

Phase fractionation at South Eugene Island Block 330

PETER MEULBROEK^{1*}, LAWRENCE CATHLES III^{1†} and JEAN WHELAN^{2‡}

¹Department of Geological Sciences, Snee Hall, Cornell University, Ithaca, NY 14853, U.S.A. and

²Department of Marine Chemistry, Woods Hole Oceanographic Institute, 360 Woods Hole Rd MS#4, Woods Hole, MA 02543, U.S.A.

Abstract—Persistent gas flux can dissolve, remobilize and alter reservoir or migrating oil through a process of phase fractionation. Moving gas, when flowing through an oil, can dissolve large fractions of that oil. The composition of the oil dissolved in the gas is dependent on the pressure–temperature conditions of the oil and the fluid flow history of the basin. The composition of the residual oil can be interpreted to yield both the depth at which the oil fractionated and the volume of gas required to fractionate the oil. South Eugene Island Block 330 in the U.S. Gulf Coast is a hydrocarbon province that has recently experienced large gas fluxes. Some of the oils in the region show signs of progressive fractionation and remobilization by gas transport. For example, the oils are more aromatic and less paraffinitic than unfractionated oils of similar maturity from the same area. The altered oils are also depleted of light *n*-alkanes. We have developed a computer-based model of oil alteration based on a fluid phase equilibria algorithm to simulate progressive fractionation of oil by gas. Application of the model to the South Eugene Island Block 330 area shows that several of the oils in the area have compositions that are compatible with alteration caused by equilibrating with approximately 12 to 14 mol of gas per mol of oil (2 to 2.7 g of gas per g of EI oil). The oils appear to have fractionated at approximately the depths of their present reservoirs. The model has great potential to examine hydrocarbon fluids for evidence of past migration and mixing. © 1998 Elsevier Science Ltd. All rights reserved

Key words—equation of state, Eugene Island, evaporative fractionation, fluid phase equilibrium, gas washing, geochromatography, phase fractionation, separation migration

INTRODUCTION

Maturing hydrocarbons in the subsurface generally start as a single-phase mixture. As the hydrocarbon fluids migrate, the changing pressure and temperature regimes they experience can induce the fluids to separate into distinct fluid phases (liquid and vapor). Phase separation can also be caused by mixing of separate single-phase fluids. Phase fractionation is the general process that describes the compositional changes caused by phase separation and subsequent physical separation that occur to a chemical mixture, such as a mixture of hydrocarbons in the subsurface. In the subsurface, these events are caused by fluid movement. Phase fractionation is distinct from simple phase separation in that it includes the physical separation of the two phases, and thus describes an open system.

One scenario of fluid movement and mixing in the subsurface occurs when a mobile fluid invades and mixes with a relatively immobile fluid (perhaps trapped in a reservoir), causing the mixture of the

two to fractionate into liquid and vapor phases. If the mobile fluid is a gas that periodically interacts with an immobile liquid (oil), the process can be referred to as “gas washing” (see Fig. 1). Increasing degrees of fractionation result as increasing amounts of gas mix with the oil and remove the most soluble components of the oil. The gas stream leaving the oil contains some fraction of dissolved oil, and can be thought of as a low-temperature condensate. This stream can either be trapped in a reservoir at a shallower depth, or vent out of the system. Evidence for this venting occurs throughout the Gulf of Mexico as pockmarks and seafloor hydrothermal vents (Roberts and Carney, 1997). In this paper, we will present a model of the phase fractionation that results from gas washing, and relate that model to a case study of gas washing at Eugene Island Block 330.

Gas washing occurs in many locations around the world. There is evidence that gas migration-induced fractionation occurs at the U.S. Gulf Coast (Thompson, 1987), offshore Taiwan (Dzou and Hughes, 1993), the South China Sea (Quanxing and Quming, 1991), offshore Indonesia (Schoell *et al.*, 1985), offshore Alaska (Kvenvolden and Claypool, 1980) and the North Sea (Larter and Mills, 1991) amongst other places. More generally, gas washing should occur wherever a free gas phase can form and migrate in a hydrocarbon province.

*To whom correspondence should be addressed. Present address. Department of Marine Chemistry, Woods Hole Oceanographic Institute, 360 Woods Hole Rd MS#4, Woods Hole, MA 02543; E-mail: pmeulbroek@whoi.edu.

†E-mail: cathles@geology.cornell.edu

‡E-mail: jwhelan@whoi.edu

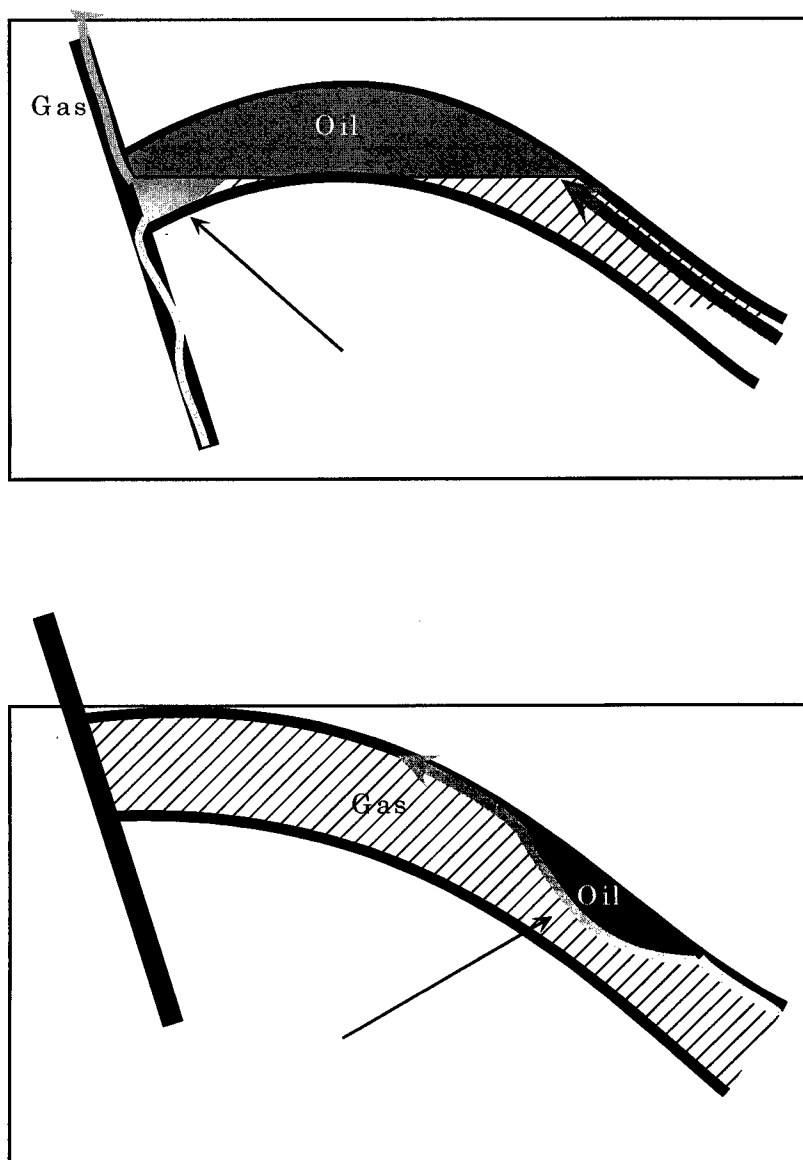


Fig. 1. Two examples of gas "flowing through" oil. In the figure, flowing gas remains proximate to oil for a sufficient period of time to equilibrate with that oil. In (a) the oil is trapped in a reservoir, while in (b) a low saturation oil is migrating, albeit slower than the gas migrates. In both figures, the black arrow indicates the region in which gas "flows through" oil.

Models of gas washing in the subsurface are not common in the literature. Though reservoir engineers commonly calculate the effects of gas caps separating from trapped hydrocarbons using equations of state (see reviews in Edmister and Lee, 1988, Ahmed, 1989 and Reid *et al.*, 1985) the published work generally apply these equations to discuss the effects of phase separation within closed systems in which all phases remain proximate, such as within a reservoir. Gas washing, which includes the physical segregation and migration of the separated phases, occurs in an open system. The gas that washes the oil generally migrates towards the oil in order to

wash it, then migrates away from the oil. This process can occur within a leaky reservoir, or as the hydrocarbon mixture migrates outside a confining reservoir.

Gas washing has appeared sporadically in the literature. Silverman (1963) and Silverman and Plumley (1963) describe the process of separation-migration, which is defined as a phase separation in an oil reservoir caused by changes in pressure and temperature, followed by migration of the two phases along separate paths. McAuliffe (1979) predicts the fractionation effects resulting from oil migrating in a water solution, which are quite

different from the fractionation effects from migrating in a gas solution, but are controlled by the same theoretical constraints.

Thompson (1987, 1988) has suggested that many of the gas condensates in the Gulf of Mexico basin result from evaporative fractionation, which is a restricted example of gas washing. Evaporative fractionation results when a mixture of hydrocarbons is invaded by a single body of gas, followed by equilibration between the fluids and subsequent migration of the vapor phase. Thompson proposed that the vapor phase of the evaporative fractionation products has a composition similar to, but distinguishable from a thermal (high maturity) gas condensate. The liquid phase resulting from the evaporative fractionation is a residual oil depleted in light hydrocarbons. Thompson found that this process tends to alter the residual oil such that there is:

1. an increase the modal *n*-alkane of the oil,
2. an increase in the aromaticity (defined by Thompson as the ratio of toluene to *n*-heptane) of the oil,
3. an increase in the normality (amount of unbranched alkanes and cycloalkanes relative to branched alkanes) of the oil and
4. a decrease of the oil's paraffinicity (defined by Thompson as the ratio of *n*-heptane to methylcyclohexane).

Thompson's concepts and experimental work are supported by Larter and Mills (1991), who performed experiments to determine the compositional changes that a migrating fluid undergoes.

Krooss *et al.* (1991) describe gas washing as "gas-liquid geochromatography", where a mobile vapor phase equilibrates with and then fractionates a (relatively) stationary liquid phase. They find the process analogous to separation techniques utilized in gas- or liquid-chromatography. The limited numeric model presented by the authors describing the effects of a one-step fractionation between a mobile and a stationary phase shows that the fractionation between two phases is proportional to the "sorption affinity", which in two fluid phase systems is equivalent to solubility.

In this work, we will use the term gas washing to describe the fractionation caused by multiple events or continuous mixing between oil and gas. Gas washing can be distinguished from evaporative fractionation, which is caused by a single mixing event. Thompson's observations on the effects on hydrocarbon composition of a single fractionation event should apply to more general cases of gas washing. We do expect, however, that multiple or continual fractionation effects will cause more profound compositional changes in an oil than a single fractionation event.

The literature on gas washing to date has been focused on conceptual, experimental or observational reports. No detailed numeric or quantitative models of gas washing have been developed. This paper presents a numerical model that quantitatively predicts the effects of gas washing on hydrocarbon fluids under realistic conditions, and relates the results to an example of fractionation found at South Eugene Island Block 330 (EI 330) in the U.S. Gulf Coast. We use the results from this model to

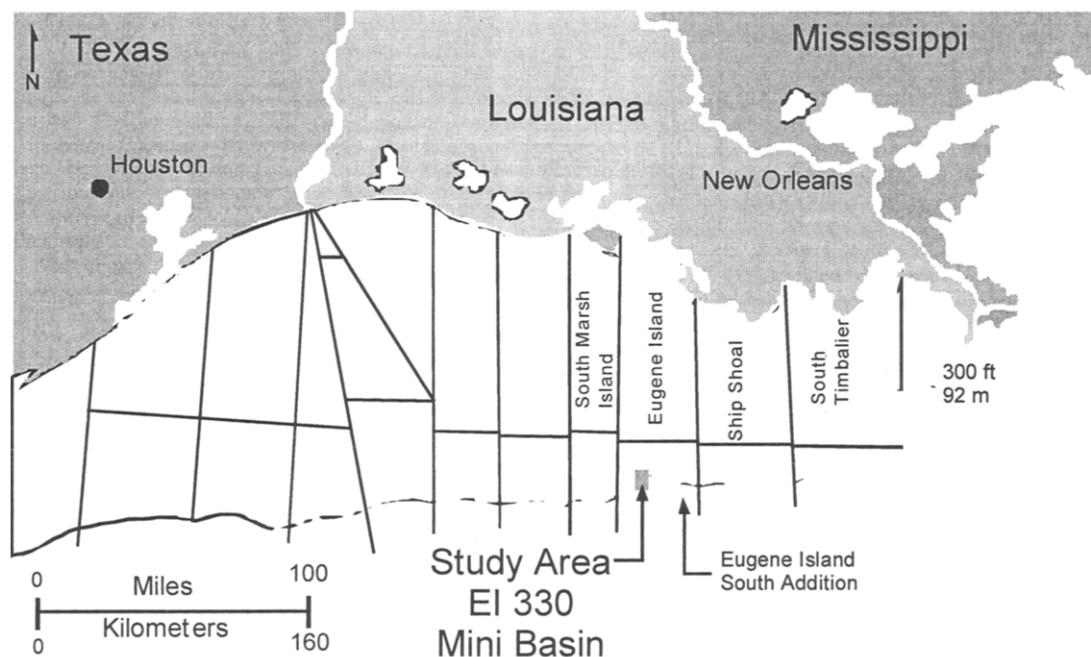


Fig. 2. Location of Eugene Island South Block 330. From Anderson *et al.* (1993).

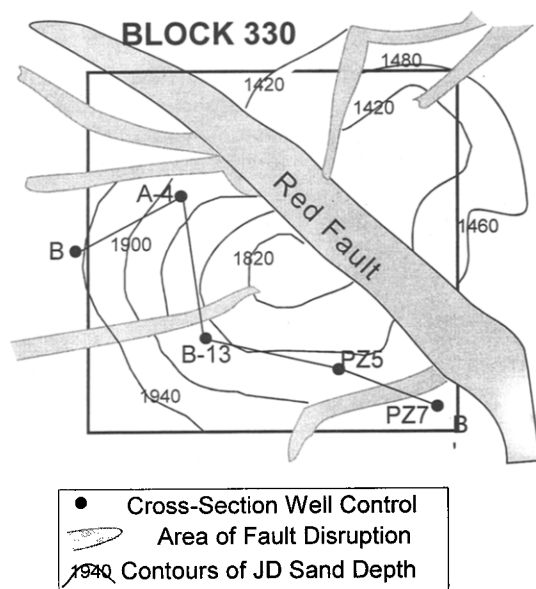


Fig. 3. Map view of South Eugene Island Block 330 at the JD sand, based on Coelho's interpretation of a Pennzoil 3-D seismic survey (Coelho, 1997). The shaded areas represent the major faults in the area. Structure contours of the JD sand are in black, with depth listed in meters.

relate the fluid history of oils in the EI 330 reservoirs to oils that are in adjacent or underlying reservoirs. Relating oils to deeper fluids can be used to understand the fluid flow history of a basin, and to predict the existence of deeper fluids.

EUGENE ISLAND OILS: EXAMINATION OF A DATA SET OF WHOLE OIL ANALYSES

In this paper we utilize a data set of whole oil analyses of oils from South Eugene Island Block 330 (EI 330) performed at Woods Hole

Oceanographic Institute for the Global Basin Research Network (Whelan *et al.*, 1993, 1994).

The South Eugene Island Field is located on the U.S. Gulf Coast Shelf, offshore Louisiana (see Fig. 2). The South Eugene Island Block 330 field is the largest Pleistocene oil field in the world (Holland *et al.*, 1990). It has been the focus of Global Basins Research Network (GBRN) studies for the past 8 years, and hence is well studied both geologically and geochemically.

Structurally, the EI 330 area is a minibasin bounded on the north and east by the "red" fault (a regional growth-fault system), and on the south by the "blue" fault (a counter-regional compensation fault), as shown in Fig. 3. The stratigraphy consists of alternating sequences of Plio-Pleistocene sands and shales that overlie deepwater distal fan deposits from the ancestral Mississippi river delta (Alexander and Flemings, 1995). Each of the major sand layers in the minibasin form rollover anticlines on the downthrown side of the faults. These anticlines are filled with oil and gas. The deepest reservoirs are geopressed, while shallower reservoirs are hydrostatically pressured. The transition to overpressure (from hydrostatic to a near lithostatic gradient) generally takes place within or just above the OI sand, at approximately 2.0 km depth (see Fig. 4, modified from Coelho, 1997).

The producing sands in the field are lettered according to depth. In this study, we only consider the reservoirs from the IC sand, at approximately 1.7 km depth, to the OI sand, which can be as deep as 2.7 km. The cross-section in Fig. 4 shows the depth to the various sands on the downthrown side of the Red fault in EI Block 330. The location of the cross section in Fig. 4 is shown in Fig. 3.

The EI 330 oil data were assembled to investigate the concept of present day migration into the reservoirs at EI 330. The evidence for present-day mi-

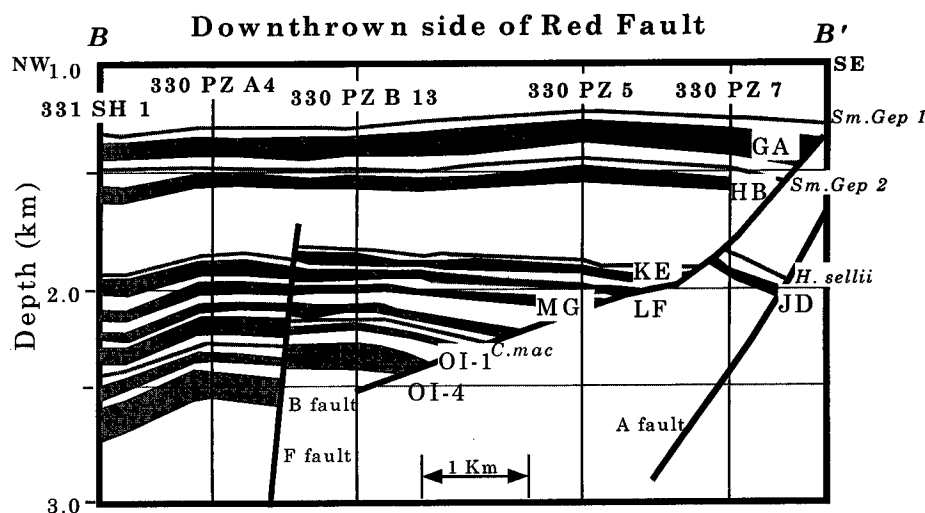


Fig. 4. Geological section of South Eugene Island Block 330. After Coelho (1997).

gration of low molecular weight fluids includes active hydrocarbon seeps in the area that occur at the surface expression of the major growth faults (Anderson *et al.*, 1993). Also, compositional changes in the hydrocarbons in shallow reservoirs imply that the injection of wet gas and gasoline range hydrocarbons into those reservoirs is presently occurring (Schumacher, 1993; Whelan *et al.*, 1994). The migration of low molecular weight fluids (most probably gas) implies that the oils from EI 330 might show the effects of gas washing. The data analyzed in this paper consist of 110 oil samples from Eugene Island Block 330, collected during 1993 and 1994. The samples are analyzed for approximately 60 *n*-alkane, isoalkane and gasoline range (light aromatic and naphthene) concentrations, as published in Whelan *et al.* (1993, 1994).

Evidence of fractionation

Much of the analysis performed here will examine the distribution of molar concentration with carbon number of the *n*-alkanes in the EI 330 oils. Kissin (1987) states that an unfractionated, unaltered oil shows an exponential relationship between molar concentration and carbon number. Kissin found that the mole fraction of *n*-alkanes in most of the world's oils are exponentially distributed with carbon number, which might relate to the mechanism by which *n*-alkanes are formed in source rocks (Fabuss *et al.*, 1964; Thompson, personal communication, 1996). This distribution can be modeled as

$$y_i = A \exp[ax_i], \quad (1)$$

where y_i is the molar concentration of the *n*-alkane of carbon number x_i , A is a scaling factor, a is the exponential "slope factor", which is generally negative. When the log of molar concentration is plotted against carbon number, the slope factor is equivalent to the slope of the best fit line though the distribution of *n*-alkane concentrations. Deviations of *n*-alkane concentrations from this line are typically quite small (Thompson, personal communication, 1996) reports R^2 values of up to 0.99 for unaltered oils.

Kissin states that the slope factor is a function of an oil's maturity. Immature oils have a slope factor near zero. More mature oils have smaller (more negative) slopes. The typical range for slope factors is shown in Table 1, after Kissin (1987).

The oils in Eugene Island can be characterized as one of the two types based on their *n*-alkane distribution.

1. Pristine oils, defined as those oils with *n*-alkanes that follow an exponential relationship, gas condensates with no secondary alteration, with *n*-alkanes that also follow an exponential relationship.

Table 1. Kissin slope of different oil types

Range	Oil type
-0.5- -0.2	wet gas to condensate
-0.19- -0.16	normal oil
Greater than -0.1	heavy, waxy oil

2. Altered oils with *n*-alkane concentrations that deviate from an exponential relationship, which we interpret as oils that have been washed by gas.

The *n*-alkane concentrations in the altered oils show a very regular pattern. Their heavier *n*-alkanes are exponentially distributed, with an exponential slope factor similar to that of the pristine oils. The lighter *n*-alkanes in the oil all have approximately equal concentrations and plot as a horizontal line in a semi-log plot. There is an abrupt transition between the two sections. Hence, when the *n*-alkanes of a fractionated oil are plotted in a semi-logarithmic plot, the curve appears as two linear sections that are joined. An example of this can be seen in Fig. 5, which shows the plot of oils from the LF sand at EI 330. Note that oils that show evidence of biodegradation, such as from the GA and HB sands, are not included in this study. The pattern of *n*-alkanes in biodegraded oils deviate from the scheme presented here.

To quantify the deviation in the *n*-alkane distributions from an exponential distribution, each of the *n*-alkane distributions in the EI 330 data set is fit with a curve that defines the distribution as the union of two line segments. We use this function to fit the distributions since it describes the pattern seen in most of the altered oils. The fit function is defined by the following formula:

$$\begin{aligned} y &= mx + b, & \text{if } x > a \\ y &= ma + b, & \text{if } x \leq a, \end{aligned} \quad (2)$$

where m , a and b are determined by linear regression, x is the carbon number and y is the log[mole fraction] for each *n*-alkane. The a value in the equation we will refer to as the break number, because it is the carbon number at which a "break" occurs in the best fit curve. Note that a is not necessarily an integer and hence has no direct physical meaning. The m value is the slope factor of the heavy *n*-alkanes (those with carbon numbers greater than a), and reflects the slope factor of the original oil.

Figure 5 shows a plot for *n*-alkanes in the LF sand. The population here consists of four unaltered oils (the B4, B5ST, B6ST and the A21), one altered oil (the B14) and one heavy condensate (the B7). The B4 oil, though referred to as unaltered, actually has a slope break at about C₉. Though this might be an indication of mild alteration, we will

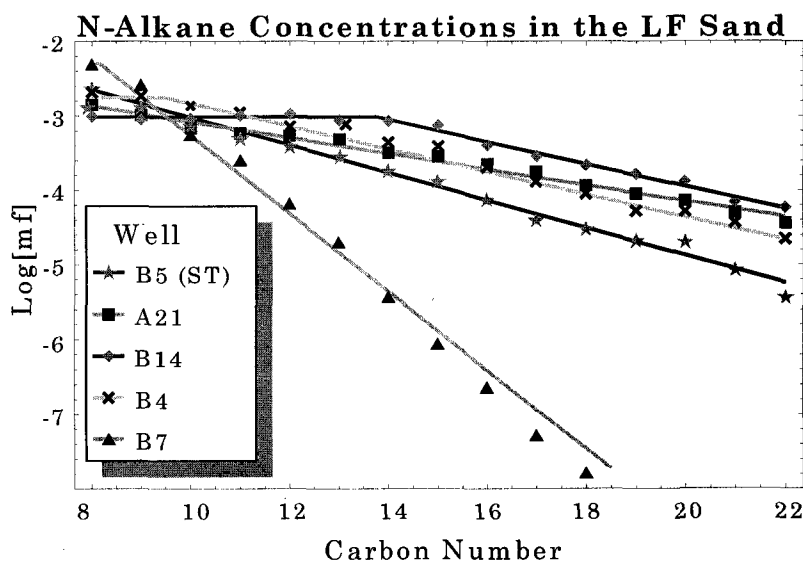


Fig. 5. Plot of carbon number vs. the log of mole fraction for the *n*-alkanes in oils from the LF Sand, South Eugene Island Block 330.

consider any slope break less than 9 to be unaltered by gas washing. We choose a slope break of 9 as the cutoff value to eliminate the fractionation introduced during production of the EI 330 fluids, as well as any fractionation attributable to gas-cap separation.

Interpretation of fractionation

The EI 330 oils all seem to be of the same maturity and source, based on biomarker analysis done elsewhere (Whelan *et al.*, 1993, 1994). The gases at EI Block 330 (C_1 and C_2) are somewhat more mature, as determined by their $\delta^{13}C$ isotopic values. This single maturity amongst the oils should result in equal slope factors for all the oils in EI 330. Hence, variations in the oil must arise from processes other than maturation. To quantify these variations, we analyze the distribution of *n*-alkanes

in each sample using equation 2. Note that we use the value m from equation 2 as the slope factor of the oil, since this represents the original slope factor of the oil regardless of postmaturation alteration.

Figure 6 shows the slope factor for all oils in the GBRN database. The distribution here is trimodal, with peaks at -0.7 , -0.35 and -0.1 . As defined by list of tables. As described by Table 1, the first two peaks correspond to condensates, and the -0.1 peak corresponds to a normal oil. Thus, the population of all samples from EI 330 can be divided into condensates and normal oils based on their slope factor.

The normal oils can be subdivided into two categories (unaltered and altered) based on their slope break, a from equation 2. Figure 7 shows the distribution of slope break factors for all the oils in the GBRN data set. The figure clearly shows a bimodal

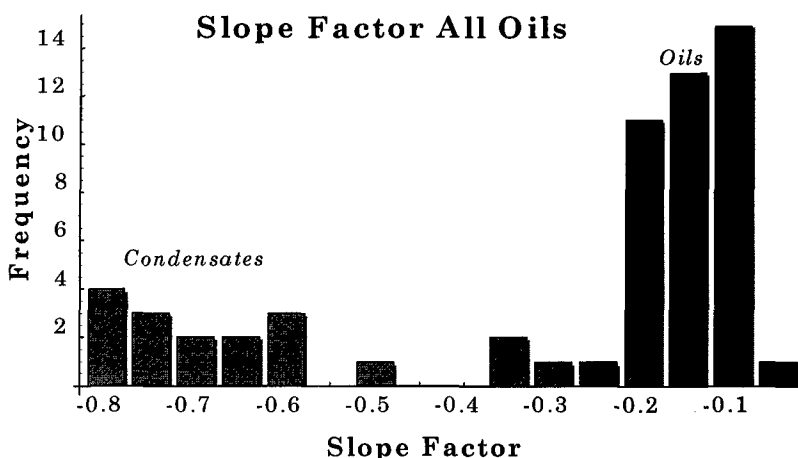


Fig. 6. The slope factor for all oils in the GBRN database, as defined by equation 2.

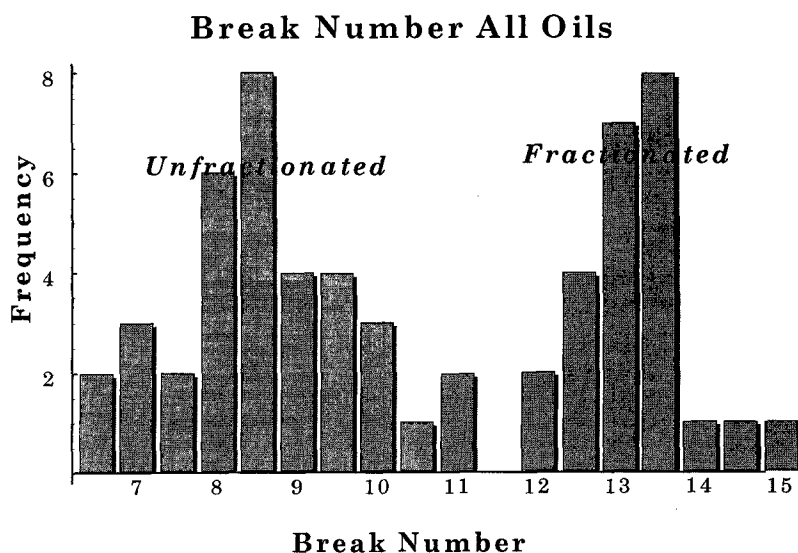


Fig. 7. Break number for all oils in the GBRN database, as defined by equation 2.

distribution. The first peak in the distribution at slope break values of less than 10 includes all the unaltered oils and all the condensates. The second peak, at 13, includes the altered oils.

Thus, the oils of EI 330 seem to fit into three categories: condensate, unaltered oil and altered oil. The condensates can be distinguished from the oils based on their slope factor. The oils can be divided into altered and unaltered based on their break number. Note that these categories should be very sensitive to mixing. The slope factor and slope break are determined from the relative abundance of *n*-alkanes in a fluid. If two fluids with different slope factors mix, the *n*-alkane concentrations would very quickly reach an average value, and

hence deviate from an exponential distribution. These indexes can be used to distinguish fluids in a reservoir that have not interacted or mixed, which can be an indication of reservoir continuity.

We propose that the oils at EI 330 with a break number greater than 10 are the products of phase fractionation (gas washing), caused by the equilibration of these oils with large volumes of gas, most probably, methane. A considerable body of evidence shows that the EI 330 area is at present discharging large volumes of gas generated below the present reservoirs to the surface (Whelan *et al.*, 1997). This gas fractionates the EI 330 oils as it migrates towards the surface. The deviations in the *n*-alkane concentrations from an exponential distri-

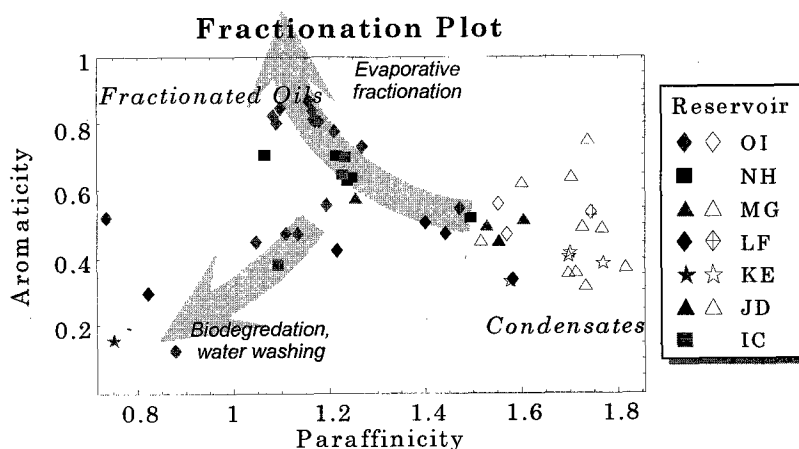


Fig. 8. Aromaticity (toluene/*n*-heptane) vs. paraffinicity (*n*-heptane/methyl-cyclohexane) for Eugene Island Oils. The light gray line shows the line of increasing alteration according to Thompson. Symbols indicate each fluid's reservoir. Condensates are shown with hollow symbols and normal oils are shown using solid symbols.

bution can be used as a quantitative indicator of fractionation.

Relating the categories to phase fractionation

In mixtures of hydrocarbons at typical reservoir conditions (e.g. 100 bar, 60°C), *n*-heptane preferentially fractionates into a methane-rich gas phase compared to either methylcyclohexane or toluene (Thompson, 1987). Hence, as an oil is increasingly fractionated by a methane gas stream, it should show a decline in paraffinicity (defined by Thompson as *n*-heptane/methylcyclohexane) and an increase in aromaticity (defined by Thompson as toluene/*n*-heptane) as the concentration of *n*-heptane declines relative to both methylcyclohexane and toluene. This result is numerically verified in Meulbroek (1997). Contrawise, the condensate (vapor phase fractionate) is enriched in *n*-heptane, and hence shows an increase in paraffinicity and a decrease in aromaticity when compared to the original fluid.

The oils in the GBRN data set from EI Block 330 show evidence for phase fractionation. Figure 8 shows a plot of aromaticity vs. paraffinicity for the GBRN data set. The gray lines superimposed on the plot show the alteration expected for residual oils and for biodegradation/water-washing as demonstrated by Thompson, and discussed for the EI 330 case by Whelan *et al.* (1994). In this figure, an increasingly fractionated or repeatedly gas-washed oil should move from the center of the diagram to the upper left corner along the line marked "evaporative fractionation" as the oil becomes depleted in *n*-heptane relative to methylcyclohexane or toluene. The corresponding vapor-phase condensate should plot towards the right side of the diagram, since it would be enriched in *n*-heptane relative to both the original oil and the liquid fractionate. Water washing tends to decrease the aro-

maticity of the oil, accompanied by a slight decrease in the paraffinicity of the oil.

The condensates from EI 330 plot towards the right of the diagram, and fractionated oils (as defined by their break number) plot towards the upper left. Unfractionated oils plot in the center of the diagram. This agreement between the EI 330 data and the Thompson trend is strong evidence that these oils are altered by gas washing.

We next show that the proposed indices of fractionation, slope break and slope factor, are related to the aromaticity and paraffinicity of the oils at EI 330. Figure 9 shows the aromaticity vs. calculated slope break for all hydrocarbon samples in the GBRN data set. Fractionated oils tend to have high aromaticity and high slope break. Condensates have (on average) a lower aromaticity than unfractionated oils, and have an insignificant slope break ($a < 9$). Figure 9 shows a somewhat ambiguous relationship between aromaticity and slope break for both the oils and the condensates at EI 330. Not shown on this figure are four wells with quite abnormal aromaticity values (ranging up to 23). The high concentration of toluene in these wells, and the low values of aromaticity for some of the other fractionated oils imply that aromaticity values of the fluids in the are have been altered by other processes in addition to gas washing.

To reinforce this point, Table 2 shows the correlation coefficients between aromaticity, paraffinicity, slope break (a) and slope factor (m) for the EI 330 fluids. The table reports separate correlation coefficients for oils and condensates. The table shows no significant relationship between aromaticity and slope break for either the oils or condensates in the GBRN data set. The only statistically significant correlation involving aromaticity is between aromaticity and slope factor for the oils. This relationship

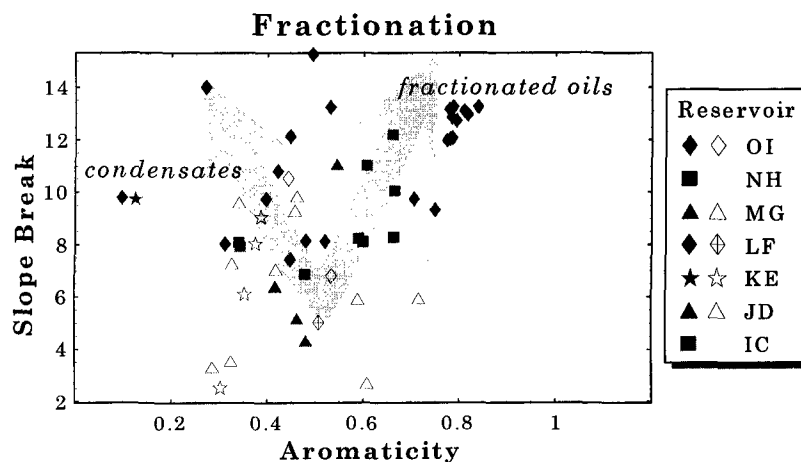


Fig. 9. Aromaticity (toluene/*n*-heptane) vs. slope break (a from equation 2) for the EI 330 data set. The gray lines show the path of increasing alteration from continual gas washing. Note that slope break values below 8 are considered unfractionated for the purposes of this work.

Table 2. Correlation coefficients for EI 330 data set. Significance is measured by a Student *t*-test at the 95% confidence interval

	Paraffinicity	Slope break	Slope factor
Correlation coefficients for oils (slope factor > -0.3)			
Aromaticity	0.10	-0.10	0.36
Significance	false	false	true
Paraffinicity	-	-0.68 true	0.02 false
Slope Break	-	-	0.22 false
Correlation coefficients for condensates (slope factor < -0.3)			
Aromaticity	-0.10	-0.01	-0.02
Significance	false	false	false
Paraffinicity	-	0.09 false	-0.55 true
Slope break	-	-	0.21 false

arises from a group of high aromaticity oils with a slope factor of 0.1 from the OI sand.

The relationship between paraffinicity and slope break is much clearer than the relationship between aromaticity and slope break. Figure 10 plots slope break vs. paraffinicity for all hydrocarbon samples in the GBRN data set. Fractionated oils have low paraffinicity and high slope break. The condensates have a higher paraffinicity than unfractionated oils. Figure 10 shows a clear trend of decreasing paraffinicity with increasing slope break in the oils of the GBRN data set. Table 2 reinforces this observation,

showing that paraffinicity is negatively correlated with slope break for the oils. No significant relationship between slope break and paraffinicity exists in the condensates.

The relationship between slope break and paraffinicity is consistent, both with the results of earlier modeling (Meulbroek, 1997) and with the experiments of Thompson (1988). The carbon number of the highest *n*-alkane affected by fractionation (the slope break) is positively correlated with both depth and the amount of gas that washes the oil. Similarly, the paraffinicity of an altered oil is negatively correlated with the amount of gas that washes the oil.

The relationship between slope break and slope factor is explored in Fig. 11. In this figure, condensates plot on the left, and all oils plot on the right. Note that all slope break values less than 9 are not considered significant. Though a slight positive relationship may be seen between slope break and slope factor in both the condensates and the oils, this relationship is not statistically significant, as reported in Table 2.

MODELING-DEVELOPMENT OF MODELS THAT CAN PREDICT FRACTIONATION

The FlowTube model used in this paper is described in detail in Meulbroek (1997), modified from Prausnitz *et al.* (1986) and Mathias (1983). The FlowTube numerically simulates the fractionation that occurs when a mobile fluid flows past and equilibrates chemically with a series of relatively immobile fluids. We use the term "flow through" to represent the interaction of gas and liquid similar in concept to experiments of Thompson (1987). In the model, gas "flows through" an immobile oil in the sense that it inter-

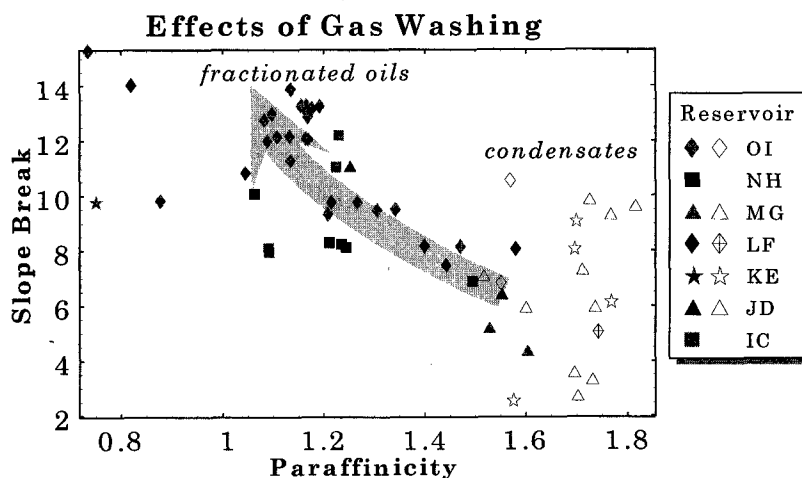


Fig. 10. Paraffinicity (*n*-heptane/methyl-cyclohexane) vs. slope break (*a* from equation 2) for the EI 330 data set. The gray lines show the path of increasing alteration from continual gas washing. The different symbols refer to each sample's reservoir.

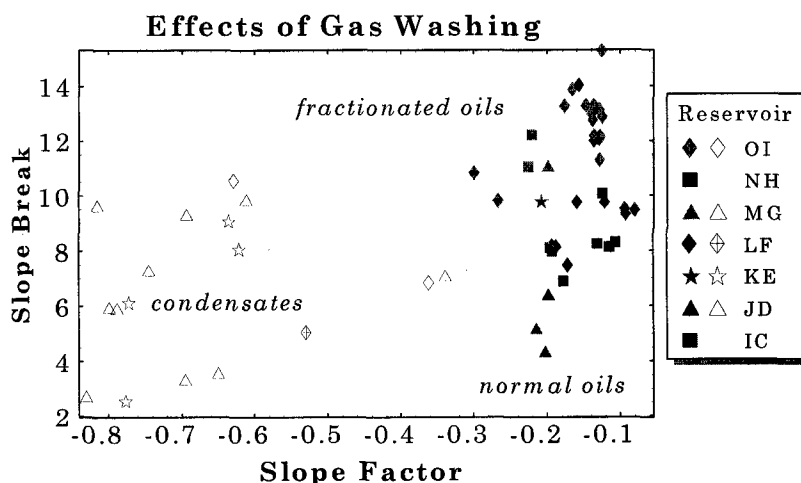


Fig. 11. Slope Factor (m from equation 2) vs. slope break (a from equation 2) for the EI 330 data set.

acts with the oil sufficiently to reach chemical equilibrium, then moves away from the chemically altered immobile oil (see Fig. 1). Gas may "flow through" oil by passing through it physically, or by remaining proximate to the oil until the gas and oil equilibrate.

The FlowTube can simulate gas flowing through oil at a single location, or past several locations (nodes) that contain oil. Each location is represented by a node and is assigned a pressure, temperature and starting oil composition. The nodes are modeled as fluid systems at thermodynamic equilibrium, using a fluid phase equilibria model (Michelsen, 1982a,b; Prausnitz *et al.*, 1986) that relies on the Mathias equation of state (Mathias, 1983), a Redlich-Kwong-Soave (RKS)-type cubic equation of state. RKS-type equations have seen widespread acceptance as a method for calculating fluid properties (Shibata and Sandler, 1989). In general, RKS-type equations of state produce adequate volume predictions for nonpolar mixtures provided that pressure and temperature conditions are far from the mixture's critical point.

The FlowTube model can reproduce experimental density data within a few percent, and predict experimental composition with an average deviation (d) of 15% when compared to flash PVT experiments performed on the reservoir fluids, which is defined by the following equation:

$$d = \sum_i |p_i - e_i|, \quad (3)$$

where p_i is the mole fraction of the i th component predicted by the model and e_i is the measured mole fraction of each component. Given that the compositional changes predicted by the model span orders of magnitude, an error of 15% is acceptable.

The nodes in the FlowTube can be thought to either represent an oil reservoir, or a migrating oil whose velocity is lower than that of the gas stream.

For the EI 330 simulations, a FlowTube model utilizing a single node adequately matches the known hydrocarbon compositions. This conclusion is reinforced by the observation that none of the condensates at Eugene Island Block 330 are derived from previously-fractionated oils.

The FlowTube model runs used in this paper simulate the conditions in which an aliquot of gas enters the FlowTube, equilibrates with the oil located in the system, then passes out of the system. This occurs numerically by adding an amount of gas to the deepest node, calculating the equilibrium phase separation of the mixture in the node, and allowing any excess volume of gas to pass upward to the next node. At each node, equilibrium occurs when the fugacity of each component of the mixture at that node is constant across all phases (Michelsen, 1982a). For the purposes of this paper, only single phase and two-phase (liquid, vapor) systems are considered.

EI BLOCK 330 FLOWTUBE SIMULATION

We verify that the EI 330 compositional variations could result from gas washing by analyzing the results of several FlowTube simulations. These simulations show that some the composition of the EI 330 oils located in the IC through OI reservoirs can be produced by phase fractionation. By comparing the simulations to the current compositions of oils from EI 330, both the depth at which oils fractionated and the amount of gas required to cause their fractionation can be determined.

The simulations test the fractionation scenario that each of the oils at EI 330 was washed by a gas stream composed of pure methane. Methane is chosen as the washing fluid for simplicity. Though a more common washing fluid in a sedimentary basin might be a wetter gas (gas with some amount of dissolved oil); early model runs in Meulbroek

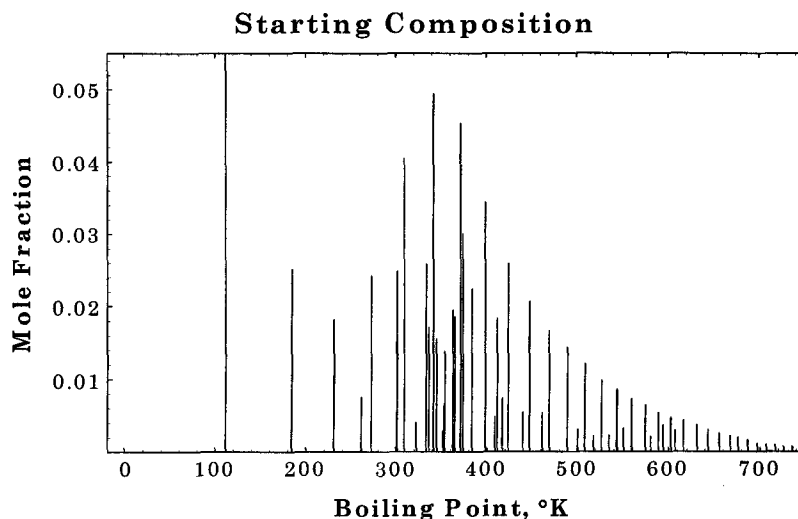


Fig. 12. Composition of the unfractionated fluid used in FlowTube models. The figure plots the mole fraction of each species vs. boiling point, which is proportional to retention time.

(1997) suggest that using a wet gas composition does not significantly change the predicted effects of gas washing on oil composition. We assume that neither the gases nor the oils mix after they are washed, but either fraction might migrate to a shallower depth after washing. Two reservoir sands at EI Block 330 above the IC sand (the GA and HB sands) do show the addition of light material, which would imply mixing. However, these reservoirs are severely biodegraded, and so it is difficult to separate the effects of enrichment from the background of biodegradation. We have elected to not

include these reservoirs in the sample set analyzed in this work.

The simulations are carried out for a range of depths between 2.0 and 3.6 km, which allows us to estimate the effect of depth (i.e. pressure and temperature) on fractionation. Pressure is assumed to follow a hydrostatic gradient from the surface to a depth of 2.0 km. Below 2.0 km, pressure follows a lithostatic pressure gradient. Temperature follows a 25°C/km gradient, with a surface temperature of 15°C. These are the conditions currently observed at Eugene Island Block 330. The FlowTube is filled

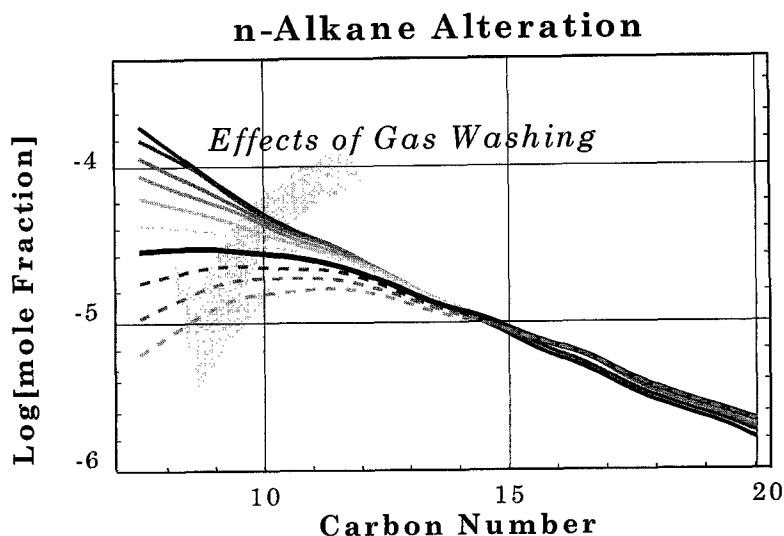


Fig. 13. Effects of gas washing on *n*-alkane concentrations in a FlowTube Simulation (at 2.0 km). Shown is the log[mole fraction] for *n*-alkanes in the liquid phase (oil) plotted vs. carbon number. Shading in the figure represents the amount of gas that has washed the oil, running from 0 to 16 (mol gas/mol oil). Each line shows the effects of washing by an additional 1.6 mol of gas/mol of oil. Compositions with alteration less than that seen in the fractionated oils of Eugene Island are unbroken. Compositions with alteration greater than that seen at Eugene Island are shown as dashed. The thick black line represents a composition with a degree of alteration comparable to some of the EI oils.

with 1 mol of the fluid from the A3 well of the NH sand, reconstructed as in Meulbroek (1997). This fluid is the least fractionated in our sample set, as established by both a low slope break and the Thompson (1988) criteria. The simulation proceeds by injecting sequential aliquots of 1/5 mol of methane through the oil. The composition of this starting oil is represented in Fig. 12, which shows an impulse plot of the mole fraction of species vs. their boiling point, which is proportional to retention time (Altgelt and Boduszynski, 1994).

Washing an oil with methane removes components from that oil in proportion to their solubility in methane (more precisely, in proportion to their fugacity in a methane-rich mixture). Hence, the most soluble components are removed quickly, while the removal of less soluble components requires more methane. The solubility of *n*-alkanes in methane is a function of carbon number.

The effects of gas washing on the distribution of *n*-alkanes are shown in Fig. 13. In this figure, the log of the *n*-alkane mole fraction is plotted vs. carbon number for a FlowTube simulation at 2.0 km. It can be seen that light *n*-alkanes are removed from the oil more quickly than heavy *n*-alkanes. With increasing gas throughput, the distribution of *n*-alkanes moves away from exponential (which would plot as a straight line on this diagram) to a kinked line similar in form to that described by equation 2. High carbon number *n*-alkanes are not affected by the gas washing, while low carbon number *n*-alkanes are completely removed.

The tendency for a portion of the *n*-alkanes to shift away from an exponential distribution with increasing amounts of gas washing results in compositions similar to those found at EI Block 330. It can be seen from Fig. 13 that *n*-alkane distributions

of an oil that is washed by a gas appear similar to those shown in Fig. 5.

The effect of gas washing on the aromaticity and the paraffinicity of the oil is shown in Fig. 14. In this figure, both paraffinicity and aromaticity of the fractionated oil are plotted vs. the amount of gas that washes the oil for a FlowTube simulation at 2.0 km. Both these ratios can be used as linear measures of the amount of gas that washes the oil. Aromaticity smoothly increases in the fractionated oil, while paraffinicity smoothly decreases. Hence, any of the EI 330 oils that have been fractionated at 2.0 km should have paraffinities and aromaticities that fall along these curves, and these two measures of fractionation should quantitatively indicate how much gas has washed those oils.

The solubility of oil components in a gas stream is strongly affected by the depth at which that gas stream washes the oil. In general, the solubility of all oil components in methane increases with increasing depth; i.e. higher pressure and temperature (Price *et al.*, 1983). However, the solubilities of individual components do not increase equally with depth. The change in solubility of components with lower solubility in gas is greater than the change in solubility of components with higher solubility. In mathematical terms, the change in concentration of an oil component in a gas stream with depth is a decreasing function of concentration. This implies that the curves shown in Figs 13 and 14 are not general, but instead are depth-specific. Each of the indices of fractionation described here (aromaticity, paraffinicity and slope break) should respond uniquely to changes in depth. Hence, it is possible to combine two of the indices to determine both the amount of gas that has washed the fractionated

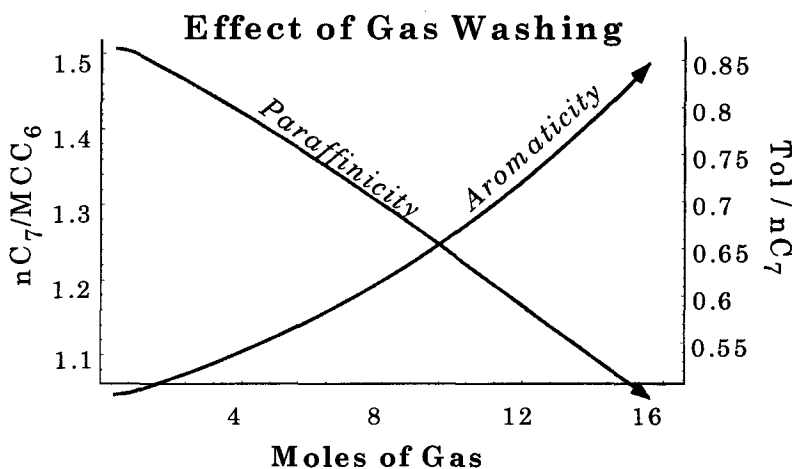


Fig. 14. Effects of gas washing on the aromaticity and paraffinicity of a fractionated oil in a FlowTube simulation (at 2.0 km). In the figure, the aromaticity and paraffinicity of a fractionated oil is plotted vs. the amount of gas that washes that oil (in mol of gas/mol of oil). "Tol" refers to the toluene mole fraction in the oil, "MCC6" refers to the methyl-cyclohexane mole fraction in the oil and "nC7" refers to the *n*-heptane mole fraction in the oil.

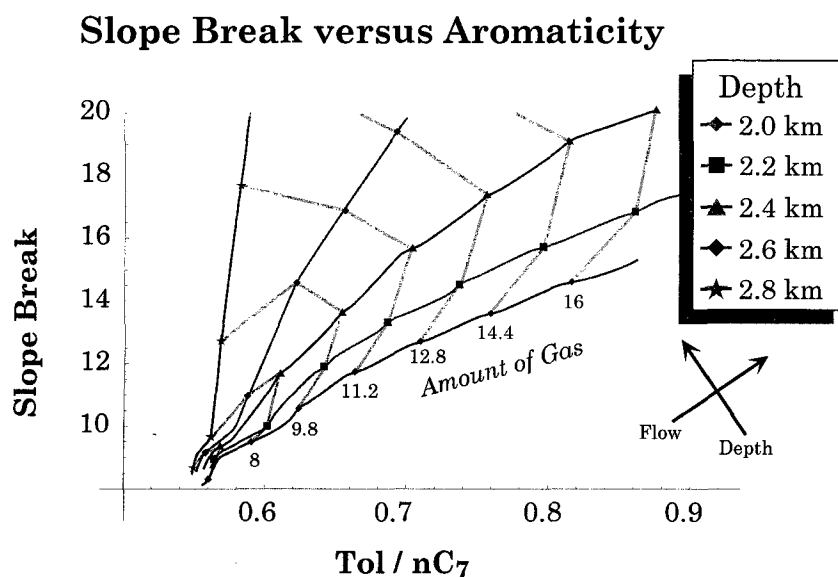


Fig. 15. Predicted slope break vs. aromaticity. This figure shows the results of several FlowTube simulations in which the slope break of a fractionated oil is plotted against that oil's aromaticity. The depth of the simulation is indicated by symbol, and the amount of gas is indicated by the gray tie lines and labeled. The alteration history of an oil can be estimated by comparing the measured slope break and aromaticity to this figure. "Tol" refers to the toluene mole fraction in the oil and "nC7" refers to the *n*-heptane mole fraction in the oil.

oils, and the depth at which those oils have been washed.

One such combination is shown in Fig. 15, which plots the aromaticity of the fractionated oils vs. their slope break for various depths of interaction. The depths range between 2.0 and 2.8 km. The

amount of gas (in mol/mol oil) required to cause the indicated fractionation is indicated by the gray tie lines. This figure can be compared directly to Fig. 9 to determine both the depth of fractionation and the amount of gas necessary to fractionate the oils of EI Block 330. For example, the alteration of

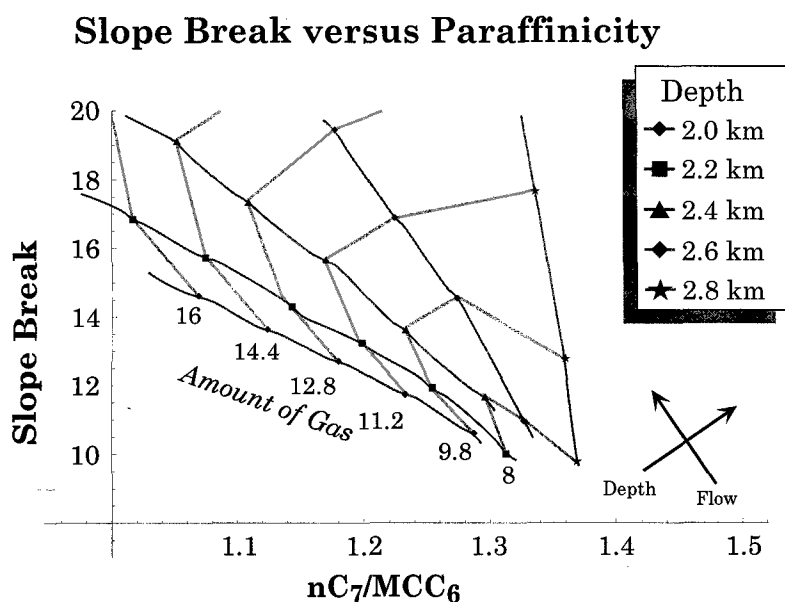


Fig. 16. Predicted slope break vs. paraffinicity. This figure shows the results of several FlowTube simulations in which the slope break of a fractionated oil is plotted against that oil's paraffinicity. The depth of the simulation is indicated by symbol, and the amount of gas is indicated by the gray tie lines, and labeled. The alteration history of an oil can be estimated by comparing the measured slope break and aromaticity to this figure. "MCC6" refers to the methyl-cyclohexane mole fraction in the oil, and "nC7" refers to the *n*-heptane mole fraction in the oil.

residual oils in Fig. 9 with aromaticity of 0.8 and slope break of 14 requires about 15 mol of gas at 2.0 km depth. Some of the outlying points from Fig. 9 do not plot on Fig. 15, reinforcing that these oils might have undergone a more complex flow history than modeled here. A different pressure gradient (such as a normal pressure regime) would lead to different depth estimates.

Comparison of Figs 9 and 15 reveals that the only reservoirs that have experienced significant gas washing at Eugene Island Block 330 are the IC, MG and the OI sands. The estimation of fractionation depths ranges from 1.7 km (for most of the OI oils) to 2.1 (for the MG oil). The estimation of amount of gas ranges from 10 mol gas/mol oil (for the MG oil) to approximately 16 mol gas/mol oil (for the OI oils).

The paraffinicity of all FlowTube simulations is plotted against slope break for different depths of alteration in Fig. 16. The amount of gas (in mol/mol oil) required to cause the indicated fractionation is indicated by gray tie lines. This figure can be compared directly to Fig. 10 to determine both the depth of fractionation and the amount of gas necessary to fractionate the oils of EI Block 330. For example, the alteration of residual oils in Fig. 10 with paraffinicity of 1.2 and slope break of 13 (similar to the OI oils) requires about 12 mol of gas at 2.2 km depth. As with Fig. 15, the depth estimate derived from the FlowTube modeling is dependent on the pressure gradient assumption used to design the simulations. Both Figs 15 and 16 produce similar results for estimates of depth and required gas for each sample in the EI database, resulting in a robust estimation of the alteration history of each oil.

DISCUSSION

According to the model results, about 40% the oils at Eugene Island have been washed by a gas stream. These fractionated oils come from the IC, MG and OI reservoirs. In general, the OI oils have been washed by more gas (approximately 12–14 mol gas/mol oil) at a shallower depth (1.7 km) than have the oils from shallower reservoirs.

This difference in fractionation depth could indicate that the OI reservoir filled earlier (shallower) than the sands above it. However, using an oil with a somewhat higher initial aromaticity and somewhat lower initial paraffinicity in the simulations would eliminate the differences in predicted depth of fractionation between the OI oils and the IC/MG oils.

The oils from the OI sands might well have derived from a fluid with lower initial paraffinicity and higher aromaticity than the oils from the IC/MG sands. The NH reservoir oils show the least amount of fractionation of any reservoir at Eugene

Island Block 330. These oils have paraffinicity values that range from 1.2 to 1.5 and aromaticity values that range from 0.5 to 0.7. According to Fig. 14, these ranges would require the fluids to be washed by approximately 8 mol of gas/mol of oil. Since the oils have low break numbers (and hence do not show evidence of much gas washing), the ranges in aromaticity and paraffinicity shown in the NH reservoir oils may be attributed to factors other than gas washing, and add uncertainty to their use as indicators. This variance might indicate that the original (prior to washing) fluids that fill the EI 330 reservoirs were slightly heterogeneous in composition, though of very similar maturity and source rock. In light of this, the difference in fractionation depth between the IC/MG oils and the OI oils is probably not significant. This heterogeneity might relate to subtle source differences, or indicate that the oils underwent slightly different migration histories.

In this work, we chose to ignore the effects of water on fractionation and only examine two phase flow. There are two effects caused by the presence of a third phase. The first is a thermodynamic effect in which the separation conditions and compositions are changed by the presence of water. There is some evidence in the literature that liquid–vapor separation in hydrocarbons is not significantly altered by the presence of water (Pendersen *et al.*, 1984). Note that a mobile water phase would cause alteration, as more water-soluble components (e.g. such monoaromatic compounds as benzene and toluene) are removed from the hydrocarbon liquid phase (McAuliffe, 1979). Though this point will be pursued in later work, we believe that a two phase model provides a foundation on which to build.

The second effect that water has on fractionation is a mass transport effect, in which the interactions of the vapor phase with the liquid hydrocarbon phase are modified by the presence of a separate aqueous phase. At some scale, migrating gas that is proximate to oil will equilibrate with that oil, and hence “flow through” some amount of that oil (in the sense that we use the term). The presence of the third phase can affect the amount of contact that the gas experiences with the oil, as well as the relative velocities of gas and oil, and hence the duration of contact of the two phases. These two effects dictate with how much oil a migrating gas can equilibrate. Hence, the presence of water only affects the scale of the washing phenomena.

As with any phase equilibria model that depends on an equation of state to calculate fugacity of individual species, the values predicted by the model show some scatter when compared to PVT cell simulations. For example, model simulations of PVT experiments in the area give average deviations in composition of 15%. Though this limitation should be recognized, the compositional changes

noted in this work are well within the predictive limit of our model. For example, Fig. 13 shows an order of magnitude change in C_8 concentration caused by gas washing.

ALTERNATIVE EXPLANATIONS

We propose that the compositions of oil from Eugene Island Block 330 show the effects of gas washing. Other possible causes of the unusual chemistry patterns described above include:

Separator-induced alteration

It should be noted that the a value, as calculated above, can be changed during the production of an oil. A reservoir fluid passing through a separator "fractionates" into a stock tank oil and a separator gas. Though this might shift a to higher values, this production-induced fractionation should not induce a values greater than 7. This can be verified qualitatively by examining a plot of n -alkane vapor pressure vs. carbon number. Figure 17 shows a plot of the vapor pressure of the n -alkanes n -butane (C_4) through n -eicosane (C_{20}) at 70 F, a typical separator temperature. This figure shows that the vapor pressure of n -alkanes above C_7 is negligible, and so significant production induced fractionation should not occur at carbon numbers greater than 7 for fresh oil samples. The vapor pressures plotted were calculated using the Antoine equation (Reid *et al.*, 1985), which predicts the vapor pressure of a pure species as:

$$\log(p) = A - \frac{B}{T + C}, \quad (4)$$

where p is the vapor pressure of the species, T is the absolute temperature (K) and A , B and C are experimentally determined species-specific parameters. Larter and Mills (1991) confirm that the effects of separator-induced fractionation is small above C_7 .

Gas cap separation/separation migration

Formation of a gas cap and subsequent preferential gas migration can cause some fractionation. However, separation migration can only cause the loss of intermediate n -alkanes (C_9 – C_{14}) for oil mixtures that are near their critical point. Otherwise, the fugacities of intermediate n -alkanes at typical reservoir conditions are simply too low to result in significant loss from a liquid phase during phase separation.

Furthermore, the vapor phase formed by near-critical phase separation resembles a light oil with a slope factor of -0.3 to -0.4 . Three condensates from EI Block 330 have this slope factor, but 14 condensates have slope factors of -0.6 to -0.8 , which are better explained by gas washing (see Fig. 6). Though separation migration might have caused the lower carbon number breaks (below C_9) seen in some of the EI oils, the process would not cause higher carbon number breaks, as seen in the more fractionated oils from EI 330.

Solid-liquid geochromatography

In this scenario, the fluid oil is progressively altered during migration through selective sorption of aromatic and more polar species to the mineral matrix. Though this process undoubtedly occurs widely in the subsurface, it probably is not the primary cause of the alteration in the EI Block 330 oils. As reported by Krooss *et al.* (1991), oils altered by the process of solid-liquid geochromatography show progressive loss of aromatic and polar species, but this loss is not species specific. In particular, ratios of compounds within a homologous series tend remain constant during fractionation. Krooss *et al.* attribute the decline in fractionation to the presence of water, which spoils the absorption ability of the rock matrix. Hence, the fractionation among the n -alkanes of the oils at EI Block 330 is probably better explained by gas washing.

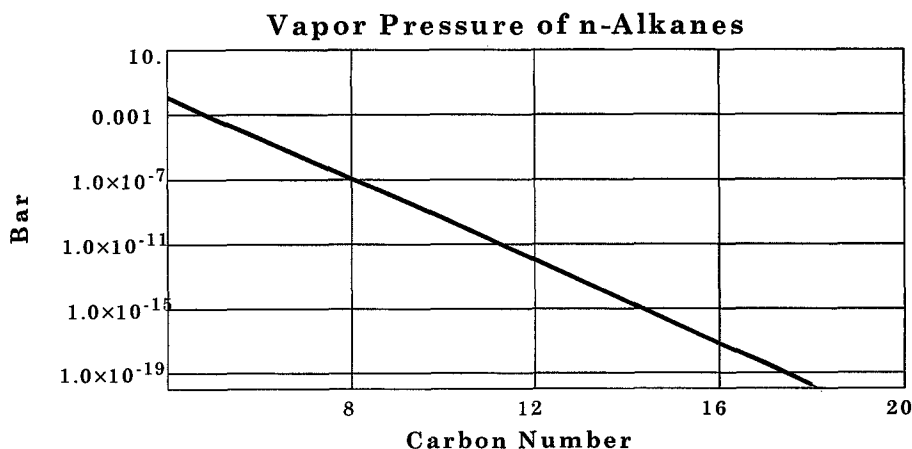


Fig. 17. Vapor pressure of n -alkanes, as calculated by the Antoine equation (Reid *et al.*, 1985).

Molecular diffusion

In this scenario, light, mobile species diffuse away from the main oil pool, leaving the heavy species behind. This process cannot explain two aspects of the composition of the EI 330 fluids. First, it cannot explain the relationship between aromaticity and paraffinicity of the fractionated oils. Diffusion coefficients are (to zeroth order) proportional to species the product of mole fraction (x_i) and the square root of molecular weight (mw_i):

$$D_i \propto x_i \sqrt{mw_i}. \quad (5)$$

Toluene, methylcyclohexane and *n*-heptane are have similar molecular weights, (84, 98 and 100, respectively), and their mole fractions are also quite similar (since the values of paraffinicity and aromaticity are close to 1). Fractionation based on diffusion in these circumstances is a very slow process, which probably has not had cause significant changes in composition since the reservoirs were filled (which must have occurred since the reservoirs formed, i.e. within the last 150,000 years).

Secondly, diffusion would not cause the *n*-alkane fractionation seen in the EI 330 oils. Since diffusion coefficients are proportional to the square root of molecular weight, no strong compositional differences would be expected between heavier *n*-alkanes (e.g. C₁₀+) where the difference between diffusion coefficients becomes small. For example, diffusion probably does not explain a fractionated oil with a break number of 12 that has lost a significant amount of C₁₀ and C₁₁, but very little C₁₂.

CONCLUSION

Alteration by a gas stream causes predictable changes in an oil's chemistry. In particular, those changes are reflected in the distribution of *n*-alkanes, as well as in the aromaticity and paraffinicity in the oil. An oil's *n*-alkane content is sensitive to both the amount of gas that washes an oil, and also to the depth at which that oil was washed. Both of these factors cause the *n*-alkane content of an oil to deviate from an exponential distribution.

This paper introduces a model that can simulate phase fractionation in hydrocarbon fluids and quantitatively predict the effect that one example of phase fractionation, gas washing, has on fluid chemistry. Oils from South Eugene Island Block 330 show varying degrees of gas washing. The simulations show that the alteration seen at EI 330 is consistent with a series of independent washing events at approximately 2.0–2.6 km depth, which are the depths of the current reservoirs. The oils do not seem to be the result of a flow through system where a single gas stream fractionates deeper and then shallower oils sequentially. Rather, the oils seem to be fractionated by methane gas streams

that independently affected different oils at different depths. Variations in compositions of approximately 40% of the oils in the EI Block 330 data set we examined can be attributed to by gas washing. The slope break in the *n*-alkanes and the changes in aromaticity and paraffinicity in these oils indicate that 12–15 mol of methane per mol of oil is required to fractionate these oils. The agreement between the independent fractionation indexes lends strong support to this conclusion.

The method presented here is a powerful tool for describing the history of hydrocarbon fluid flow in sedimentary basins. With this tool, we can identify scenarios that are consistent with the available data, and reject those that are not. Gas washing is clearly an important process that can control the composition of hydrocarbon fluids in the subsurface, and the FlowTube model is a tool that can aid in quantifying the effects of this process.

Acknowledgements—The authors would like to acknowledge the Gas Research Institute (GRI 5093-260-2689) for funding this work as well as additional support from the Global Basins Research Network. We would also like to acknowledge Dr Keith Thompson for his many helpful comments and contributions particularly to the early parts of the work reported here, and to the useful comments of the reviewers.

REFERENCES

- Ahmed, T. (1989) *Hydrocarbon Phase Behaviour*. Gulf, Houston.
- Alexander, L. and Flemings, P. B. (1995) Geologic evolution of a Pliocene–Pleistocene salt-withdrawal minibasin: Eugene Island block 330, offshore Louisiana. *American Association of Petroleum Geologists Bulletin* **79**, 1737–1756.
- Altgelt, K. H. and Boduszynski, M. M. (1994) *Composition and Analysis of Heavy Petroleum Fractions*. Marcel Dekker, New York.
- Anderson, R. N., Flemings, P. B., Losh, S., Whelan, J., Billeaud, L. B., Austin, J. and Woodhams, R. (1993) *The Pathfinder Drilling Program Into A Major Growth Fault in Eugene Island 330: Implications for Behavior of Hydrocarbon Migration Pathways*. Lemont-Dorhety Earth Observatory Press, New York.
- Coelho, D. F. (1997) Three-dimensional analysis of the temperature field in Block 300, South Eugene Island, Gulf of Mexico. Ph.D. thesis, Cornell University.
- Dzou, L. I. and Hughes, W. B. (1993) Geochemistry of oils and condensates, k field, offshore Taiwan: a case study in migration fractionation. *Organic Geochemistry* **20**, 437–462.
- Edmister, W. C. and Lee, B. I. (1988) *Applied Hydrocarbon Thermodynamics*. Gulf, Houston.
- Fabuss, B. M., Smith, J. O. and Satterfield, C. N. (1964) Thermal cracking of pure saturated hydrocarbons. In *Advances in Petroleum Chemistry and Refining* 9, ed. McKetta. Interscience Publications, New York, pp. 157–201.
- Holland, D. S., Leedy, J. B. and Lammelin, D. R. (1990) Eugene Island block 330 field, U.S.A., offshore Louisiana. In *Structural Traps III, Tectonic Fold and Fault Traps*, ed. E. A. Beaumont and N. H. Foster. American Association of Petroleum Geochemists, Tulsa, pp. 103–145.

- Kissin, Y. V. (1987) Catagenesis and composition of petroleum: origin of *n*-alkanes and isoalkanes in petroleum crudes. *Geochimica et Cosmochimica Acta* **51**, 2445–2457.
- Kvenvolden, K. E. and Claypool, G. E. (1980) Origin of gasoline-range hydrocarbons and their migration by solution in carbon dioxide in Norton Basin, AK. *American Association of Petroleum Geologists Bulletin* **64**, 1078–1106.
- Krooss, B. M., Brothers, L. and Engel, M. H. (1991) Geochromatography in petroleum migration: a review. In *Petroleum Migration, Geological Society Special Publication No. 59*, eds England W. A. and Fleet, A. J. The Geological Society, London, pp. 149–163.
- Larter, S. and Mills, N. (1991) Phase-controlled molecular fractionations in migrating petroleum charges. In *Petroleum Migration, Geological Society Special Publication No. 59*, ed. England and Fleet. The Geological Society, London, pp. 137–147.
- Mathias, P. M. (1983) A versatile phase equilibrium equation of state. *Industrial Engineering Chemical Process Design Development* **22**, 385–391.
- McAuliffe, C. D. (1979) Oil and gas migration: chemical and physical constraints. *American Association of Petroleum Geologists Bulletin* **63**, 761–778.
- Meulbroek, P. (1997) Hydrocarbon phase fractionation in sedimentary basins. Ph.D. thesis, Cornell University.
- Michelsen, M. L. (1982a) The isothermal flash problem. 1. Stability. *Fluid Phase Equilibria* **9**, 1–19.
- Michelsen, M. L. (1982b) The isothermal flash problem. 2. Phase-split calculation. *Fluid Phase Equilibria* **9**, 21–40.
- Pendersen, K. S., Fredenslund, Aa. and Thomassen, P. (1989) *Properties of Oils and Natural Gases*. Gulf, Houston.
- Pendersen, K. S., Thomassen, P. and Fredenslund, Aa. (1984) Thermodynamics of petroleum mixtures containing heavy hydrocarbons. 1. Phase envelope calculations by use of the Soave–Redlich–Kwong equation of state. *Industrial Engineering Chemical Process Design and Development* **23**, 163–170.
- Prausnitz, J. M., Lichtenthaler, R. N. and de Azevedo, E. G. (1986) *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, Englewood Cliffs.
- Price, L. C. W., Lloyd, M., Ging, T. and Blount, C. W. (1983) Solubility of crude oil in methane as a function of pressure and temperature. *Organic Geochemistry* **4**, 201–221.
- Quanxing, Z. and Quming, Z. (1991) Evidence of primary migration of condensate by molecular solution in aqueous phase in Yacheng field, offshore South China. *Journal of Southeast Asian Earth Sciences* **5**, 101–106.
- Reid, R. C., Prausnitz, J. M. and Poling, B. E. (1985) *The Properties of Gases and Liquids*. McGraw-Hill, New York.
- Roberts, H. H. and Carney, R. S. (1997) evidence of episodic fluid, gas and sediment venting on the northern Gulf of Mexico continental slope. *Economic Geology* **92**, 863–879.
- Schoell, M., Durand, B. and Oudin, J. L. (1985) Migration of oil and gas in the Mahakam Delta, Kalimantan: evidence and quantitative estimate from isotope and biomarker studies. In *14th Indonesian Petroleum Association Convention Proceedings 2*. Indonesian Petroleum Association, Jakarta, pp. 49–56.
- Shibata, S. K. and Sandler, S. I. (1989) Critical evaluation of equation of state mixing rules for the prediction of high-pressure phase equilibria. *Industrial and Engineering Chemical Research* **28**, 1893–1898.
- Schumacher, D. (1993) Eugene Island block 330 field, offshore Louisiana: geochemical evidence for active hydrocarbon recharging. In *American Association of Petroleum Geologists Annual Convention Abstracts*. American Association of Petroleum Geologists, New Orleans.
- Silverman, S. R. and Plumley, W. J. (1963a) *Separation–Migration, an Hypothesis for Explaining Compositional Differences Among Related Petroleum, Research Report No. 809*. California Research Corporation, La Habra.
- Silverman, S. R. (1963) Migration and segregation of oil and gas. *American Association of Petroleum Geologists Bulletin* **47**, 2075–2076.
- Soave, G. (1972) Equilibrium constants from a modified Relich–Kwong equation of state. *Chemical Engineering Science* **27**, 1197–1203.
- Thompson, K. F. M. (1987) Fractionated aromatic petroleum and the generation of gas-condensates. *Organic Geochemistry* **11**, 573–590.
- Thompson, K. F. M. (1988) Gas-condensate migration and oil fractionation in deltaic systems. *Marine and Petroleum Geology* **5**, 237–246.
- Whelan, J. K., Kennicutt, M. C., Brooks, J. M., Schumacher, D. and Eglinton, L. B. (1994) Organic geochemical indicators of dynamic fluid flow processes in petroleum basins. *Organic Geochemistry* **22**, 587–615.
- Whelan, J., Eglinton, L., Requejo, R. and Kennicutt, M. C. (1993) Pathfinder Well organic geochemistry indicators of oil source and maturity and fluid flow mechanisms. In *The Pathfinder Drilling Program Into A Major Growth Fault in Eugene Island 330: Implications for Behavior of Hydrocarbon Migration Pathways*. Lemont-Dorhety Earth Observatory Press, Palisades.
- Whelan, J. (1997) The dynamic migration hypothesis, how fast are oil and gas leaking to the ocean floor and replenishing themselves in some reservoirs? *Sea Technology* **38**, 10–18.
- Whelan, J. K., Kennicutt, M. C., Cathles, L. M., Eglinton, L., Meulbroek, P., Coelho, D., Losh, S., Wian, Y., Thompson, K. F. M. and Requejo, A. G. (1997) Scenario for dynamic injection of oil and gas into U.S. LA gulf coast Eugene Island 330 reservoirs. In *18th International Meeting on Organic Geochemistry, September 1997, Maastricht, Extended Abstracts*. Forschungszentrum Jülich GmbH, Jülich, pp. 227–228.