, but with a slightly lower correlation coefficient. This illustrates why it is occasionally quite difficult to distinguish homologous oils using this type of plot only.

Other light hydrocarbon ratios and interpretive plots are not grossly affected by evaporative losses possibly as a result of compensation by differential rates of evaporation of the compounds used in these relationships. Evaporation does not alter the genetic relationships inferred from interpretation of certain source-specific and invariant plots such as [2MH + 2,3DMP] versus [3MH + 2,4DMP] (invariant plot parameters) and P2 versus N2/P3 (source specific plot) (Mango, 1987, 1990b) even though there is a change in concentration of various compounds used in these plots (Fig. 9a and b). Further examination suggests that in the invariant plot, the principal dis-

Table 4
C$_7$ weight percent and calculated Ctemp of 9 light oils from southeast of México, including sample intentionally evaporated

Sample	22DMP	24DMP	223TMB	33DMP	2MH	23DMP	3MH	11DMCP	c13DMCP	t13DMCP	3EP	t12DMCP	nC7	MCH	ECP	TOL	Ctemp
O1	0.0065	0.0167	0.0017	0.0051	0.1493	0.0779	0.1932	0.0119	0.0299	0.0296	0.0164	0.0569	0.5898	0.3198	0.0490	0.3481	116.9
O2	0.0133	0.0348	0.0035	0.0100	0.2891	0.1529	0.3703	0.0235	0.0575	0.0551	0.0309	0.1086	1.0814	0.5669	0.0846	0.5710	117.8
O3	0.0251	0.0617	0.0064	0.0167	0.4580	0.2356	0.5666	0.0363	0.0859	0.0814	0.0476	0.1593	1.5123	0.7627	0.1114	0.6875	119.9
O4	0.0155	0.0402	0.0041	0.0113	0.3236	0.1688	0.4098	0.0256	0.0631	0.0598	0.0339	0.1184	1.1710	0.5953	0.0889	0.5894	118.5
O5	0.0221	0.0556	0.0057	0.0154	0.4275	0.2214	0.5338	0.0334	0.0804	0.0766	0.0447	0.1504	1.4527	0.7269	0.1071	0.6643	119.3
O7	0.0195	0.0479	0.0051	0.0137	0.3780	0.1932	0.4721	0.0296	0.0719	0.0684	0.0390	0.1310	1.2913	0.6666	0.0985	0.6097	119.1
O8	0.0122	0.0334	0.0029	0.0091	0.2663	0.1400	0.3387	0.0210	0.0503	0.0477	0.0282	0.0959	0.9971	0.4857	0.0727	0.5251	118.5
O9	0.0211	0.0543	0.0054	0.0143	0.4116	0.2123	0.5131	0.0324	0.0777	0.0737	0.0422	0.1446	1.4187	0.6975	0.1031	0.6681	119.5
O6 (0 h)	0.0203	0.0531	0.0052	0.0142	0.4106	0.2137	0.5157	0.0323	0.0781	0.0738	0.0421	0.1466	1.4502	0.7109	0.1058	0.6916	119.1
O6*(5 h)	0.0328	0.0855	0.0100	0.0290	0.9196	0.4629	1.2035	0.0686	0.1802	0.1671	0.0971	0.3454	3.9041	2.0423	0.3183	2.1580	114.7
O6*(10 h)	0.0535	0.1470	0.0000	0.0628	2.1441	1.1001	2.9782	0.1617	0.4211	0.4331	0.2526	0.8749	11.4073	6.3306	1.0446	7.5369	109.8
O6*(15 h)	0.0000	0.1794	0.0000	0.0000	3.5713	1.8897	5.2529	0.0000	0.7687	0.7527	0.4644	1.4830	23.8781	14.1763	2.3542	19.5317	104.7
O6*(20 h)	0.0000	0.0000	0.0000	0.0000	4.2425	2.2479	6.3321	0.0000	0.9577	0.9261	0.6016	1.8126	31.5024	18.8619	3.2056	29.0250	nd

O6* intentionally evaporated oil; nd = not determined.

criminating compounds are the methylhexanes, which are not grossly affected by incipient evaporation, whereas 2,4-DMP is particularly susceptible to even minor evaporative losses. In the source-specific plot, P2 is composed of the methylhexanes, whereas N2 is composed of the cyclical daughter products of P2 (Mango, 1987). 1,1-DMCP is the most volatile of the N2 compounds having completely evaporated by the completion of the 15 h experiment. P3 is composed of the dimethylpentanes plus 3-EP, all of which have variable volatilities. Overall, the evaporative loss of the P3 compounds is partially offset by the decrease in concentration of 1,1-DMCP in N2. While P2 increases systematically, its increase does not alter the interpretation of the oils being in a homologous oil family, only their predicted maturities. The partially evaporated oils appear to be less mature than the unevaporated samples.

It is concluded that these plots are a good means to classify oils even when some evaporation has occurred, but care must be taken if these data are used in maturity assessments. By comparing results from these latter two plots to light hydrocarbon plots that do show variable classification of the same oils, the effects of evaporation can be evaluated. For example, comparison of the invariant plot or the P2 vs. N2/P3 plot to the Thompson plot would show that differences exist among the oils. However, because the oils group as a single homologous oil type, the variation is suggested to be due to some form of alteration, possibly evaporation. In addition the maturity of the oils would be underestimated from these data. If variations among the various plots are not identified, i.e., there are no alteration effects whether evaporation or some other phenomenon, the differences in a homologous oil set would be due only to maturation differences.

3.4. Effect on Ctemp (oil expulsion temperature)

As Mango (1987) demonstrated, both the ratios of [2,4-DMP/2,3DMP] and [2MH/3MH] are temperature indicators and, consequently, reflect levels of thermal maturity of a homologous oil family. The Ctemp calculation (oil expulsion temperature) (BeMent et al., 1994; Mango, 1997) was derived by comparison of these ratios to thermal maturity and thermal histories as determined from basin modeling (BeMent et al., 1994). However, as a result of differential evaporation rates for the DMPs, Ctemp rapidly decreases with only minor evaporation (Table 4, Fig. 10). An average initial temperature calculated for all the oils is 119°C, including the unaltered O6 oil. However, even after only 5 h of open top evaporation and with a modest concentration of 2,4-DMP remaining, the Ctemp value of O6* has dropped to 115°C. After 10 and 15 h the Ctemp value has dropped
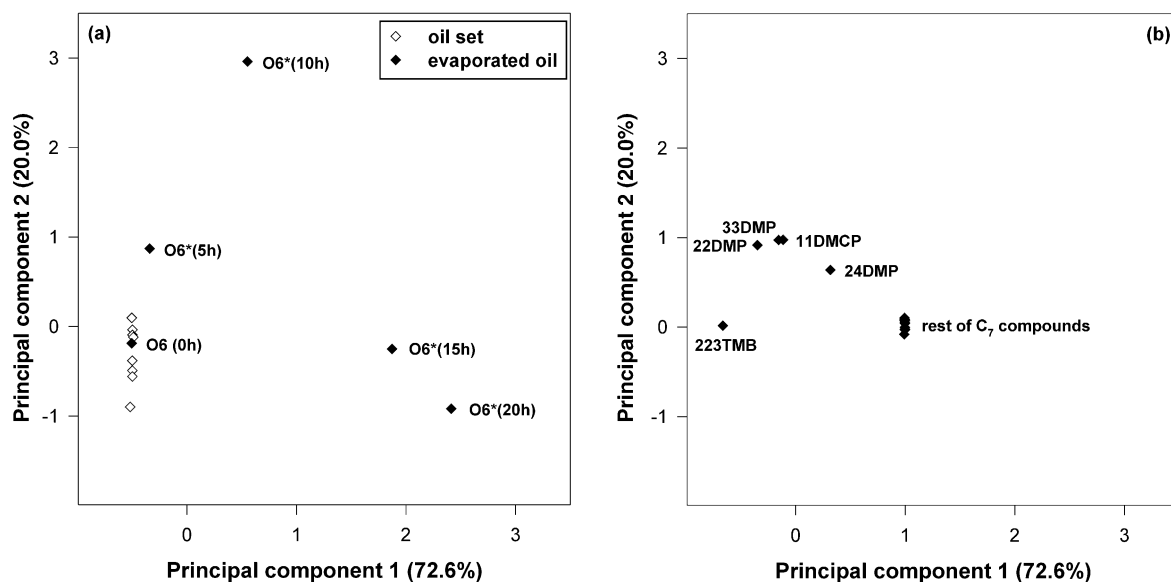
Fig. 4. Principal component analysis obtained from the data in Table 4 for the O1–O9 oils: (a) scores (b) loadings. The two largest principal components explain 92.6% of the total cumulative variance of the data.
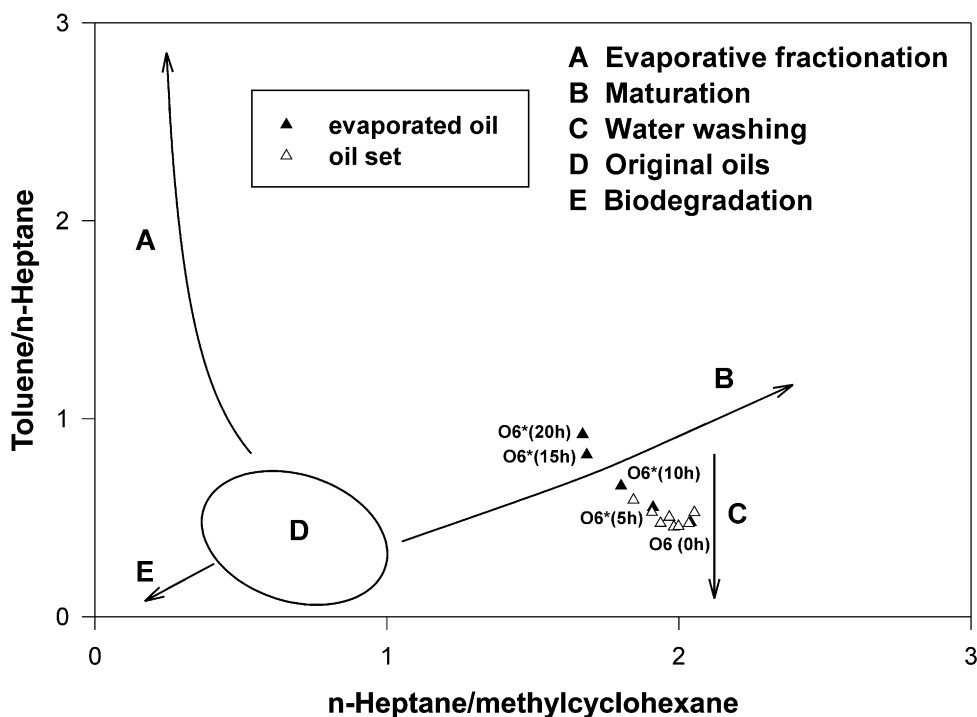

Fig. 5. Paraffinicity vs. aromaticity plot for the O1–O9 oils (modified from Talukdar and Dow, 1990).

to 110 and 105 °C, respectively. At 20 h 2,4-DMP is completely evaporated. Thus, when 2,4-DMP was present in sufficient amount to be quantified by gas chromatography, Ctemp was 5–15 °C lower than Ctemp on the original oil.

While the MHs are enriched following evaporation of the more volatile C_7 hydrocarbons, the ratio of [2MH/3MH] also changes rapidly with evaporation as seen from data in Table 4. Thus, this ratio cannot be substituted for the standard Ctemp calculation of

(a)

(b)
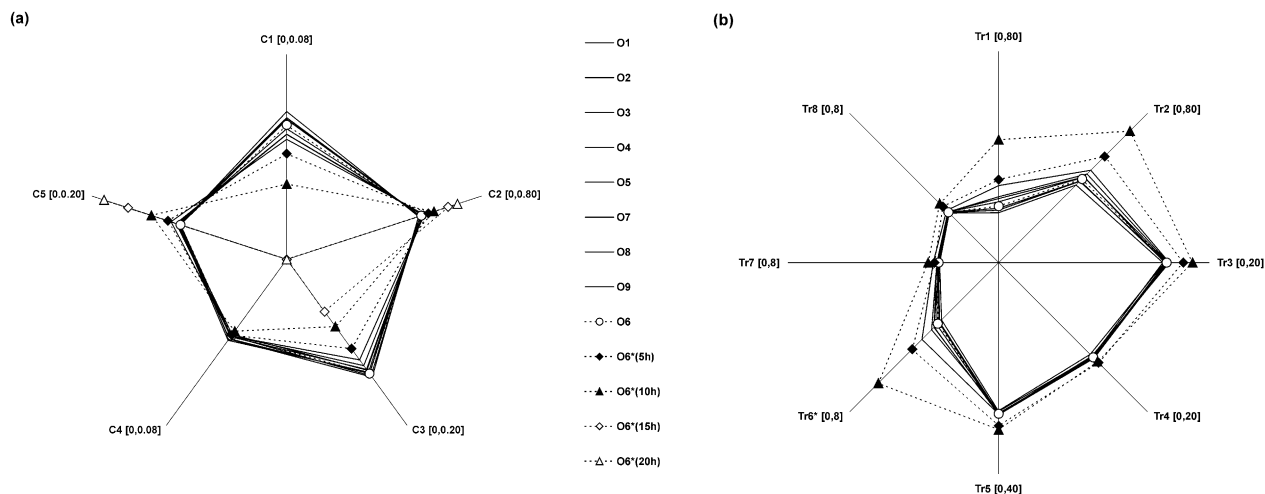
Fig. 6. C_7 oil correlation and transformation diagrams (Halpern, 1995). (a) correlation star diagram of the O1–O9 oils using C_7 compounds including the O6* sample that was altered by laboratory evaporation at 5, 10, 15 and 20 h. (b) behavior of the same samples using an oil transformation star diagram. The numbers between parentheses refer to the scale of each axis.
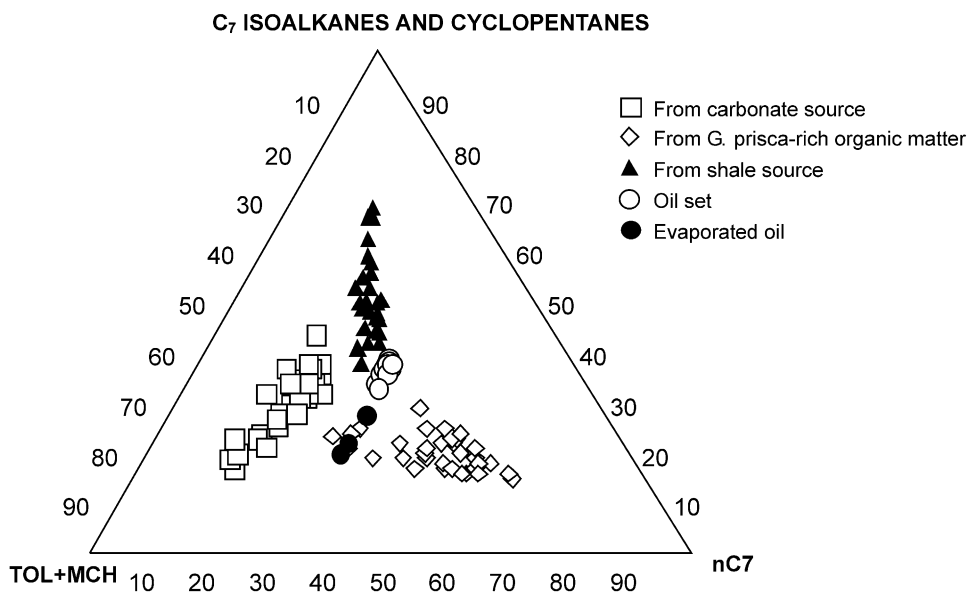
C$_7$ ISOALKANES AND CYCLOPENTANES

Fig. 7. Type and inferred lithofacies ternary plot using all C_7 hydrocarbons shows the O1-O9 group together, whereas the samples altered by evaporation would type apart from the original oils and might suggest mixing of two unrelated oil types (modified from Jarvie, 2001).

BeMent et al. (1994), although it is slightly more stable than the temperature prediction using the DMPs. Thus, the interpretation and application of Ctemp values must be carefully assessed with regard to alteration especially evaporation using the techniques cited in this paper.

It is important to emphasize that the effect of evaporation on the light hydrocarbon assessments can become more critical, as the tests of evaporation in the laboratory were only conducted at 20°C over a period of 26 h. More problematic assessments might be derived from oils stored under reasonably good conditions but
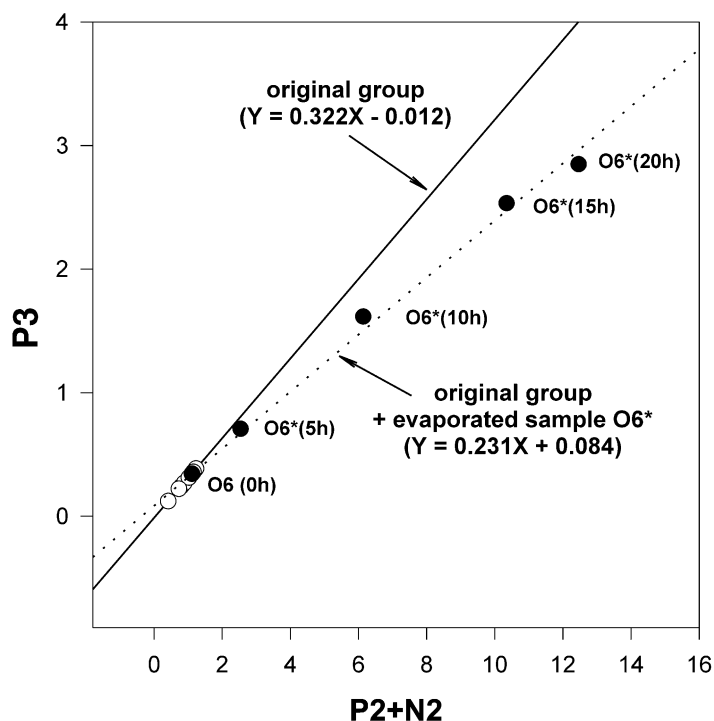
Fig. 8. P3 vs. P2 + N2 Mango graph for the original oil set and including O6* evaporated sample at different times.
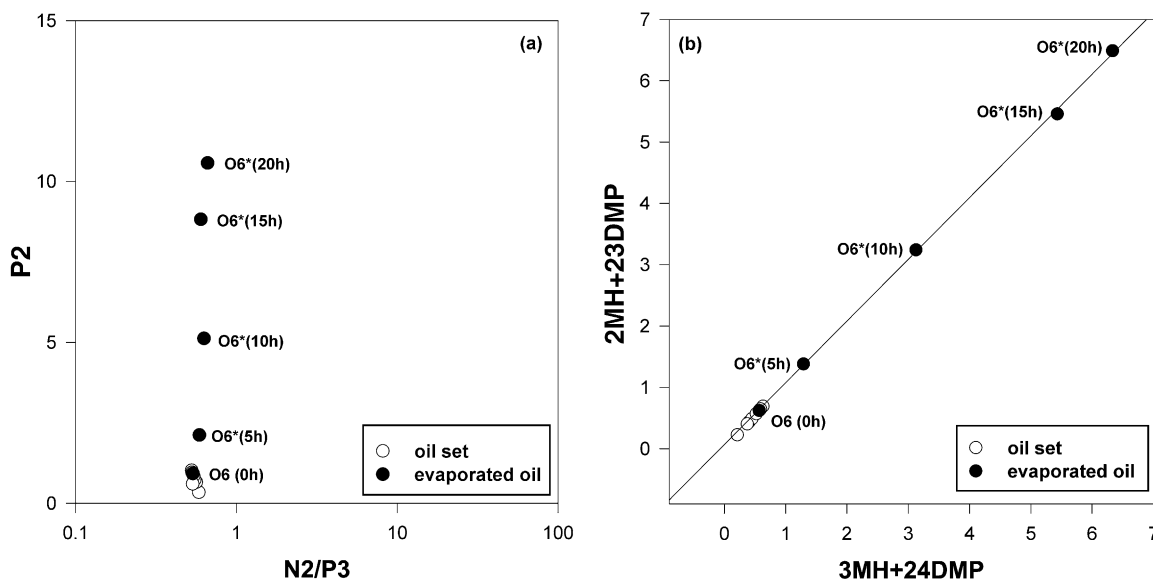

Fig. 9. (a) P2 vs. N2/P3, and (b) 2MH + 2,3DMP vs. 3MH + 2,4DMP Mango graphs for the original oil set and including O6* evaporated sample at different times.

over long periods of time where evaporation rates could occur at very low rates.

Studies have sometimes shown poor correlation between oil families determined by biomarkers versus those determined by light hydrocarbons. It is evident from the data reported herein that even slight evapora-

tion of oil samples will affect correlations using light hydrocarbons. It is also evident that some frustration with use of light hydrocarbons for such correlations is due to poor sample quality likely brought about by partial evaporation of the samples during shipping, handling, and storage.
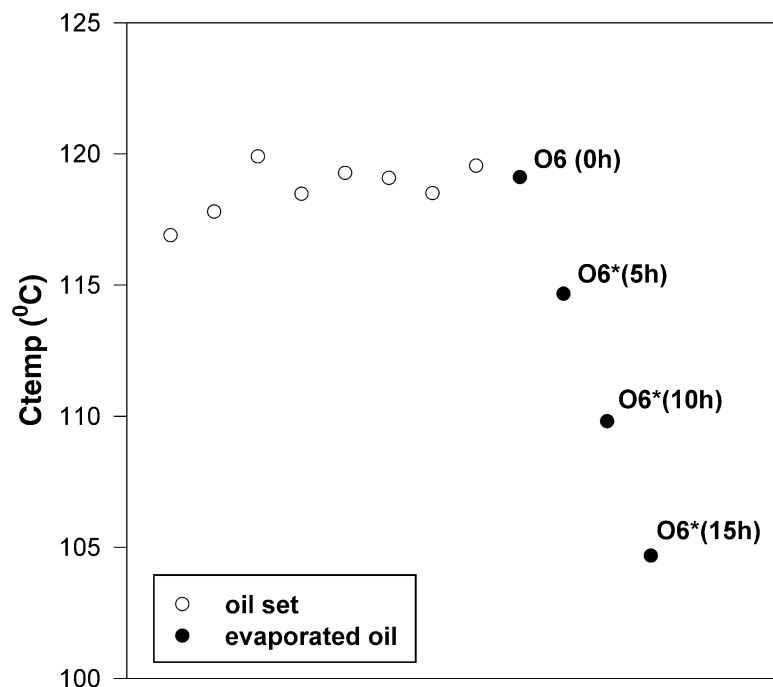
Fig. 10. Plot of calculated temperature Ctemp on O1–O9 oils showing the reduced values on the partially evaporated O6 oil sample (for equation see Appendix).

4. Conclusions

The application of C_7 light hydrocarbons is a fundamental means to correlate oils, assess alteration effects, predict thermal maturity of the light hydrocarbon fraction, and assess oil expulsion temperatures. However, as the C_7 and all light hydrocarbons are highly susceptible to evaporation, caution must be exercised when interpreting C_7 parameters commonly used in geochemical studies. The results reported in this paper demonstrate that typical C_7 light hydrocarbon parameters used to group oils or assess alteration such as PCA, paraffinicity/aromaticity, selected C and TR ratios of Halpern (1995), P3 vs. P2 + N2, and certain ternary plots will be affected by poor preservation of samples. It should also be noted that original papers reporting good source-specific indicators and temperature relationships utilized oils that were properly collected and stored in air-tight containers (Mango, 1987; 1990b; 1994).

However, even after some evaporation has occurred, certain relationships of the C_7 hydrocarbons that are typically represented graphically for assessing homologous oil families are still valid, such as P2 vs. N2/P3 and [2MH + 2,3DMP] vs. [3MH + 2,4DMP]. Evaporation does alter the concentration of these compounds and their ratios or concentrations and will provide a faulty maturity assessment. Combining these homologous oil typing plots with other ratios and plots that are altered by evaporation provides a means to assess whether differences are due to evaporative artifacts rather than source, in-reservoir alteration, or maturity. Thus, sound interpretations may still be derived if the limitations of such alterations are properly assessed.

Maturity assessments and Ctemp values decrease as a result of differential rates of evaporation of 2,4-DMP and 2,3-DMP as shown by these controlled evaporation experiments. Decreases of 5–15 °C were noted in Ctemp values from oils having undergone partial evaporation before the complete loss of 2,4-DMP occurred. While the MHs are more resistant to the effects of evaporation and provide a slightly broader window for temperature calculations, this ratio also will be ultimately altered, and will result in misleading thermal maturity assessments.

In order to use light hydrocarbon data with confidence, the extent and impact of evaporation must be considered. Strict procedures used for sampling, transport, subsampling, analysis, and storage must be implemented since even minor evaporation will affect overall data quality. These results strongly suggest that oil samples be stored in sealed vessels to minimize evaporation of light hydrocarbons and to maximize data and interpretive quality that can be derived from high resolution analysis of the light hydrocarbons.

Appendix

C$_7$ hydrocarbons

Peak	Compound	Abrev.
1	2,2-Dimethylpentane	22DMP
2	2,4-Dimethylpentane	24DMP
3	2,2,3-Trimethylbutane	223TMB
4	3,3-Dimethylpentane	33DMP
5	2-Methylhexane	2MH
6	2,3-Dimethylpentane	23DMP
7	1,1-Dimethylcyclopentane	11DMCP
8	3-Methylhexane	3MH
9	*cis*-1,3-Dimethylcyclopentane	c13DMCP
10	*trans*-1,3-Dimethylcyclopentane	t13DMCP
11	3-Ethylpentane	3EP
12	*trans*-1,2-Dimethylcyclopentane	t12DMCP
13	n-Heptane	nC$_7$
14	Methylcyclohexane	MCH
15	*cis*-1,2-Dimethylcyclopentane[a]	c12DMCP
16	Ethylcyclopentane	ECP
17	Toluene	TOL

[a]Coelutes with methylcyclohexane but is present in constant proportion to t−1,2-dimethylcyclopentane.

Thompson's parameters
aromaticity = (Toluene/n-C$_7$)
paraffinicity = (n-C$_7$/methylcyclohexane)

Mango's parameters
P1 = heptane
P2 = 2-methylhexane + 3-methylhexane
P3 = 2,2-dimethylpentane + 2,4-dimethyl pentane + 2,3-dimethylpentane + 3,3-dimethyl pentane + 3-ethylpentane,
N1 = ethylcyclopentane + 1,2dimethylcyclopentane (*cis* + *trans*)
N2 = 1,1-dimethylcyclopentane + 1,3-dimethylcyclo pentane (*cis* + *trans*)

Halpern's parameters
Tr1 = toluene/1,1-dimethylcyclopentane
Tr2 = n-heptane/1,1-dimethylcyclopentane
Tr3 = 3-methylhexane/1,1-dimethylcyclopentane
Tr4 = 2-methylhexane/1,1-dimethylcyclopentane
Tr5 = P2/1,1-dimethylcyclopentane
Tr6 = 1-*cis*-2-dimethylcyclopentane/1,1-dimethyl-cyclopentane
Tr7 = 1-*trans*-2-dimethylcyclopentane/1,1-dimethyl-cyclopentane
Tr8 = P2/P3
C1 = 2,2-dimethylpentane/P3
C2 = 2,3-dimethylpentane/P3
C3 = 2,4-dimethylpentane/P3
C4 = 3,3-dimethylpentane/P3
C5 = 3-ethylpentane/P3

Maximum temperature of burial (Ctemp)
Ctemp(°C) = 140 + 15[ln(24DMP/23DMP)]

Biomarkers ratios
%RoEq = Absolute vitrinite reflectance value determined by optical measurement.

$$\%Rc = \frac{1.5^*(3MP + 2MP)}{P + 9MP + 1MP}$$

$$Pr/C_{17} = \frac{2, 6, 10, 14\text{-tetramethylpentadecane}}{n - C_{17}}$$

$$Phy/C_{18} = \frac{2, 6, 10, 14\text{-tetramethylhexadecane}}{n - C_{18}}$$

$$Pr/Phy = \frac{2, 6, 10, 14\text{-tetramethylpentadecane}}{2, 6, 10, 14\text{-tetramethylhexadecane}}$$

$$Hop/St = \frac{\begin{matrix} Ts + Tm + H28 + H29 + H29ts + DH30 + H30 \\ + H31(S + R) + H32(S + R) + H33(S + R) \\ + H34(S + R) + H35(S + R) \end{matrix}}{\begin{matrix} D27(\beta\alpha + \alpha\beta)(S + R) + D28\beta\alpha(SS + RR + SR + RS) \\ + S27\alpha\alpha\alpha(S + R) + \beta\beta\_D29S + S27\alpha\beta\beta S + D29\beta\alpha R \\ + S28(\alpha\alpha\alpha + \alpha\beta\beta)(S + R) + S29(\alpha\alpha\alpha + \alpha\beta\beta)(S + R) \end{matrix}}$$

$$Tric/Hop = \frac{\begin{matrix} Tr19 + Tr20 + Tr21 + Tr22 + Tr23 + Tr24 \\ + Tr25(S + R) + Tr26(S + R) + Tr28 \\ (S + R) + Tr29(S + R) + Tr30(S + R) \end{matrix}}{\begin{matrix} Ts + Tm + H28 + H29 + H29ts + DH30 \\ + H30 + H31(S + R) + H32(S + R) + H \\ 33(S + R) + H34(S + R) + H35(S + R) \end{matrix}}$$

$$Ts/Ts + Tm = \frac{C27\ 18\alpha\ (H)\text{-trisnorneohopane}}{\begin{matrix} C27\ 18\alpha\ (H)\text{-trisnorneohopane} + \\ C27\ 17\alpha\ (H)\text{-trisnorhopane} \end{matrix}}$$

$$HopC29/HopC30 = \frac{17\alpha(H)\ 21\beta(H) - 30 - \text{norhopane}}{17\alpha(H)\ 21\beta(H) - \text{hopane}}$$

$$\text{Dia/Reg. Col.} = \frac{\text{D27 } \beta\alpha \text{ (S + R)}}{\text{S27 } \alpha\alpha\alpha \text{ (S + R)}}$$

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