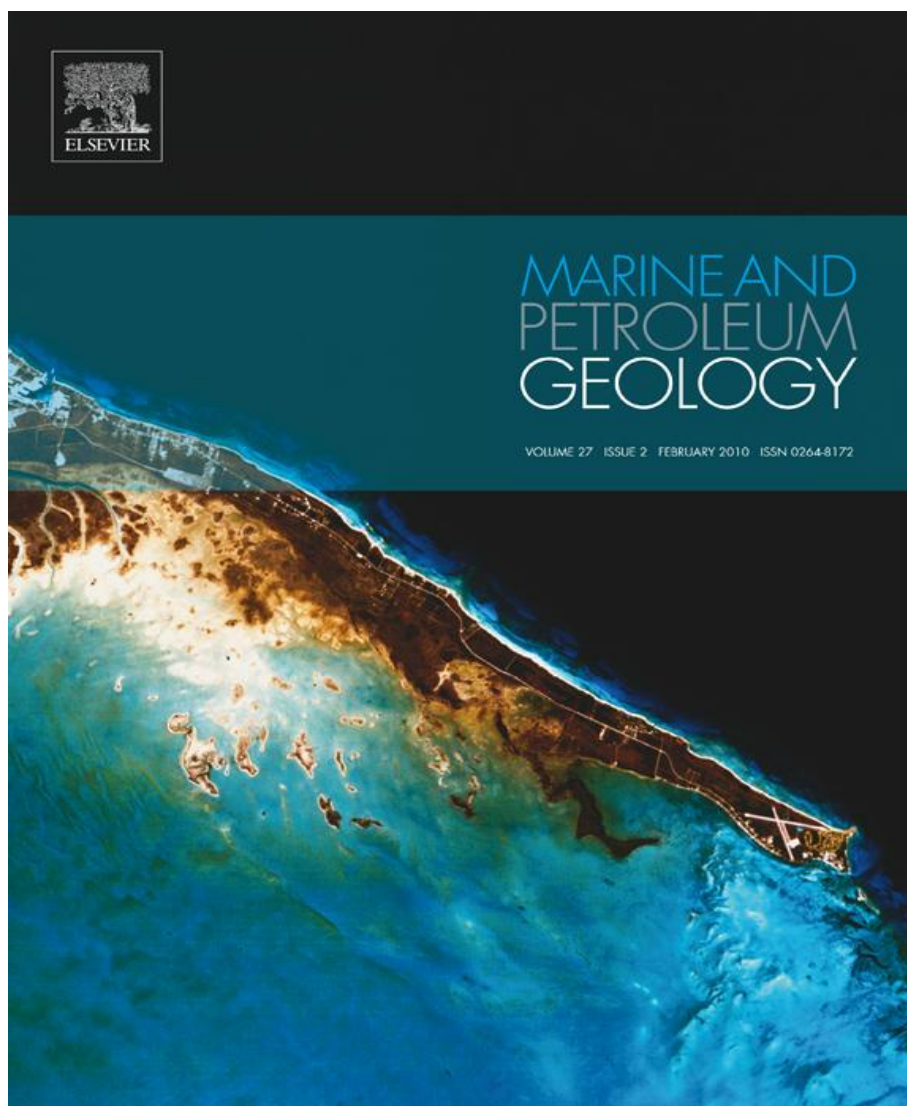


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Phase fractionation and oil-condensate mass balance in the South Marsh Island Block 208–239 area, offshore Louisiana

Steven Losh^{a,*}, Lawrence Cathles III^b

^a Dept. of Chemistry and Geology, Minnesota State University, FH 241, Mankato, MN 56001, United States

^b Dept. of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, United States

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ABSTRACT

Phase fractionation can strongly deplete oil of its volatile compounds in a regular and characteristic fashion. This process has affected oils to a remarkably uniform extent throughout the 30×15 km South Marsh Island 208–239 and Vermilion 30–31 area (including the Tiger Shoal, Starfak, Mound Point, Lighthouse Point, Amber, Trinity Shoal, and Aquamarine fields) just offshore Louisiana. Fractionation of the original “parent” oil likely occurred in the deep, relatively flat-lying Rob L sand that underlies the area, and produced gas-washed oils (mean API 33°) and gas condensates (mean API 50°) in a volume ratio of 1:3.5. Both fractionated oil and vapor migrated from the fractionation site to shallower reservoirs. However, the estimated ultimate production ratio of gas-washed oil to gas condensate in this group of fields is 1:0.32, about 11 times higher than would be expected on mass balance considerations alone. Thus, there is an apparent deficiency of producible gas condensate relative to the amount of producible oil for the entire study area and for every field in that area. In the case of the Tiger Shoal field, the ratio of industry-estimated ultimately producible oil to gas condensate is 1:1.1. Based on the production data, we conclude that either there is an additional 6.4×10^6 m³ (43 MMbbl) of undiscovered and/or unproduced condensate in the area or that condensate has escaped preferentially in vapor form to the seafloor. The well-studied and nearly depleted Tiger Shoal field provides a good example of how chemical data can be analyzed in a way that contributes insight into the phase fractionation process and the remaining exploration potential of an area.

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1. Introduction

Phase fractionation of gas and oil in the subsurface has been recognized for decades as a mechanism for generating gas condensates and depleting oil in light-end compounds (Silverman, 1965; Thompson, 1987; Larter and Mills, 1991; Curiale and Bromley, 1996; Meulbroek et al., 1998; Meulbroek, 2002; Losh et al., 2002). Phase fractionation can work in either direction. Vapors may condense liquids as pressure and/or temperature drop, or alternatively, a “parent” liquid may lose volatile compounds to a vapor phase, a process known as separation migration (Silverman, 1965) if the vapor exsolved directly from the oil (e.g., solution gas), and evaporative fractionation (Thompson, 1987; later referred to as “gas washing” by Meulbroek et al. (1998), Losh et al. (2002), and herein) if the gas was introduced into the oil as a mobile, external stream. Curiale and Bromley (1996) proposed that light-end depleted oils

produced at the top of overpressure from the Vermilion 39 field offshore Louisiana had undergone migration fractionation, a combination of migration separation and evaporative fractionation. Phase-fractionated oils are depleted in light-end compounds (e.g., C₆–C₁₄) relative to the coexisting vapor into which the light ends have been fractionated, and in the oil, the fractionation process concentrates aromatic compounds relative to *n*-alkanes having the same number of carbon atoms (Thompson, 1987). Thompson (1987), Holba et al. (1996), Meulbroek et al. (1998), and Losh et al. (2002) documented evaporative fractionation of oils on the Louisiana shelf. In this study, we examine the strongly fractionated liquids from the South Marsh Island Blocks 208–239 area offshore Louisiana to better understand controls on the phase fractionation process and to apply this knowledge to resource evaluation.

Knowledge of phase fractionation at a particular location can have economic implications. Generally, the value of a fractionated oil is diminished relative to that of an unfractionated oil by the removal of its light compounds, which are commonly more valuable, into a vapor phase that is more mobile and that can

* Corresponding author. Tel.: +1 507 389 6323; fax: +1 507 389 5625.

E-mail address: steven.losh@mnsu.edu (S. Losh).

preferentially leak to the surface. Prediction of this effect in an area could refine economic evaluations. Equally importantly, if the gas condensates in an area are genetically related to phase-fractionated oils in the vicinity, the relative masses of oil and gas condensate can be predicted and potential undiscovered resources identified based on mass balance. For example, if a field produces equal volumes of phase-fractionated oil and gas condensate, say 10^7 m^3 (65 MMBBL) each (we use the term 'gas condensate' for relatively high API liquid ($>45^\circ$) that condenses from vapor at the separator), and mass balance in the system is such that each cubic meter of oil should be paired with two cubic meters of gas condensate, then the known amounts of oil and gas condensate suggest that additional accumulations of the latter could be found; in this example, 10^7 m^3 . Whether the 'missing' gas condensate is still trapped in the subsurface or has vented to the surface is not addressed by this method.

Compositional data for genetically related phase-fractionated oils and gas condensates can be used in conjunction with known partitioning of a particular compound or group of compounds to determine the mass balance relationships between the two liquids in an area. Here we compute the partitioning of *n*-alkanes between fractionated oil and genetically related gas condensate, utilizing the method of Losh et al. (2002), described below. Whole-liquid analyses (PIN – paraffins, isoalkanes, and naphthenes and SARA – saturates, aromatics, resins, and asphaltenes) of fractionated oil and gas condensate samples from the South Marsh Island Block 208–239 area, described in the next section, are then used to determine the relative masses of the fractionated oil and gas condensate that were derived from the parent oil. We discuss the nature of the oils and gas condensates in the studied area and show how the fractionated oil–gas condensate mass balance relationships can be used to estimate undiscovered potential resources and understand aspects of migration systematics. This area is unusually well-characterized in terms of geochemical and ultimate production data, and is well-suited for this analysis.

2. Measuring the missing oil

Regardless of the mechanism of phase fractionation, fractionated oils show regular and systematic patterns relative to unfractionated "parent" oils that permit the determination of the relative mass of "parent" oil that has been fractionated into a vapor phase. These fractionation patterns can be studied in terms of variations

within homologous series having fugacities in the vapor phase that vary regularly with carbon number. The most useful series for this type of analysis is the *n*-alkane series, although other homologous series can also be instructive (Meulbroek, 2002). As determined by Kissin (1987), normal, unaltered, mature crude oils are typically characterized by an exponentially decreasing abundance of *n*-alkanes with increasing carbon number, at least for carbon numbers greater than six (Fig. 1a).

The composition of a fractionated oil (Fig. 1b) clearly differs from that of the unfractionated oil, and its gas chromatographic spectrum can be divided into two parts: a high-carbon number portion that has not been affected by fractionation and that is characterized by the aforementioned exponential decrease in *n*-alkane abundance with increasing carbon number, and a lower-carbon number portion characterized by depletion of *n*-alkane (and other compound type) abundance with respect to the unaltered oil. The depletion increases in a regular fashion with decreasing carbon number. Biodegradation can be ruled out as an explanation for this depletion, as there is no 'hump' of biodegradation products and Pr/nC_{17} in this sample is much less than one (e.g., Curiale and Bromley, 1996). Significant water washing is also precluded because aromatics, which are more soluble in water than *n*-alkanes (Palmer, 1984; Lafargue and Barker, 1988), are enriched relative to *n*-alkanes in this sample. Although more-volatile compounds are increasingly fractionated into the vapor phase in all cases, highly fractionated oils are characterized by systematic decrease in absolute abundance of progressively more-volatile compounds, for instance having less nonane than decane. The carbon number of the lightest unfractionated *n*-alkane is defined as the '*n*-alkane break number,' and is positively correlated with the pressure and temperature at which the oil was fractionated (e.g., Meulbroek, 1997, 2002; also Price et al., 1983). The 'break number' is readily identified on a plot of the natural logarithm of *n*-alkane mole fraction vs *n*-alkane carbon number ('molar fraction plot' of Losh et al., 2002; Fig. 2); it is generally not the same as the carbon number of the most-abundant *n*-alkane in the fractionated oil. Because pressure and temperature both increase with depth, Meulbroek (1997) and Losh et al. (2002) concluded that the break number, to a first approximation, serves as a proxy for depth of fractionation.

The mass of "missing oil" (Fig. 1b, 2), that is, compounds that have been fractionated from parent oil into a vapor phase, can be computed in terms of a mass depletion fraction, first for the *n*-alkanes (Losh et al., 2002), then for the whole oil. To minimize

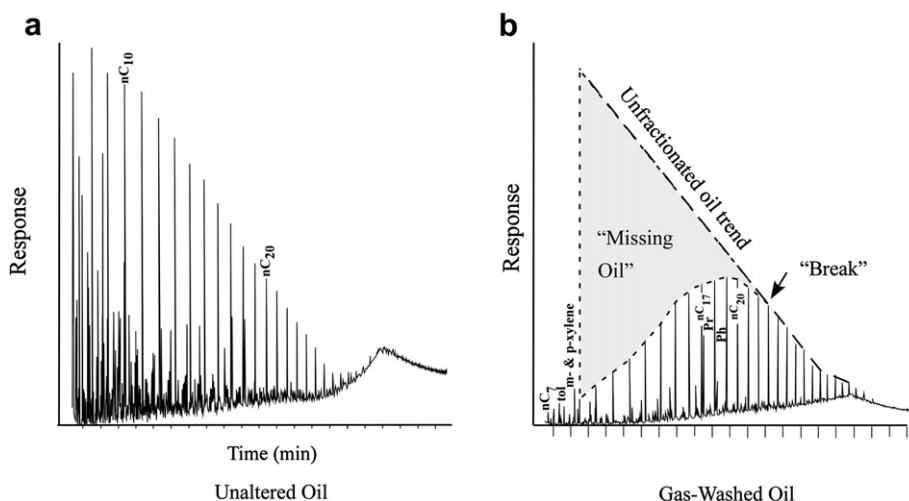


Fig. 1. Whole-oil–gas chromatograms comparing unaltered "parent" oil (a, left) with phase-fractionated oil (b, right; Gulf of Mexico samples). Fractionated oil exhibits systematic depletion of compounds more volatile than the compound at the "break".

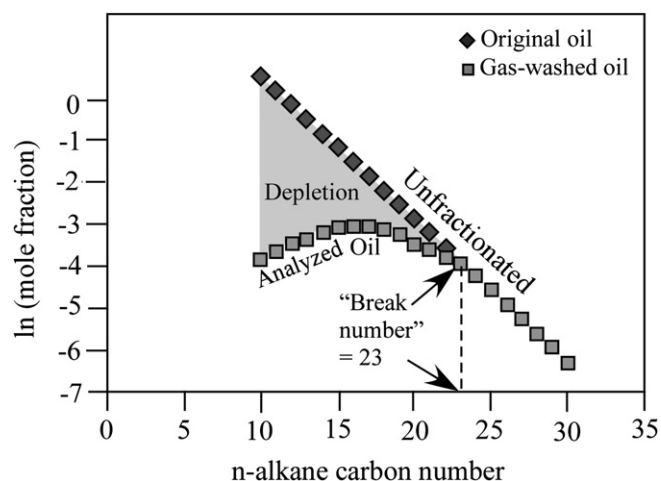


Fig. 2. Plot of $\ln(\text{mole fraction of } n\text{-alkane})$ vs $n\text{-alkane carbon number}$ ('molar fraction plot'). Break number is defined as the carbon number of the lightest $n\text{-alkane}$ that is not fractionated. The unfractionated oil trend has been shifted according to the methodology of Losh et al. (2002). Sample is from the Tiger Shoal field.

complications due to sampling artifacts and post-collection handling and storage effects, the $n\text{-alkane}$ mass depletion fraction is determined only for compounds having carbon number of 10 or higher. Phase fractionation depletes oil in lighter compounds even

more strongly than it does the C_{10+} compounds, so the calculated mass depletion fraction is a minimum estimate. If the abundances of $n\text{-alkanes}$ in both the fractionated oil and the 'daughter' gas condensate are known (e.g., from PIN data), the mass of fractionated oil relative to the mass of oil that was fractionated into the vapor phase ('missing oil' in Fig. 1b) can be computed provided that the vapor did not introduce compounds that remained in the oil after the vapor separated from it. Because we base our analysis of fractionation on the oil's C_{10+} compounds, addition of compounds to the oil by the vapor, assumed to be a wet gas consisting of C_1 – C_5 compounds, in the compositional range of interest in this study is not considered likely. A fractionated oil and gas condensate is considered to be genetically related if the two have similar chemical 'fingerprints' such as dimethylcyclopentane isomer ratios (Mango, 1990) or whole-oil $\delta^{13}C$ values. In addition, fractionated oil has greater aromaticity (toluene/ $n\text{-heptane}$) and lower paraffinicity ($n\text{-heptane/methylcyclohexane}$) than does the gas condensate that is genetically related to it (Thompson, 1987).

To compute mass balance between phase-fractionated oil and gas condensate (specifically, the 'missing oil' shown in Fig. 1b), consider that phase fractionation divides the components in 1 mass unit (i.e., one kilogram) of original parent oil into masses in the fractionated oil and a vapor (gas condensate) according to the relation:

$$M^L + M^V = M^0 = 1. \quad (1)$$

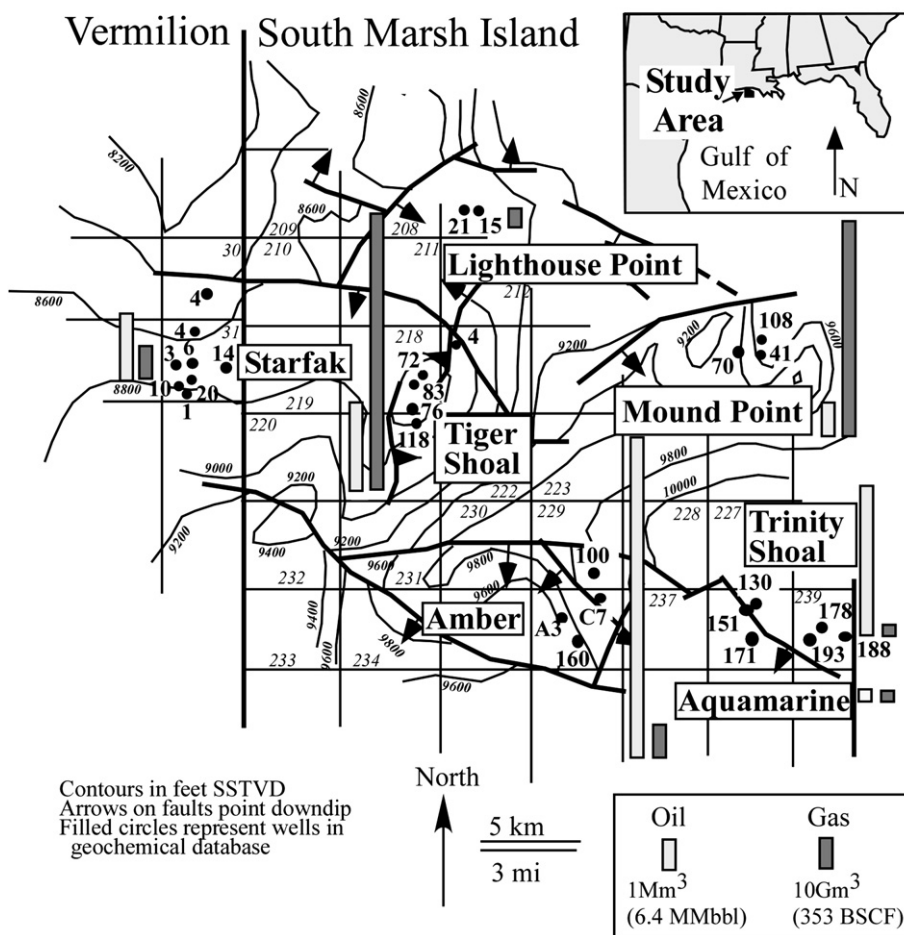


Fig. 3. Structure contour map on Textularia L horizon, SMI 208–239 area, interpreted from 3D seismic data. Shown are locations for wells from which geochemical data were obtained and OCS lease block numbers. Bars represent amounts of ultimately recoverable oil and gas (in 10^6 m^3 and 10^{10} m^3 , respectively) in fields that comprise the SMI 208–239 area.

Here M^L is the mass of all components in the fractionated liquid oil with carbon number equal to or greater than 10, and M^V is the mass of all components in the gas condensate that were 'stripped' from this oil with carbon numbers equal to or greater than 10. The mass of n -alkanes in the vapor constitutes some fraction, d_{nalk} , of the n -alkanes in the original oil:

$$M_{\text{nalk}}^V = d_{\text{nalk}} M_{\text{nalk}}^0 \quad (2)$$

The n -alkane mass depletion fraction d_{nalk} can be determined from the analysis of fractionated oil by the method of Losh et al. (2002). The mass of n -alkanes in the vapor phase also equals the mass fraction (X_M , to distinguish the term from the conventional mole fraction X) of n -alkanes in the vapor phase, $X_{M_{\text{nalk}}}^V$, times the mass of the vapor phase M^V , which, using (1), can be written:

$$M_{\text{nalk}}^V = X_{M_{\text{nalk}}}^V (1 - M^L). \quad (3)$$

Equating (2) and (3) we find:

$$d_{\text{nalk}} M_{\text{nalk}}^0 = X_{M_{\text{nalk}}}^V (1 - M^L). \quad (4)$$

For the fractionated oil, using the same reasoning as above,

$$M_{\text{nalk}}^L = (1 - d_{\text{nalk}}) M_{\text{nalk}}^0, \quad (5)$$

$$M_{\text{nalk}}^L = X_{M_{\text{nalk}}}^L M^L, \quad (6)$$

and:

$$(1 - d_{\text{nalk}}) M_{\text{nalk}}^0 = X_{M_{\text{nalk}}}^L M^L. \quad (7)$$

Combining (4) and (7) to solve for M^L yields:

$$M^L = \frac{\left(\frac{1}{d_{\text{nalk}}} - 1\right) X_{M_{\text{nalk}}}^V}{\left(\frac{1}{d_{\text{nalk}}} - 1\right) X_{M_{\text{nalk}}}^L + X_{M_{\text{nalk}}}^L} \quad (8)$$

M^L is the mass of the fractionated oil with the convention that the original parent oil had a mass of 1 unit. M^L is defined in terms of d_{nalk} , the mass depletion fraction of n -alkanes, and the mass fractions of n -alkane in the vapor (gas condensate) and fractionated oil. These are all parameters that are readily measured or determined from the fractionated oil and the gas condensate; $X_{M_{\text{nalk}}}^V$ and $X_{M_{\text{nalk}}}^L$ are determined from PIN data. The fractions of other compound types (isoalkanes, naphthenes, aromatics, and asphaltenes) in the parent oil and their mass depletion fractions can also be readily calculated from the foregoing equations in combination with SARA and PIN data, but in this paper we focus on analysis of bulk fractionation.

3. Geology of the South Marsh Island 208–239 Area

The South Marsh Island 208–239 and Vermilion 30–31 area (referred to for simplicity as the SMI 208–239 area) comprises a 30-km by 15-km tract that includes the Tiger Shoal, Starfak, Lighthouse Point, Mound Point, Trinity Shoal, Amber, and Aquamarine fields (Fig. 3) in the South Marsh Island and Vermilion protraction areas just offshore Louisiana. Taken together, these fields comprise a geochemically similar cluster, geographically separate from neighboring fields and whose contents share a common migration history. Thus, the fields are considered in aggregate form for part of this analysis, with one field, the Tiger Shoal field, being considered in more detail.

Cumulative production in this nearly depleted area is $20.6 \times 10^6 \text{ m}^3$ oil, $6.7 \times 10^6 \text{ m}^3$ condensate, and $195 \times 10^9 \text{ m}^3$ gas at

STP (133 MMBBL, 43 MMBBL, and 6.9 TSCF, respectively) mostly from four-way closures and fault traps in middle to late Miocene deltaic sands at depths between 1800 and 4300 m (Fig. 4). Below 3600 m, the section is predominantly massive shale, although a deep sand, the Rob L at about 4400 m (14,400 ft) depth, has produced oil in the Starfak field and likely underlies the entire area. Salt domes are absent, although features that appear to be salt sills and pillows can be seen below the reservoirs in seismic data (O'Connor and Weimer, 2004). The fields have been operated by Texaco (now Chevron) since the early 1960s, and most of the reservoirs are now largely depleted.

East–west faults divide the area. Individual faults have up to 300 m of down-to-the-south displacement at the level of the deepest productive sands. These faults, as well as several subsidiary faults, can be traced to the seafloor on seismic data, and so appear to be presently or recently active. Many other faults do not cut significantly above the Bigenerina 'A' (6.3 Ma) marker (Fig. 4). The greater activity of faulting during the Miocene is consistent with sedimentation rates that were somewhat higher then (0.3 mm/yr) than they have been since 'Big A' time (0.2 mm/yr).

Fluid pressures are hydrostatic to a depth of about 3000 m throughout the area. 'Hard' overpressures (0.7 times lithostatic) are encountered at Mound Point and Starfak at about 3300 m, compatible with the shale-rich nature of the stratigraphic section at and below this depth (Fig. 4). The petroleum sample set analyzed in this paper straddles the top of overpressure: at the Tiger Shoal field, pre-production pressures range from 24.8 MPa (3650 psi) in the N sand at ~2600 m depth (a hydrostatic fluid pressure gradient) to 85.0 MPa (12,500 psi) in the Rob L at ~4500 m depth ('hard overpressure'). In the Tiger Shoal field, reservoir temperatures range from 85 °C (N sand) to 102 °C ('12,000 sand'); the deepest sampled reservoir, the Robulus L ('Rob L') sand in the Starfak field, is at a temperature of 147 °C.

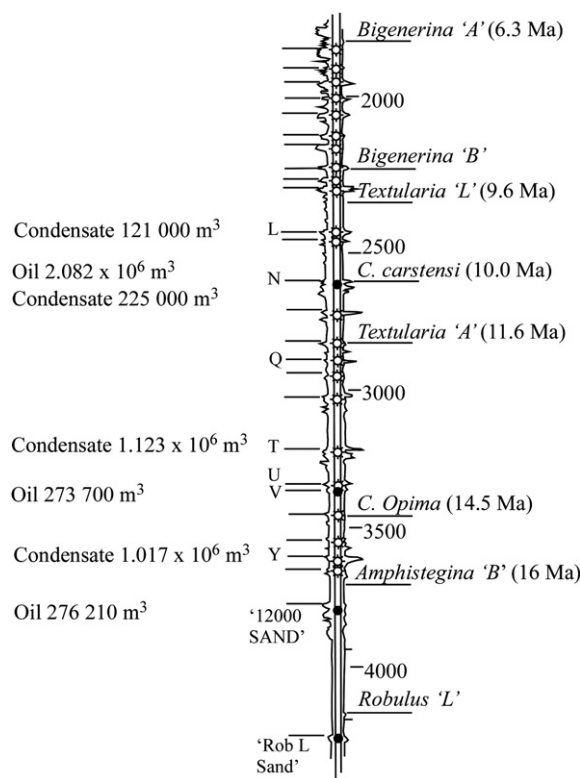


Fig. 4. Type well log (SP on left, long normal resistivity on right), Tiger Shoal field, showing main oil and gas condensate volumes in the Tiger Shoal field. Depths are in meters SSTVD.

4. Petroleum distribution and chemistry in the SMI 208–239 area

Gas and oil are irregularly distributed throughout the area (Fig. 3). The southernmost fields in the area, Amber, Trinity Shoal, and Aquamarine, contain more than half of the area's petroleum liquids but less than a tenth of its gas. About $15.4 \times 10^6 \text{ m}^3$ (99 MMbbl) of ultimately recoverable petroleum liquids, nearly all of which is black oil (average API 35°), lay in these fields, in contrast to $11.5 \times 10^6 \text{ m}^3$ (74 MMbbl) liquids, much of which is gas condensate, in the area's northern fields, consisting of Starfak, Tiger Shoals, Lighthouse Point, and Mound Point. The three southern fields contained initial reserves of $17 \times 10^9 \text{ m}^3$ (0.6 TSCF) gas in comparison with the northern fields' reserves of $179 \times 10^9 \text{ m}^3$ (6.3 TSCF).

Within the Tiger Shoal field, oil and gas are irregularly distributed. Oil is found in three sands, the '12000', the V, and the N (Fig. 4). All gas-producing reservoirs, regardless of oil content, produce gas condensate. Most gases have gas/ liquid condensate ratios between 18,000 and 72,000 m^3/m^3 (100 and 400 MSCF/bbl), regardless of reservoir size. The condensates contain compounds as

heavy as eicosane. As noted, ultimate production for the entire study area is $6.7 \times 10^6 \text{ m}^3$ (43 MMbbl) gas condensate and $20.6 \times 10^6 \text{ m}^3$ (133 MMbbl) residual oil, for a condensate : oil ratio of 0.32:1. At the Tiger Shoal field, the volumes are $2.93 \times 10^6 \text{ m}^3$ (18.9 MMbbl) gas condensate and $2.65 \times 10^6 \text{ m}^3$ (17.1 MMbbl) of fractionated oil, giving an ultimately recoverable gas condensate:residual oil ratio of 1.1:1.

4.1. Composition of oils and gas condensates

Relevant data for 36 black oils and gas condensates from the SMI 208–239 area are reported in Table 1. Production-related changes in oil and condensate composition are thought to be relatively minor for our sample set, as the fluids were collected early in the history of the field, before large pressure drops had been experienced (P. Kelley, pers comm.). Furthermore, the liquids were analyzed shortly after collection, minimizing evaporation-related modifications to composition during storage.

Liquid petroleum in the study area (representative gas chromatograms shown in Fig. 5a and b) originated from an early Tertiary shale source (Hood et al., 1995; Losh et al., 2002), which

Table 1

Oil and gas condensate data, SMI 208–239 area. Analyses performed at Texaco EPTD, Houston, Texas.

Sand	Well	Depth (m SSTVD)	API	Fluid type	Para**	Aro**	Pr/nC ₁₇	$\delta^{13}\text{C}$	Break no	d _{nalk}	%n-alkanes
<i>Tiger Shoals</i>											
N1 MDL/300	72	2600		Oil	0.532	0.776	.746	−26.4	23	0.86	39
Q-1/390	172	2888	51.4	Cond.	0.762	1.151	.837	−26.2	n/a	n/a	39.1
T-1/250	4	3209	50.9	Cond.	0.818	0.939	.818	−26.0	n/a	n/a	33
T-1/900	83	3209	49.1	Cond.	0.799	1.032	.799	−26.2	n/a	n/a	59.7
U N-1/300	72	3542	34.7	Oil	0.416	3.915	.740	−26.4	23	0.86	9.5
V/550	76	3418		Oil			.388	−26.7	23	0.91	–
V/580	121	3418	34.3	Oil	0.459	3.067	.395	−26.7	23	0.91	26.5
Y/400	118	3626	43.3	Cond.	0.709	1.452	.629	−26.3	n/a	n/a	34.2
12000A/150	186	3720	35.5	Oil	0.614	2.153	.572	−26.7	24	0.83	25.1
<i>Starfak</i>											
T2A/475	V31/1	3299	33.7	Oil	0.555	2.239	.398	−26.8	23	0.87	21.3
U/450 (9921)	V30/4	3373	34.7	Oil	0.53	1.843	.706	−26.5	23	0.85	33.9
U/450 (10960)	V30/4	3373	35.3	Oil	0.565	1.928	.619	−26.7	–	–	27.4
U/500	V31/14	3373	–	Oil	0.477	1.836	.652	−26.7	23	0.87	25.5
U/670	V31/20	3373	31.6	Oil	0.33	2.097	.518	−26.6	23	0.87	45.3
12000A/670	V31/6	3869	48.4	Cond.	0.737	0.106	.708	−26.7	n/a	n/a	40.6
ROBL1/655	V31/3	4357	49.6	Cond.	0.807	0.785	.609	−26.6	n/a	n/a	45.1
ROBL2/670	V31/4	4352	39.6	Oil	0.7	0.802	.569	−27.0	24	0.88	29.8
ROBL2/650/1*	V31/10	4352	41.2	Oil	0.638	0.785	.597	−26.9	23	0.88	35.9
ROBL2/650/2*	V31/10	4352	–		0.629	0.83	.409	−27.1	–	–	37.2
<i>Trinity shoals</i>											
J/250	171	2951	36.3	Oil	0.571	0.424	.826	−26.5	23	0.87	21.8
N/100	130	3154	37.4	Oil	0.665	0.771	.692	−26.5	23	0.86	6.1
N/100	151	3154	36.7	Oil	0.633	0.824	.675	−26.6	23	0.85	23
N/100	178	3154	34.6	Oil	0.468	0.97	.682	−26.5	23	0.82	11.3
N/100	188	3154	35.2	Oil	0.514	0.822	.726	−26.5	23	0.86	18.1
N/100	193	3154	48.4	Cond.	0.733	0.783	.727	−25.8	n/a	n/a	40.3
<i>Amber</i>											
N/360	C7	3082	30.8	Oil			.668	−26.4	23	0.90	11.5
N/144	160	3082	33.1	Oil	0.391	1.422	.713	−26.4	23	0.87	17.3
TexL4/310	100	2881	33.2	Oil	0.449	0.644	.242	−26.6	22	0.79	10.3
TexL4/110	A3	2881	34.4	Oil	0.51	2.134	.590	−26.3	23	0.85	21.5
<i>Mound point</i>											
M/500	41	2617	–	Oil	0.25	0.455	1.84	−26.3	23	–	63.5
M/500	70	2617	–	Oil	0.42	0.54	.622	−26.4	23	0.82	15.2
Q1/250	108	3043	–		0.779	0.275	.896	−26.2	–	–	35.3
<i>Lighthouse point</i>											
Q1	21	2856	47.6	Cond.	0.783	1.14	.503	−26.4	n/a	n/a	39.3
Q2/800	15	2884	49.1	Cond.	0.802	0.803	.528	−26.4	n/a	n/a	14.3
<i>Aquamarine</i>											
TexL1/500	153	2741	36.9	Oil	0.618	0.469	.774	−26.5	23	0.87	23.7
J/500	196	2784	37.1	Oil	0.588	0.45	1.05	–	23	0.83	16.5

*1 – sample no 9926, /2 – sample no 10962; **para = paraffinicity; n-heptane/methylcyclohexane; Aro = aromaticity; toluene/n-heptane (both from Thompson, 1987).

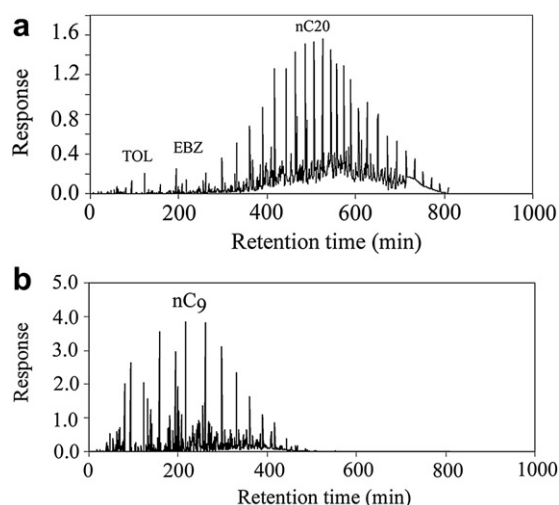


Fig. 5. Gas chromatogram of (a) fractionated oil and (b) gas condensate, both from the Tiger Shoal field. Selected peaks are labeled (TOL = toluene; EBZ = ethylbenzene; *n*-alkanes as shown).

now lies at a depth of about 12 km below sea level in the studied area (e.g., McBride, 1998). Methylphenanthrene isomer ratios in the sampled oils generally lie between 1.0 and 1.2% R_c (from MPI1 and MPI3), indicative of middle to late oil window generation (Radke, 1988; Curiale and Bromley (1996) showed that many biomarkers are useful even in highly fractionated oils). Gas condensates are characterized by a similar range of maturities. At high carbon numbers (greater than 24), the sampled oils all show similar relative abundance of lighter compared to heavier *n*-alkanes as shown

by steep '*n*-alkane slopes' (as determined on a semilog plot such as Fig. 2; analogous to Thompson's (2002) slope factor) of -0.29 to -0.33 , which Kissin (1987) noted as typical of oils of middle to late oil window maturity. Gas condensates are also similar to one another in terms of *n*-alkane distribution, having '*n*-alkane slopes' of -0.8 to -1.05 . Aromaticity (ratio of toluene to *n*-heptane (Thompson, 1987); Table 1) of sampled oils is generally high (greater than 0.5), and indicates that aromatics have not been preferentially removed from the oil due to water washing (Thompson, 1987; Palmer, 1984; Lafargue and Barker, 1988). Biodegradation is also absent in these oils, as demonstrated by the lack of Unresolved Complex Mixture in whole-oil gas chromatograms as well as by the nearly ubiquitous Pr/nC_{17} ratios less than one (e.g., Curiale and Bromley, 1996; Table 1). Only two samples have ratios are greater than unity, but the higher of these is likely unreliable due to low concentrations of both pristane and nC_{17} . In addition, the ratio of total *n*-alkanes to isoalkanes in these oils is at least 2:1, again indicating little to no biodegradation. The lack of biodegradation is consistent with the relatively high reservoir temperatures, which exceed the commonly accepted 80 °C upper limit of oil pasteurization temperatures (Pepper and Santiago, 2001; Larter et al., 2003).

4.2. Phase fractionation at SMI 208–239

Despite their lack of alteration by water washing or biodegradation, black oils in the SMI 208–239 study area are strongly depleted in gasoline- to diesel-range compounds (Fig. 5a). This depletion is remarkably uniform throughout the sample set (Fig. 6) and is consistent with phase fractionation. Regardless of present depth or pressure, the oils are characterized by nearly the same 'break number' (mean = 23, range 22–24) and a relatively narrow

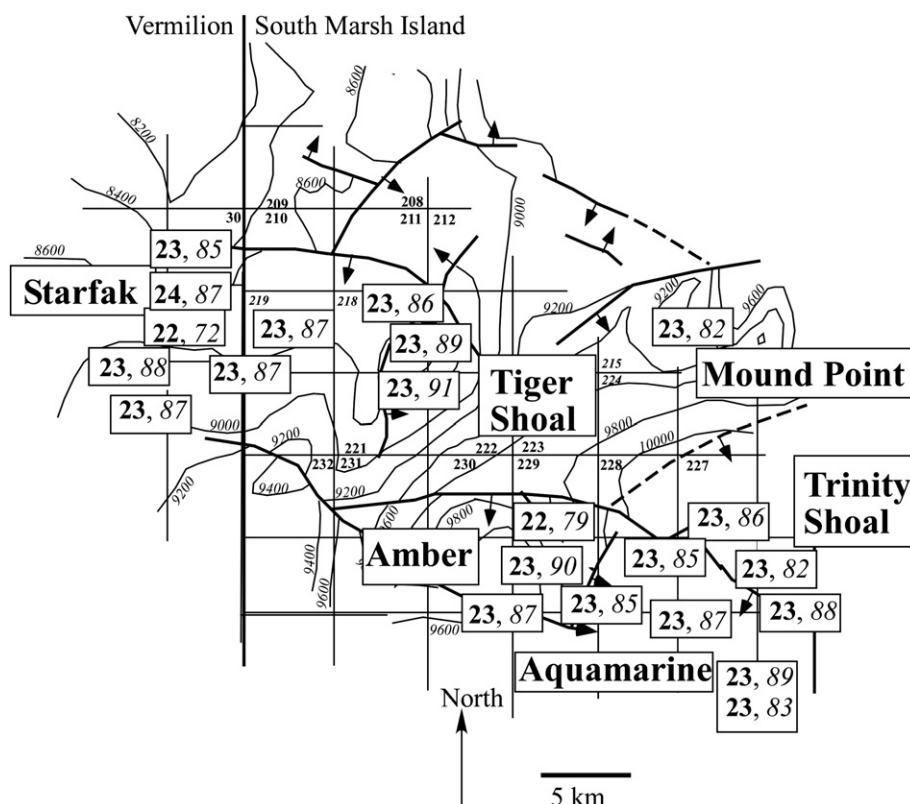


Fig. 6. Structure contour map of Tex L horizon, SMI 208–239 area, showing break number (first number) and percent *n*-alkane mass depletion (second number, italics) for sampled oils.

range of nC_{10+} n -alkane mass depletion fractions (mean 0.85, range 0.79–0.91) (Table 1, Figs. 6 and 7). The similarity in break numbers implies similar pressure–temperature conditions during the fractionation of all the oils, and the similarity in n -alkane depletion indicates similar amounts of vapor and liquid were involved in the fractionation process in spite of the evidence that each field was fed by an individual plumbing system (Chevron unpub. data).

Gas condensates and fractionated oils from SMI 208–239, including the Tiger Shoal field, appear to be genetically related. They have nearly identical whole-oil $\delta^{13}C$ values ($-26.3 \pm 0.26\text{‰}$ PDB for gas condensates, $-26.6 \pm 0.2\text{‰}$ PDB for black oils; Table 1) and ratios of particular dimethylcyclopentane isomers (Fig. 8; Mango, 1990). As noted, the two types of liquid also have the same range of maturities as determined from methylphenanthrene isomer ratios (Radke, 1988).

Black oils and gas condensates in the SMI 208–239 area are complementary with respect to their aromaticity and paraffinicity (Fig. 9), consistent with derivation of the gas condensates by phase fractionation of parent oil. As shown by Thompson (1987), gas condensates that formed by fractionation of oil are enriched in n -alkanes relative to cycloalkanes (e.g., n -heptane vs methylcyclohexane). Conversely, the fractionated oil is depleted in n -alkanes relative to other compound types such as aromatics, and thus is characterized by increased aromaticity. The presence of mainly low-aromatic paraffinic condensates at SMI 208–239, according to Thompson's (1987) model, suggests the oil fractionation was mainly a single-batch process, rather than a series of mixing-fractionation steps. However, two Tiger Shoal gas condensates (not in our dataset) show high aromaticity (K. Thompson, pers. comm., 2009), indicating that in some instances a multi-stage phase fractionation process (i.e., fractionation of an already-fractionated oil) was responsible for formation of some gas condensates in this area.

5. Discussion

5.1. Oil–gas fractionation at SMI 208–239

The existence of uniformly fractionated black oils in reservoirs spanning a wide range of pre-production pressures and temperatures poses questions as to the meaning of their compositions. Under what conditions and in what geologic setting was the parent liquid fractionated, assuming it had a 'normal' (log-linear) abundance distribution of n -alkanes and other compound types? Several observations bear on this question. First, typical fractionations at the separator may in extreme instances affect compounds as heavy as nC_{10} or so, but not diesel-range compounds. Thus the highly fractionated composition of the oils is not the result of separator-

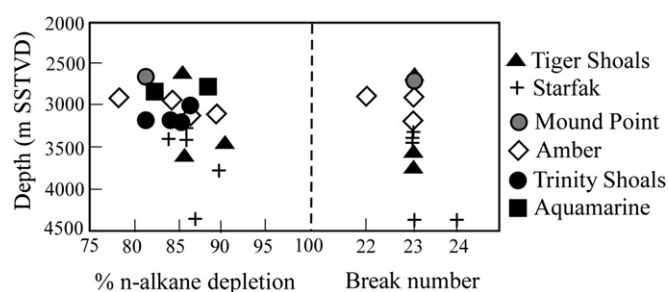


Fig. 7. Percent n -alkane mass depletion vs depth, SMI 208–239 area. Neither depletion nor break number show any evident relationship to present reservoir depth. Pre-production pressure varies from about 24.5 MPa to 81.6 MPa (3600 psi to 12,000 psi, respectively), sufficient to result in a large shift (decrease) in break number at shallower depths if fractionation took place in the reservoirs.

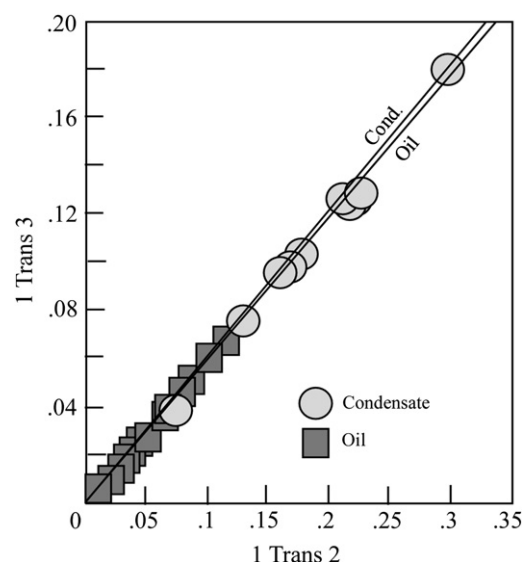


Fig. 8. Dimethylcyclopentane isomers 1Trans3 vs 1Trans2 for fractionated oils and gas condensates, SMI 208–239 area. The ratios for the two fluid types are nearly identical, indicating a common source (e.g., Mango, 1990).

related processes. Second, the uniformity of fractionation of the black oils regardless of their pre-production reservoir pressure indicates that the fractionation process and resultant observed compositional effects are not related to the pressure of the oil in the present reservoirs. Instead, the oils were fractionated at roughly the same pressure–temperature conditions. Their presence in reservoirs whose pressures vary by a factor of three means that the fractionation had to take place at some common depth, with the fractionated oils then being transported to their final positions. Third, regardless of present (pre-production) reservoir pressures, the n -alkane slopes for the unfractionated portion (carbon number > 24) of the fractionated oils lie in a narrow range, precluding any significant condensation of liquids from the vapor as it ascended (Thompson, 2002). The only explanation that reasonably accounts for all the observations is that the oils were phase fractionated at a particular depth (pressure and temperature) while they were in liquid form; that is, they were gas-washed, and by roughly the same amount of vapor in all cases. In some instances, the gas washing process involved repeated fractionation of oil, but it nonetheless happened under a rather narrow range of conditions.

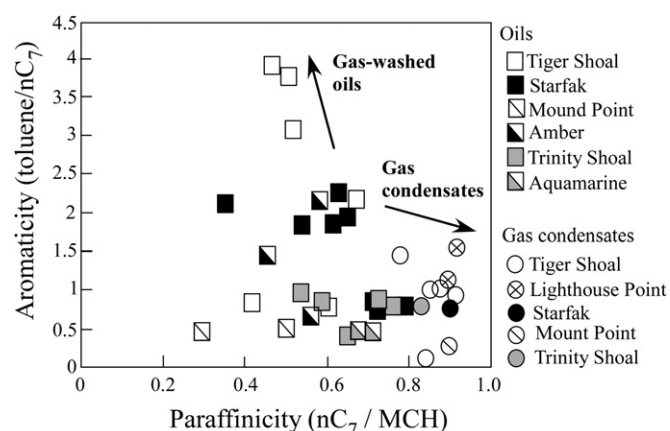


Fig. 9. Aromaticity vs paraffinicity (after Thompson, 1987) for sampled oils and gas condensates.

A late large pulse of gas, interacting with oil at higher pressure due to continued burial, may have assisted migration of the oils to their present reservoirs.

As noted, the uniformity of the SMI 208–239 oils in terms of mass depletion and 'break number' requires fractionation of all the oils at nearly the same pressure–temperature–composition (PTX) conditions. Uniformity over such a large area (>450 km²) would not be expected if fractionation occurred primarily in vertical migration conduits (e.g., faults), as such gas washing sites in an array of high-angle faults would not be expected to lie in the same narrow depth range everywhere, nor to have nearly the same ratio of washing gas to fractionated oil as reflected by the nearly uniform d_{naik} values. Depth uniformity indicates that gas washing probably took place in a relatively flat-lying horizon, most likely a sand in which the migrating gas and oil were thoroughly intermixed at relatively constant mass ratio. The presence of gas-washed oil in the Rob L sand in the Starfak field, the deepest location of gas-washed oil in the study area, indicates that the gas washing took place within the Rob L or a deeper sand. The washing scenario we envision is illustrated in Fig. 10. Although the petroleum system in the SMI 208–239 area is complex (as it is throughout much of the Gulf of Mexico), the uniformity of phase fractionation of oil throughout the area implies that at least that aspect of the migration history of the oils is relatively simple.

Gas washing may also account for the oil compositions documented in the Vermilion 39 Field by Curiale and Bromley (1996). Those workers proposed that the light-end depleted oils in that field were phase fractionated largely by the release of autochthonous gas due to a pressure drop in the reservoir. However, if this were the only source of the gas, it is difficult to explain the very high GOR and intense phase fractionation that would be needed to produce the extreme light-end depletion shown by the fractionated Vermilion 39 oils, even at elevated subsurface pressures. It is likely that these oils were phase fractionated by some other mechanism that allows for very high gas:oil ratio in the system.

5.2. Mass balance calculations for coexisting fractionated oil–gas condensate

Average mass balance. Utilizing the equations derived in Section 2 and whole-liquid (PIN) *n*-alkane data and *n*-alkane mass depletion fractions from Table 1, we determine the mass balance for

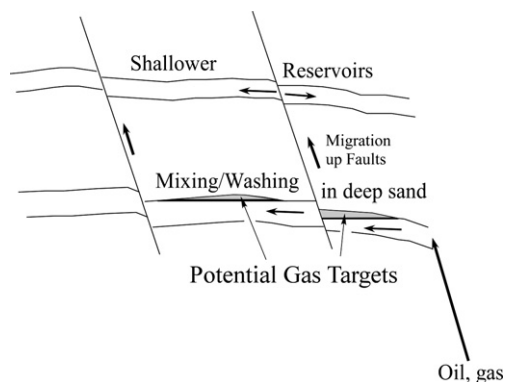


Fig. 10. Schematic gas washing model of oil (black) and gas (gray) at Tiger Shoal. Oil and gas ascend from source, mix, equilibrate, and separate in a deep (Rob L?) sand, then migrate up faults to shallower reservoirs. The 'washing sand' presumably was present beneath the entire SMI 208–239 area. Gas-washed oil accumulations have been found in the Rob L sand at Starfak. The Rob L sand is largely unexplored throughout much of the rest of the study area.

fractionated oils and gas condensates from the SMI 208–239 area. The data do not allow us to clearly distinguish different gas washing episodes in the area, and we straightforwardly apply Eq. (8) to all possible residual oil – gas condensate pairs (24 oils × 11 condensates) in the dataset. Since it is not known which oils and which condensates, if any, are paired, an M^L value was calculated for each oil paired with each condensate in the dataset, then averaged. For a mean *n*-alkane mass depletion fraction (d_{Naik}) of 0.86, the mass fraction of fractionated oil remaining after gas washing of the parent oil (M^L) is 0.24 ± 0.051 , or 24%. There is relatively low variability in this parameter considering the large range of residual oil and gas condensate compositions represented in Table 1.

On average, 76% ($1 - 0.24$) of the original oil mass has been fractionated into a separate vapor phase, which condenses liquid in the subsurface and at the wellhead. As noted previously, this calculation is based on the depletion of nC_{10+} compounds, and so represents a minimum estimate of the amount of oil fractionated into the vapor phase. To determine the ratio of gas condensate volume (V_c) to fractionated oil volume (V_o), we employ the respective densities (ρ_o for oil, ρ_c for gas condensate) as determined from their API gravities (average 35° for black oil, 50° for gas condensate):

$$\frac{V_c}{V_o} = \frac{\rho_o M_c}{\rho_c M_o} \quad (9)$$

where M_c is the mass fraction of gas condensate (here, 0.76) and M_o is the mass fraction of residual oil (0.24). Accordingly, the volume ratio of gas condensate to residual oil in the SMI 208–239 area is computed as 3.5:1. On average, each cubic meter (barrel) of residual oil is paired with 3.5 cubic meters (barrels) of gas condensate. Propagating the uncertainty of M^L results in a range of gas condensate: fractionated oil volume ratios from 2.7:1 to 5.3:1. The mean gas condensate: fractionated oil ratio is significantly affected by the extent of *n*-alkane depletion by gas washing. For example, if d_{naik} is calculated on the basis of depletion of nC_{8+} rather than nC_{10+} (resulting in an average d_{naik} value of 0.91 rather than 0.86), the mean gas condensate : fractionated oil volume ratio is calculated as 5.7:1 ($M^L = 0.16$), over 60% higher than reported above. At its high end, the gas condensate: fractionated oil volume ratio is 8.2:1.

In all cases, the amount of known gas condensate is much less than is predicted from mass balance based on the amount of fractionated oil present in the area. As noted, the volume ratio of ultimately producible gas condensate to fractionated oil is 0.32:1, or about 11 times lower than indicated by mass balance. The known amount of ultimately recoverable fractionated oil, $20.6 \times 10^6 \text{ m}^3$ (133 MMbbl), implies the initial presence of $72.2 \times 10^6 \text{ m}^3$ (465 MMbbl) (ranging from $55.7 \times 10^6 \text{ m}^3$ to $109.5 \times 10^6 \text{ m}^3$ (359–705 MMbbl)) gas condensate, about $6.7 \times 10^6 \text{ m}^3$ (43 MMbbl) of which have been produced. Taking the first of these values and using a condensate: gas ratio of 3600 m³ gas/m³ condensate (200 Mscf/bbl), typical of this area, the remaining $66 \times 10^6 \text{ m}^3$ (422 MMbbl) of condensate implies the existence of an additional $240 \times 10^9 \text{ m}^3$ (8.4 Tscf) gas. This additional gas is undiscovered, unproduced, or, in large part, has possibly vented to the seafloor over the millennia.

As noted earlier, the Tiger Shoal field is characterized by a gas condensate : fractionated oil ratio of 1.1:1, nearly the highest of all the fields in the area. However, mass balance indicates that it is nonetheless deficient in gas condensate relative to its initial reserves of fractionated oil. Based on the gas condensate and fractionated oil compositions and the average *n*-alkane mass depletion fraction (0.87) from just this field, 23 wt% of the parent oil remained as fractionated liquid after gas washing, nearly the same as is calculated for the entire area. If the Tiger Shoals field were isolated from its neighbors (which it is not), its $2.65 \times 10^6 \text{ m}^3$ (17.1 MMbbl)

of oil would be paired with $9.28 \times 10^6 \text{ m}^3$ (62 MMbbl) of gas condensate, or $6.35 \times 10^6 \text{ m}^3$ (43.1 MMbbl) more than is known in that field. The volume of undiscovered, unproduced, and/or already-vented gas that contains this condensate is on the order of $23.2 \times 10^9 \text{ m}^3$ gas at STP (820 Bscf), using the gas:condensate ratio as previously. The Rob L sand, which likely underlies the SMI 208–239 area, probably contains gas-washed oil or, more likely, gas condensate.

6. Conclusion

Mass balance computations based on the extent of *n*-alkane depletion and *n*-alkane content of paired fractionated oil and gas condensate indicate that 76 wt% of C_{10+} mass of original “parent oil” separated into a gas condensate and 24 wt% remained as a fractionated oil. The uniformity of the character and extent of gas washing over the 450-km² area indicates that gas washing took place under the same pressure and temperature conditions. A logical place for this to happen is in the deep, relatively flat-lying Rob L sand that underlies the area and that contains phase-fractionated (residual) oils. The gas washing could have occurred in a slightly deeper sand, if such exists. Rapid upward migration then charged the overlying sands with the gas-washed oil and gas condensate with no additional fractionation or separation. Chemical mass balance suggests that on average there should be $\sim 3.5 \text{ m}^3$ of gas condensate for every cubic meter of gas-washed oil. Depending on the mass depletion fraction and composition of paired gas condensate and fractionated oil, the gas condensate volume could be from 2.7 to 8.2 times the fractionated oil volume. If all the fields in the studied area comprise a single migration / fractionation system, $68.4 \times 10^6 \text{ m}^3$ (442 MMbbl) (range of $49.1 \times 10^6 \text{ m}^3$ to $103 \times 10^6 \text{ m}^3$ (316–662 MMbbl respectively)) of gas condensate is unaccounted for. Given the average industry-estimated ratio of gas condensate to fractionated oil for the Tiger Shoal field, at least $6.35 \times 10^6 \text{ m}^3$ (43 MMbbl) of gas condensate are unaccounted for in that field alone. It is likely that much of this gas condensate vented into the ocean in vapor form, but a significant amount could remain in the subsurface in producible reservoirs. Phase fractionation is a common process in basins, and the particularly well-studied and mature SMI 208–239 area provides a good example of how this sort of data can be analyzed in a way that contributes insight into the phase fractionation process and the remaining exploration potential of an area.

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