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OVERVIEW OF PETROLEUM MIGRATION PROCESSES AND ASSOCIATED COMPOSITIONAL MODIFICATIONS

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ABSTRACT

Geochemical modifications associated with the process of petroleum migration are a matter of long term debate. Although depletion trends in series of biomarker compounds associated with petroleum expulsion from source rocks have been recognized, the fractionation effects inferred as secondary migration processes are controversial and subject to restrictions. Laboratory simulation experiments examining petroleum migration through porous media have shown fractionation of selected biomarker components, but there is a lack of case histories within well-constrained geological settings. Fractionations observed in laboratory simulations are related to the extreme conditions that they are performed, where time, scale and the amount of oil involved are drastically reduced.

RESUMO

Modificações geoquímicas relacionadas ao processo de migração do petróleo constituem assunto há muito debatido. Mesmo tendo sido observadas tendências à depleção em várias séries de biomarcadores ligados à expulsão de petróleo das rochas geradoras, os efeitos do fracionamento atribuídos ao processo de migração secundária são controversos e sujeitos a restrições. Simulações em laboratório, para examinar a migração do petróleo em meios porosos, acusaram o fracionamento de determinados biomarcadores, no entanto faltam ''casos históricos'' com geologia bem controlada e conhecida. Os fracionamentos observados em simulações de laboratório estão relacionados às condições extremas nas quais foram realizados, onde tempo, escala e quantidade de óleo envolvido foram drasticamente reduzidos.

INTRODUCTION

Petroleum migration is a term used to describe the movement of hydrocarbons in the subsurface typically from source to reservoir. The expulsion of petroleum from fine-grained organic-rich source rocks to more permeable carrier beds is called primary migration and its movement through carrier beds or reservoir rocks is defined as secondary migration. Primary migration is mainly a pressure driven mechanism, but the processes that affect it are still subject of debate, whereas the phenomenon of secondary migration is principally driven by buoyancy forces.

In recent years, the process of petroleum migration has been studied by (i) laboratory simulation, (ii) computer modelling and (iii) evaluation of petroleum compositional changes due to migration. This broad range of approaches toward study of the same problem illustrates its complexity and challenging character.

Compositional modifications in bitumens related to primary migration have been observed by variations in their gross composition, accompanied by depletion of *n*-alkanes, isoprenoids and polycyclic aromatic hydrocarbons. However, there is a lack detailed observation on other biomarker compounds, especially steranes and terpanes.

Petroleum fractionation associated with secondary migration is more controversial and the active mechanisms are unclear. Long distance secondary migration effects have not been systematically investigated in any combination of studies of changes in gross composition, relative abundances of several compounds classes, and variations of the concentration of different compounds, including isomers, within a given biomarker class on a regional scale. A thorough understanding of secondary migration effects in petroleum composition is fundamental to geochemical correlation and to assessing the reliability of source and maturity parameters.

This paper is a version of the introductory chapter of a Ph.D. thesis presented at Stanford University (Trindade, 1992).

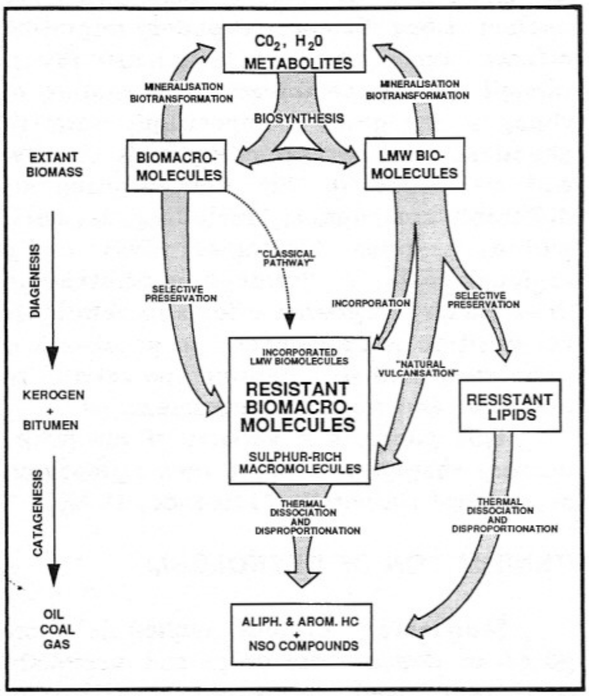
GENERATION OF PETROLEUM

Sedimentary organic matter is composed of debris from organisms variously decomposed and structurally modified by microbial activity. The conventional view of kerogen formation proposes that organic matter is transformed by polycondensation and insolubilization reactions whereby smaller molecules are converted into the larger molecules within kerogen (Tissot &

Welte, 1984). More recently, an alternative basis for the formation of kerogen has been proposed (Tegelaar et al., 1989). According to this model (Fig. 1), a significant proportion of kerogen arises from biomacromolecular structures which are buried in their protective envelopes, which are highly resistant to (bio)chemical degration and selectively preserved during diagenesis (Largeau et al., 1986; Goth et al., 1988).

In the catagenetic stage of organic matter evolution (Fig. 2), increasing temperature and pressure due to deeper burial transform the hydrogen-rich portions of kerogen into petroleum (liquid or gas). Kerogens are classified on the basis of the atomic ratios H/C and O/C (equivalent to Rock-Eval pyrolysis Hydrogen and Oxygen Indices, respectively) into the categories of Types I and II (Hydrogen rich) and III (Hydrogen poor). In simple terms, the more the kerogen is Type I in character, the larger the proportion of oil to gas (Tissot & Welte, 1984).

The onset and peak of the oil generation window of a given kerogen are dependent on temperature, heating time and pressure relationships, which are controlled by the geothermal gradient and burial history. The major controlling factor is temperature, which has an exponential influence on petroleum generation. In more advanced temperature and pressure conditions, only gas is preserved (metagenesis). A summary of organic matter evolution, from the freshly deposited sediment to kerogen, to oil generation and to the metamorphic zone is presented in Figure 2.



(modified fromTegelaar et al., 1989)

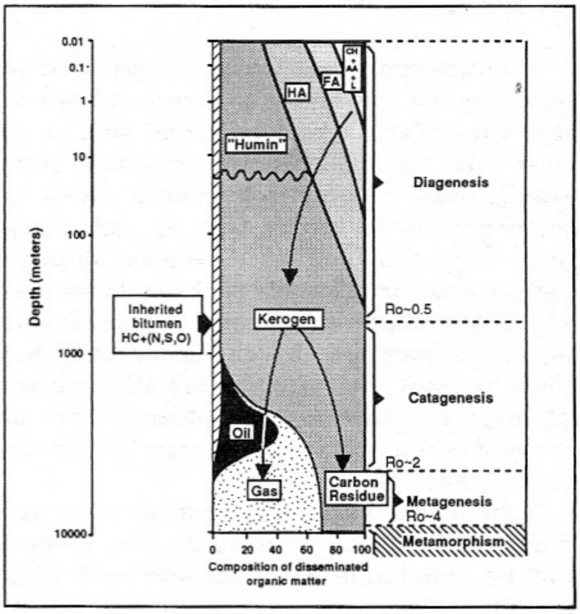
Figure 1 – Proposed mechanism for kerogen formation describing the interrelationships between extant biomass, kerogen and fossil fuel. LMW denotes low-molecular weight (modified from Tegelaar et al., 1989).

Oil generation is followed by the processes of primary and secondary migration. The first corresponds to expulsion from source rocks, and the latter is related to petroleum movement through carrier beds and reservoir rocks.

PRIMARY MIGRATION

Processes

The release of petroleum compounds



(modified from Tissot and Welte, 1984)

Figure 2 – General scheme of evolution of the organic matter from the freshly deposited sediment of the metamorphic zone. CH: carbohydrates, AA: aminoacids, FA: fulvic acids, AH: humic acids, L: lipids, HC: hydrocarbons, N, S, O: NSO compounds (non-hydrocarbons). R_o = vitrinite reflectance (%). Humin is transformed to kerogen during diagenesis of organic matter. Primary migration occur during catagenesis, but the maximum expulsion occur during the peak of oil generation (modified from Tissot & Welte, 1984).

from soil organic particles (kerogen) and its short scale expulsion from the capillaries and narrow pores of fine-grained source beds to carrier beds is called primary migration. Despite recent advances in the understanding of the factors that affect and influence primary migration (Lewan, 1987; Leythaeuser et al., 1983, 1987, 1988a, 1988b; Mackenzie et al., 1987; Talukdar, 1987) it remain a subject of debate. Many theories and hypotheses regarding the mechanism and efficiency of primary migration have been discussed (Durand, 1988), but there is a general agreement regarding the main mechanism of primary migration. In contrast, there is no consensus of opinion on the secondary role of other processes, where the following mechanisms have been proposed:

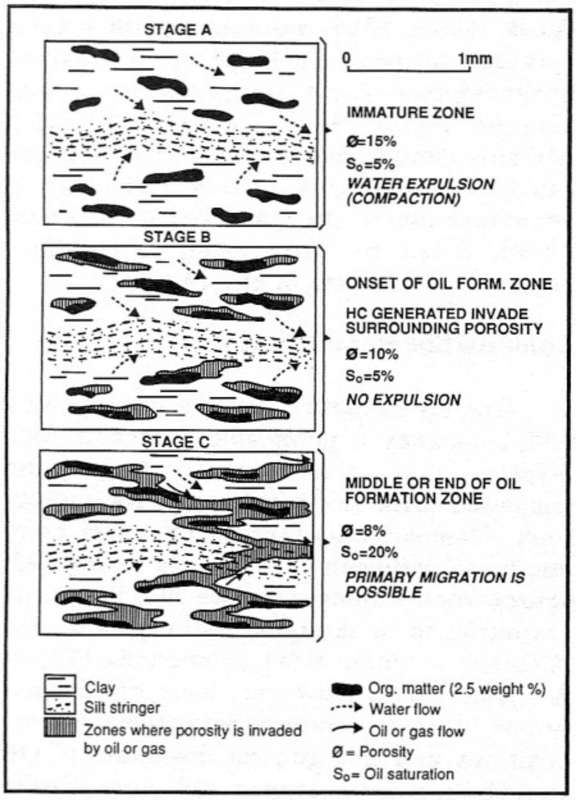
(i) Water solution: oil expulsion from source rocks was thought to take place in water solution linked to water expulsion during compaction (Dobryansky et al., 1961; Hodgson, 1980). However, improved knowledge of petroleum formation indicates that generation occurs at higher temperatures, after most water has been expelled from source-rocks (Durand, 1988). In addition, the heavier fractions of crude oils are insoluble in water (McAuliffe, 1980).

(ii) Water from smectite-illite transformation: this clay-mineral transformation proposed as a possible expulsion mechanism (Perry & Hower, 1972) does not create sufficient quantities of water and is controlled by kinetics different from those associated with petroleum generation (Durand, 1988). Furthermore, smectites are not always present in petroleum source rocks.

(iii) Molecular diffusion: petroleum generation forms high concentrations of hydrocarbons and low molecular weight compounds can migrate by molecular diffusion to some extent (Leythaeuser et al., 1980, 1982; Krooss & Schaeffer, 1987). However, molecular diffusion appears to be inefficient over the range of water saturation because it will cease, once hydrocarbon saturation in water is reached (Durand, 1988). Thus, transportation of hydrocarbons by molecular diffusion is limited by low solubility, particularly of the heavier fractions. Petroleum has also been proposed to migrate in solution in methane (Price et al., 1983).

(iv) Pressure driven: the most important mechanism for primary migration during the main phases of petroleum formation seems to be pressure-driven, discrete hydrocarbon phase movement (Tissot & Welte, 1984). Subsurface conditions that favor and permit primary migration of petroleum as a continuous oil phase are high bitumen concentrations and low water saturation in the pore space of the source rock. Under such conditions, the driving force for fluid movement is pressure gradient (Ungerer et al., 1983).

The sequence of source rock evolution with progressive burial can lead to the formation of an oil saturated network (Fig. 3). At the immature stage (diagenesis - Stage A, in Figure 3), sedimentary organic matter consists essentially of kerogen dispersed in rock and free lipids. No petroleum has been formed, but water is being progressively expelled by compaction. The nature of the kerogen influences the temperature at which generation and expulsion starts. For example, Type II-S kerogen possesses a higher proportion



(modified from Durand, 1988)

Figure 3 – Formation and expulsion of oil in a source rock (modified from Durand, 1988). The development of interconnected oil saturated pore spaces is critical.

of bonds with lower activation energies, and can therefore generate hydrocarbons at temperatures lower than those seen for other kerogen types (Tissot et al., 1987). The onset of oil generation (Stage B, in Figure 3) is associated with the physical collapse of the kerogen network and a decrease in its volume (Durand, 1988). As a result highly overpressured oil-wet networks begin to form and grow within the more porous layers of the source rock. At a more advanced degree of catagenesis (Stage C, in Figure 3), the oil forms a continuous phase in the kerogen-rich parts of the source rock. Thus, oil expulsion can proceed through this oil saturated network, aided by an increasing sedimentary load and increased thermal expulsion of water and organic phases. Eventually the rock fractures when it reaches internal pressures which exceed lithostatic pressure (Durand, 1988).

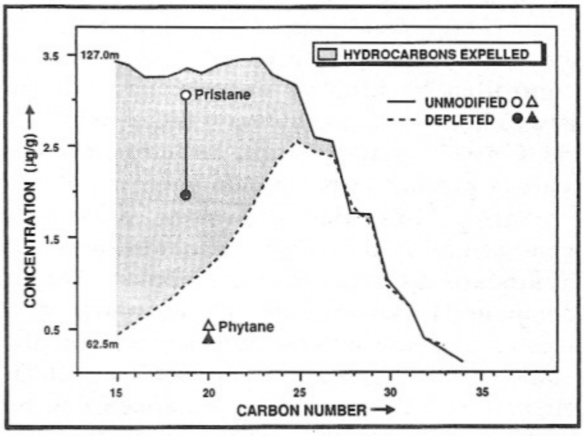
The sequence of pressure build-up, microfracturing, subsequent pressure release and finally oil expulsion appears to be a discontinuous process which may be repeated many times (Durand, 1988; Tissot & Welte, 1984) associated with several episodes of pressure build up and subsequent fracture. For a continuous network of kerogen present in a source rock which contains more permeable levels, oil and gas can be expelled without rock fracturing in an uninterrupted process (Tissot & Welte, 1984), aided by differences in capillary pressure (Mackenzie et al., 1987).

Compositional modifications

The oil expelled from a source rock which reaches a permeable reservoir rock displays changes in chemical composition compared with the bitumen of its source-rock. Comparison of gross chemical compositions between crude oils and their source rock bitumens shows that most oils are enriched in saturated hydrocarbons and depleted in polar NSO compounds (Tissot & Pelet, 1971). However, there are maturity and other constraints that influence compositions and this general observation. Oil contribution from deeper and more mature source rocks should be examined in order to avoid bias in the results.

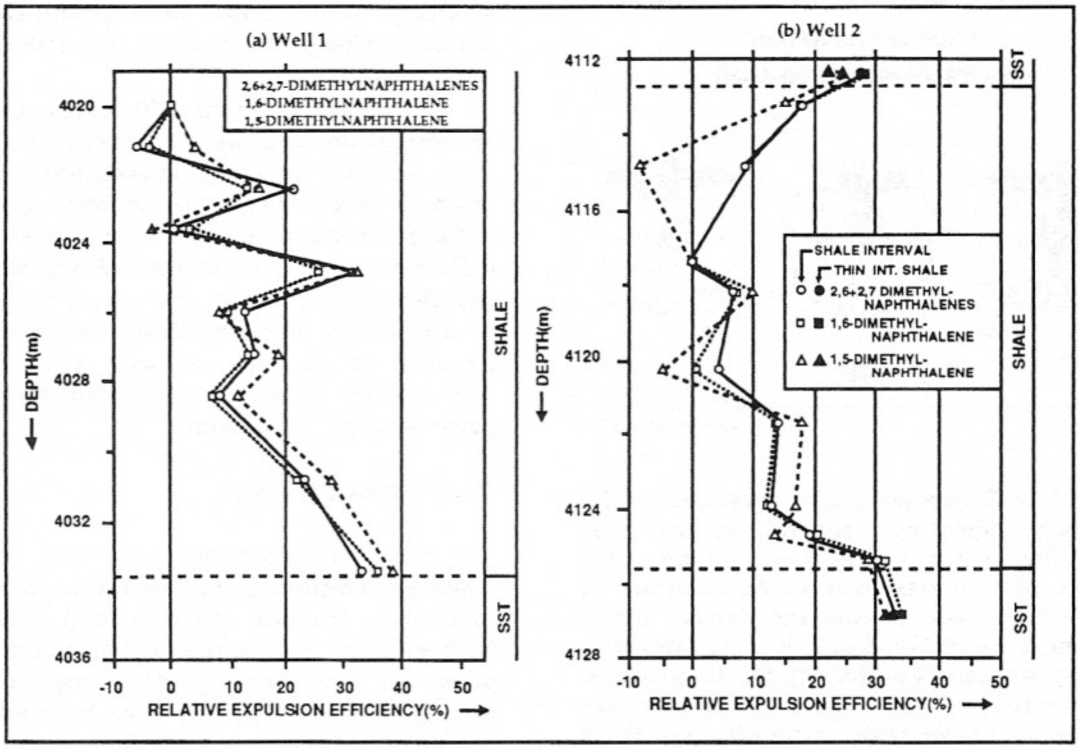
Compositional modifications in both bulk and molecular properties have been observed in close proximity to the source rock/reservoir boundary. Tissot & Pelet (1971) noted a gradual depletion in extractable bitumen of source rocks approaching a reservoir. In the Kimmeridge Clay, Leythaeuser et al. (1987, 1988a) observed: (i) depletion of the production index calculated from Rock-Eval pyrolysis, (ii) the preferential expulsion of C_{15+} saturated hydrocarbons in relation to NSO compounds, and (iii) pronounced, and often quite regular, trends of decreasing yields of C_{15+} soluble organic matter.

At a molecular level, Leythaeuser et al. (1983, 1988a, 1988b) revealed depletion of the *n*- and isoprenoid alkanes and polycyclic aromatic hydrocarbons due to petroleum expulsion over short distances in interbedded shale/sandstone sequences. They also reported, lower expulsion efficiencies of pristane and phytane compared to *n*-alkanes of comparable carbon number (Fig. 4). The greater depletion of pristane in relation to phytane can apparently be related to its higher proportion, perhaps related to different precursors. Clear depletion trends for alkynaphthalenes attributed to hydrocarbon expulsion were also observed (Fig. 5). In this instance, the compounds show comparable trends despite their significant stereochemical differences. Changes in extract yield and composition due to primary migration have also



(modified from Leythaeuser et al., 1983)

Figure 4 – Quantitative comparison of absolute amounts of individual normal and isoprenoid alkanes (µg/g sediment, based on quantitative evaluation of gas chromatograms). Concentration difference between samples (shaded area) represents hydrocarbon mixture expelled during primary migration. PRI = pristane; PHY = phytane (modified from Leythaeuser et al., 1983).



(modified from Leythaeuser et al., 1988b)

Figure 5 – Relative expulsion efficiencies (%) for selected dimethylnaphthalene isomers versus depth for samples from two continuous shale intervals investigated in detail from the Kimmeridge Clay Fm., Brae field area, North Sea: a - well 1; b - well 2. Despite the stereochemical variability, all the trends are comparable (modified from Leythaeuser et al., 1988b).

been reported for the extractable organic matter after kerogen isolation (bitumen-2 fraction) of shales (Wilhelms et al., 1990).

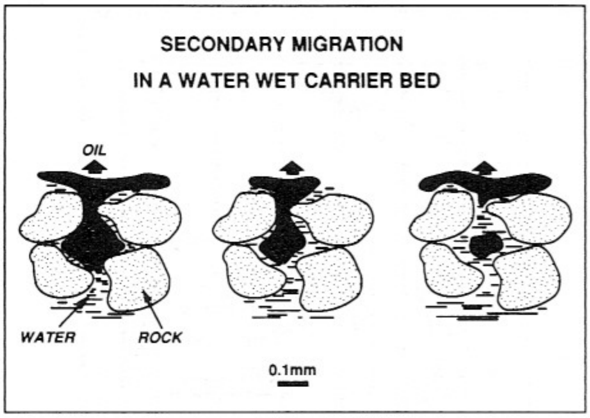
SECONDARY MIGRATION

Processes

The movement of hydrocarbons as a single continuous phase through water saturated reservoir rocks or carrier beds is called secondary migration (Schowalter, 1976). In contrast to primary migration, the factors governing secondary migration are comparatively well understood (England et al., 1987). Petroleum migration with a reservoir or accumulation is determined by the interplay between two factors. The main driving force is buoyancy, resulting from density differences between the migrating hydrocarbons and their associated water phases, modified by hydrodynamics, that can interfere with the direction of migration. The resistance to hydrocarbon migration is capillary pressure, a function of the interfacial tension between the two phases (Schowalter, 1976; Berg, 1975; Dembicki & Anderson, 1989).

Oil stringers have to deform to pass through pore throats and to move in the porous network (Fig. 6) and in this process they must overcome the interfacial tension between petroleum and water phases. Hence, the movement of petroleum stringers can occur only if the driving forces, mainly buoyancy, exceed the capillary forces, which are proportional to interfacial tension and inversely proportional to the radii of pore throats (Durand, 1988). Rocks are three dimensional porous networks, and therefore the tortuosity of the most permeable pathway will also control the direction of migration. According to Berg (1975), the vertical height of a moving oil stringer needs to be of the order of a few meters in order to overcome capillary forces.

The greater the density difference between petroleum and water, the greater the buoyant force. Thus, more mature and



(modified from Durand, 1988)

Figure 6 – Conceptual model of carrier bed for secondary migration: mineral surfaces are coated by water (water-wet surfaces). Oil droplets or stringers have to be deformed to pass through pore throats and driving forces (buoyancy, hydrodynamics) have to overcome capillary pressure. Considering the 3D character of the porous network, the migration pathway presents a considerable tortuosity (modified from Durand, 1988).

lighter oils migrating through carrier beds saturated with more saline and denser water will be more influenced by buoyancy. Oil and gas will form a pool whenever their upward movement is retarded by less permeable strata.

Compositional modifications

The amount of fractionation of petroleum components, during secondary migration is unclear, as are the mechanisms that effect such phenomena. Modifications of petroleum composition along migration pathways have been attributed to three different effects, (i) geochromatographic effects, where components are partitioned between the mobile oil phase and mineral surfaces could act as stationary phases (Seifert & Moldowan, 1981; Carlson & Chamberlain, 1986; Krooss et al., 1991), (ii) losses into solution (McAuliffe, 1980; Lafargue & Barker, 1988) and (iii) phase changes (Silverman et al., 1965; England & Mackenzie, 1989; Larter & Mills, 1991). Entrainment of anachronous compounds during migration has also been reported (Philp & Gilbert, 1982; Bac et al., 1990). Subsequent effects include in-reservoirs compositional changes related to gravitational and thermal segregation, deasphalting, and both biodegradation and water washing (England et al., 1987; Connan, 1984).

The fractionation effects attributable to migration can be obscured by factors such as differences in source rock, generation from a common source rock, but from different areas of the basin or generation at different depths, or at different times during the basin history. However, the extent of oil mixing or oil maturity variations can be used in combination with basin evolution history to assess petroleum migration pathways and directions.

Geochromatography

Geochromatography is the process whereby migrating petroleum in the subsurface is fractionated due to partitioning with mineral phases that act as a stationary phase in a chromatographic column. The term geochromatography was first used by Seifert & Moldowan (1981), and more recently, it was proposed by Krooss et al. (1991) to include both solid stationary phases (minerals and kerogen) and liquid stationary phases (sorbed films of pore water and bitumen).

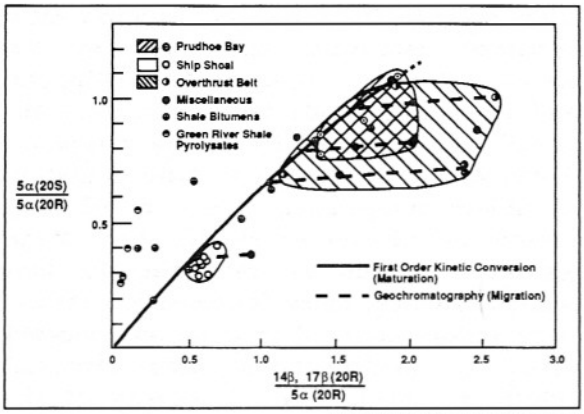
a) Field studies

Geochemical changes attributed to geochromatography were first observed in oil samples collected in an updip direction from the Quirequire oilfield in Venezuela (Silverman, 1965). Along the migration pathway, there was an increase in nonpolar hydrocarbons and a decrease in the content of asphaltenes, resins, porphyrins and other non-hydrocarbons together with a slight decrease in the $^{13}C/^{12}C$ isotope ratio. These modifications were attributed to preferential migration of non-polar components, which are enriched in ^{12}C. However, recent studies of compound-specific isotope analysis show that, depending on their origin, policyclic compounds can be isotopically lighter (e.g. hopanes, derived from methanothrophs lighter than *n*-alkanes). Also, the geologic setting of the studies was not well constrained, and neither the distribution of source rocks nor the direction of migration were clear. In addition, multiple source rocks in different areas of the basin may also occur, complicating the relationships between oils and their sources.

A biomarker migration index based on

variations in sterane stereochemistry was proposed by Seifert & Moldowan (1981) based on data from various basins. Increasing migration distances were reflected by enhanced C_{29} 14β(H), 17β(H) $20R/C_{29}$ 14α(H), 17α(H) 20R ratios, whereas the ratios C_{29} 14α(H), 17α(H) $20S/C_{29}$ 14α(H), 17α(H) 20R remained almost unaltered (Fig. 7). The latter ratio was supposed to be solely modified by thermal maturation. However, samples from several basins, with different structural styles and, consequently, different thermal histories were plotted on the same diagram. Furthermore, there is a lack of control on migration pathways and distances.

The relationship between sterane isomer distributions and migration reported by Seifert & Moldowan (1981) was also observed for North Sea oils (Miles, 1990) and in the Karamay oil field, China (Huang et al., 1990). In both cases, more migrated oils display higher relative concentrations of 14β(H), 17β(H) steranes. However, the proportion of 14β(H), 17β(H) steranes, thought to be related to migration, also increases with maturity (Mackenzie et al., 1980), and furthermore, is source dependent (Mackenzie et al., 1982), with higher concentrations of 14β(H), 17β(H) steranes occurring in hypersaline environments which can be attributed to their origin from Δ^9-sterols via spirosterenes (Peakman et al., 1989). Hence, Seifert & Moldowan's suggestion raises concerns.



(modified from Seifert and Moldowan, 1981)

Figure 7 – Comparative maturation/migration study of crude oils and bitumens using C_{29} steranes. 5α(20S) = 5α(H), 14α(H), 17α(H) 20S C_{29} sterane. 5α(20R) = 5α(H), 14α(H), 17α(H) 20R C_{29} sterane. 14β, 17β(20R) = 5α(H), 14β(H), 17β(H) 20R C_{29} sterane. (modified from Seifert & Moldowan, 1981).

Preferential migration of tricyclic vs. pentacyclic terpanes was proposed to result from the smaller molecular size of the former and consequent lower adsorption during petroleum migration (Seifert & Moldowan, 1978a). However, source, maturity and biodegradation all constrain the relative proportion of tricyclic and pentacyclic terpanes.

Migration effects were also suggested to explain a systematic increase in monoaromatic steroid versus triaromatic steroid concentrations in vertically migrated oils recovered from the Mahakam Delta, Indonesia, where there are several stacked reservoirs. The relative concentration of mono to triaromatic steroids, however, is strongly maturity dependent (Mackenzie et al., 1981). Vertical segregation of oil composition due to secondary migration in the same area is suggested by the higher proportions of the chromatographically more mobile low molecular weight *n*-alkanes and a relative increase in isoprenoids and in the pristane to phytane ratio. The mechanism proposed for the observed differentiation is analogous to elution chromatography, assisted by vertically migrating gas which would entrain liquid hydrocarbons, dissolving the lighter compounds (Vandenbroucke et al., 1983; Schoell et al., 1985). Evidence for the accumulation of overmature gases migrated from deeper source rocks in relative shallow and immature reservoirs is supported by carbon isotopic ratios of methane between -38‰ and -40‰ (Schoell et al., 1985). The isotopic composition of methane generated under lower maturity conditions, at the same depth as the reservoirs, is expected to be lighter (around -47‰).

Similar compositional variations are observed in the Samaan oil field, offshore Trinidad, another multi-play oil field where migration is dominantly vertical (Ross & Ames, 1988; Heppard et al., 1990). The shallowest reservoirs are filled with oils richer in low molecular weight *n*-alkanes, containing greater proportions of isoprenoids, and a higher pristane to phytane ratio. However, progressively more mature oils generated from a subsiding source could also explain the oil distribution observed in the basin. The higher proportion of low molecular weight *n*-alkanes in more migrated oils is also reported within the Brae Field, North Sea

(Reitsema, 1983), but the distribution of source rocks and migration pathways are not clearly defined.

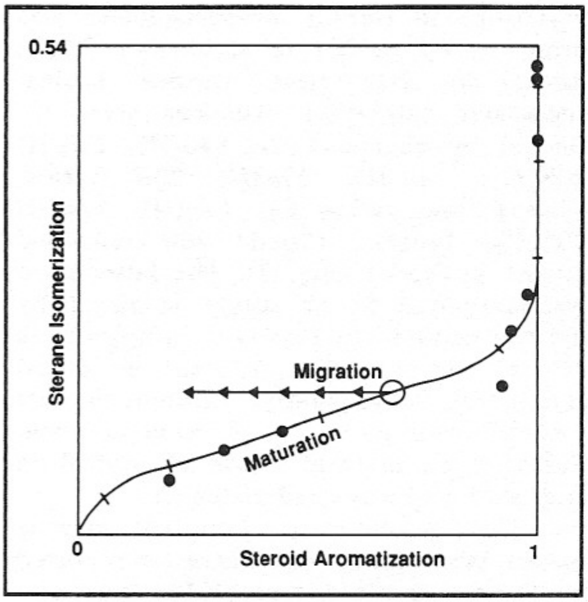
Migration of a more mature oil through an oil wet sandstone saturated with a biodegraded oil generated by the same source rock in the Campos Basin, Brazil, was suggested to promote enrichment in $<C_{15}$ *n*-alkanes with increasing distance of lateral migration within the reservoir (Trindade et al., 1987; Soldan et al., 1991). Here, the biodegraded oil, rich in polar components, could have enhanced geochromatographic effects, selectively retaining more polar compounds during the migration of the more mature oil.

Fractionation of nitrogen compounds (azarenes) was reported in oil samples from the Sarukawa oil field, Japan (Yamamoto, 1991). Preferential migration of "nitrogen-masked" isomers caused by their weak adsorption on clay minerals was suggested. However, it remains unclear if these compounds are preferentially lost in water solution or if there is any source or maturity dependence on their relative proportions.

b) Laboratory simulations

Series of laboratory simulations have been performed by several authors to evaluate geochromatographic effects of petroleum migration.

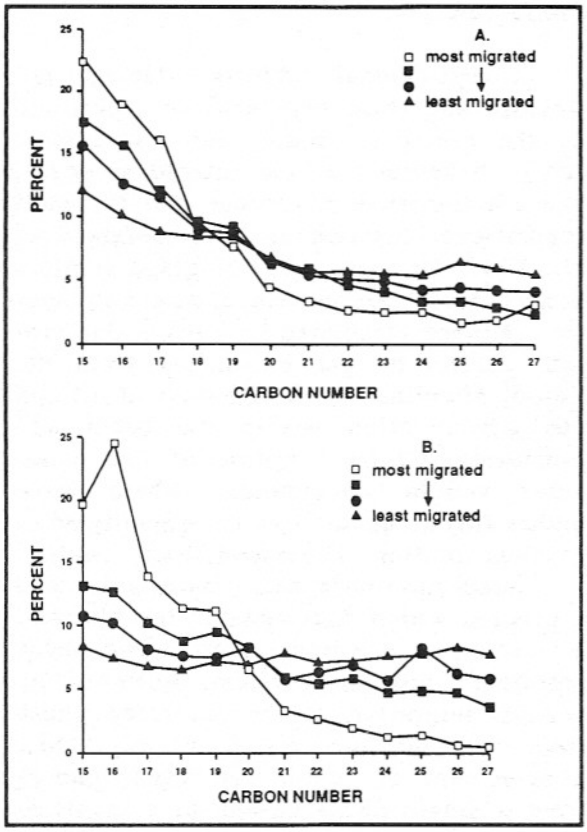
An attempt was made to evaluate the role of clay minerals as possible geochromatographic agents based on the differences between their adsorption free energies (AFE) and those of steroid biomarkers (Carlson & Chamberlain, 1986). Using clay-containing chromatographic columns, they proposed a migration trend which modifies isomerization-aromatization plots (Fig. 8) of 20S to 20R C_{29} 14α(H), 17α(H) sterane ratios (sterane isomerization) against ratios of triaromatic to monoaromatic steroids (steroid aromatization) previously defined as molecular maturity parameter (Mackenzie & McKenzie, 1983). However, sedimentary rocks are mostly water wet, and interaction between migrating petroleum charges and clay minerals is more the exception than the rule.



(modified from Carlson and Chamberlain, 1986)

Figure 8 – Predicted effect of LSC (liquid - solid chromatography) - type geochromatography upon the Mackenzie et al. (1983) C_{29} sterane isomerization (20S/20S+20R) 5α(H), 14α(H), 17α(H) 20R C_{29} sterane) and steroid aromatization (tri/tri+monoaroamatic steroids) geologically derived maturation plots. Predicted migration trend was calculated from measured AFE (adsorption free energy) differences for pertinent steroids (modified from Carlson & Chamberlain, 1986).

Laboratory simulation of petroleum migration through dry clean quartz sand and in the presence of montmorillonite produced a qualitative redistribution of the C_{15+} aliphatic hydrocarbon fraction. Specifically, low molecular weight components became greater in proportion with increasing migration distance (Bonilla & Engel, 1986; 1988). Higher quantities of montmorillonite accentuate this redistribution (Fig. 9). The carbon isotopic ratio remained relatively unchanged in the aromatic fraction, whereas both aliphatic and NSO compounds became slightly depleted in ^{13}C with increasing migration distances due to the preferential migration of lighter compounds, richer in ^{12}C. The reason for the lack of modification to the aromatic fraction is uncertain. In subsequent studies, these fractionation effects were reproduced and in addition, selected biomarker modifications were observed (Philp & Engel, 1987; Zhusheng et al., 1988), including faster elution of 14β(H), 17β(H)-steranes, tricyclic terpanes and 17α(H), 21β(H)-hopanes, compared with 14α(H), 17α(H)-steranes, pentacyclic terpanes and 17β(H), 21α(H)-hopanes, respectively. A slow migration rate for gammacerane was also recognized. These modifications were probably related to carbon



(modified from Bonilla and Engel, 1988)

Figure 9 – Distribution of *n*-alkanes in the saturate hydrocarbon fractions of an oil sample measured in experimental simulation. The stationary phase consisted of quartz sand and 5% montmorillonite (A) and quartz sand and 10% montmorillonite (B). Most migrated refers to the section of the mineral phase that is adjacent to the HPLC column exit. Least migrated refers to the section of the mineral phase that is adjacent to the column entrance. Results from dry experiments (modified from Bonilla & Engel, 1988).

number, size, ring orientation and planarity of molecules, but their quantitative recovery is required for a complete evaluation. The magnitude of component redistribution is drastically reduced when the experiments are run in water wet conditions, and results indicate that the most sensitive compounds to fractionation are basic nitrogen compounds and that oil wet systems may be expected to enhance geochromatographic effects (Brothers et al., 1991).

Simulation experiments produce more marked compositional effects than those suggested by field observations. Probably because they are performed on extreme conditions where both scale and time involved are dramatically reduced. Hence there is a lack of comparable data. In natural environments, oil fractionation is rarely observed for two principal reasons:

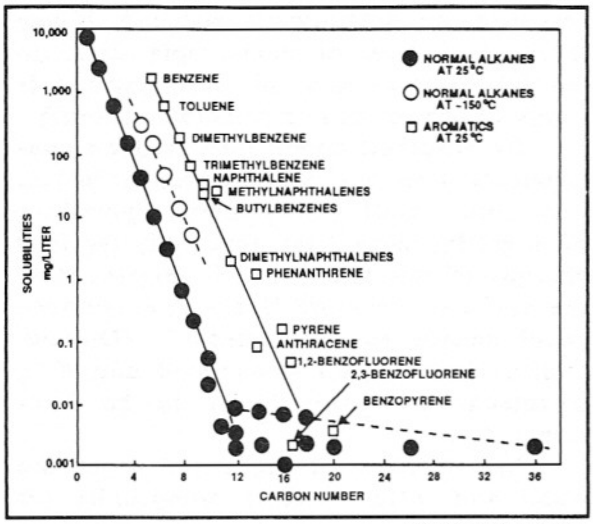
(i) adsorbed compounds will be continuously desorbed by additional oil influx. Therefore, small discontinuous quantities of migrating petroleum, especially the first charges of migration, which interact with the surfaces are more likely to experience geochromatographic effects (Durand, 1988). Hence, small amounts of migrating petroleum are more likely to be fractionated.

(ii) in most of the cases rocks are water wet, offering little opportunity for mineral surfaces to promote geochromatographic separations and suggesting a preferential loss of more soluble hydrocarbons, including gasoline range compounds (*n*-alkanes, benzene, toluene), as described by Lafargue & Barker (1988).

Losses into solution

The movement of oil particles through a water-wet system may cause polar molecules and more water-soluble hydrocarbons in the gasoline range to be preferentially lost during secondary migration (Tissot & Welte, 1984). In general, the solubility of *n*-alkanes, cycloalkanes and aromatics decrease with an increase in their molecular weight and increase with increasing temperature (Fig. 10). Reservoir temperatures are typically between 30°C and 100°C, intermediate to those depicted in Figure 10. Also, apparently aromatics are more soluble than *n*-alkanes for a given carbon number (McAuliffe, 1980), but the sequence of compounds removal by water washing experiments does not follow their solubilities, especially for higher molecular weight compounds (Lafargue & Barker, 1988). An explanation for this discrepancy is not clear, but it appears to be related to differences in the solubilities of hydrocarbons in single-component system versus multicomponent mixture.

Biodegradation usually accompanies water-washing, because aerobic bacterial degradation is enhanced during an influx of meteoric water which brings oxygen and nutrients to the system, producing effects comparable to those promoted by water washing (Connan, 1984). Also, both water-washing and biodegradation are prominent in reservoirs, after the oil is pooled



(modified from McAuliffe, 1980)

Figure 10 – Solubilities of normal alkane and aromatic hydrocarbons in water. Results show that aromatics are more soluble than saturates with the same carbon number and that solubility increases with increasing temperatures and decreases with increasing methylation (modified from McAuliffe, 1980).

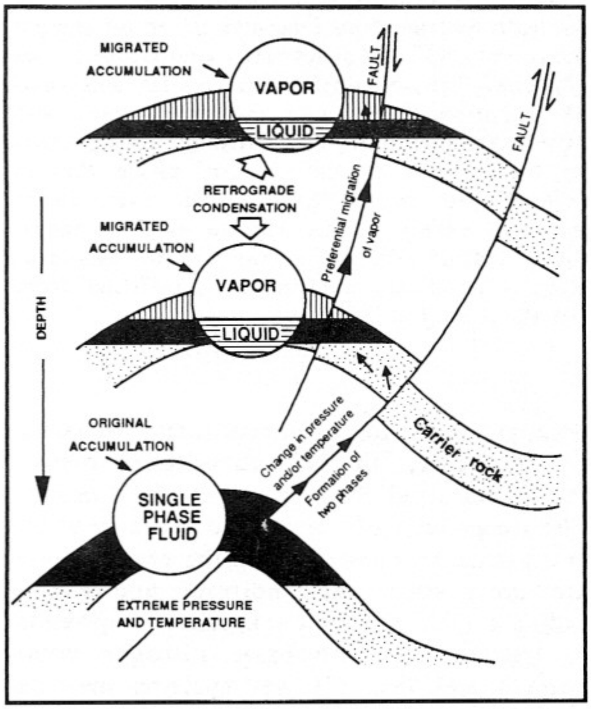
(Lafargue & Barker, 1988), limiting their use as petroleum migration indicators. Despite these limitations, depletion of benzene and toluene in relation to n-C_7 and methycyclohexane are proposed to reflect losses into solution, due to long distance lateral migration in the Anadarko Basin (Burruss & Hatch, 1989), because these are the most water soluble compounds in petroleum. However, other possible explanations were not excluded by the authors, including occurrence of other source rocks.

A model proposing accommodation of petroleum in water was tentatively suggested as partially responsible for the migration-fractionation observed in the Santa Cruz Basin, Bolivia (Illich et al., 1981), where branched and cyclic alkanes increase in relative abundance while n-alkanes and aromatics decrease. This model is not acceptable, because it requires migration in an aqueous phase, and subsequent preferential exsolution of the least soluble compounds. It has long been proved that petroleum moves as a separate phase during secondary migration (Durand, 1988) and the compositional variations can be readily explained by biodegradation.

Phase changes

Compositional effects during petroleum migration may also be controlled by the pressure, volume and temperature (PVT) behaviour of the petroleum phase, and fractionation can occur due to phase separations (Silverman, 1965; England et al., 1987; Durand, 1988; England & Mackenzie, 1989). Lower temperature and pressure regimes associated with upward migration results in gas exsolution from the liquid, affecting the distribution of oil and gas accumulation within the basin and promoting the fractionation of low molecular weight compounds, which have higher fugacities and can be remobilized in gaseous solution (Thompson, 1987, 1988).

Separation-migration was described as a process which encompasses the physical separation of one phase from a two phase petroleum reservoir system, followed by vertical migration of the separated phase from the original reservoir (Fig. 11); development of liquid and vapor phases from a single phase system as a result of



(modified from Durand, 1988)

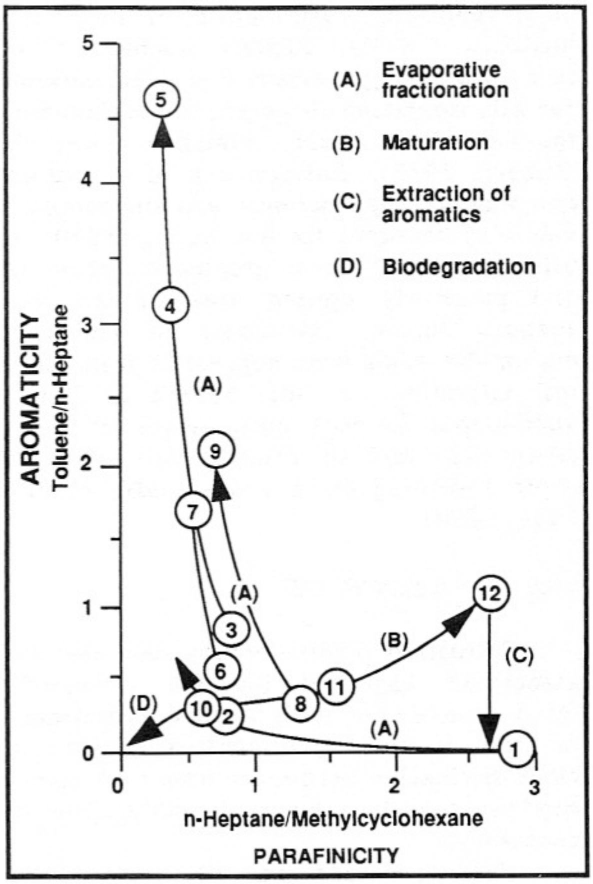
Figure 11 – Scheme of hydrocarbon phases separation (retrograde condensation) during dominantly vertical secondary and tertiary migration (from a previous existing accumulation - modified from Durand, 1988).

pressure reduction is called retrograde condensation (Silverman, 1965). More recently, the term evaporative fractionation was proposed to describe variations of intermolecular ratios in the gasoline range associated with separation of gas from oil in the subsurface (Thompson, 1987, 1988). The resulting petroleums formed by progressive gas loss are deficient of light ends but they possess abnormally high concentrations (up to 4 times) of light aromatic and naphthenic hydrocarbons (benzene, toluene, *m*-xylene, *p*-xylene, methylcyclopentane, cyclohexane and methylcyclohexane). Evaporative fractions can be estimated by a plot of the ratios of toluene/-*n*-heptane (Aromaticity) x *n*-heptane/methylcyclohexane (Paraffinicity); (Fig. 12), which compare *n*-alkane, cyclicalkane and aromatic components of similar molecular weight. Aromatics are polar structures, which form transitory complexes of high molecular weight with other molecules, limiting their ability to escape from a liquid phase (Thompson, 1987). Thus, there is an increase in aromaticity with progressive evaporative fractionation.

Oils affected by evaporative fractionation are common in the U.S. Gulf Coast (Thompson, 1988; Requejo & Halpern, 1990), where the deltaic sequence is composed of a series of stacked traps. Migration is dominantly vertical in this area, associated with intense adiastrophic tectonism related to salt movement and high pore pressures due to high sedimentation rate (Thompson, 1988). The source rock in the area is not clearly defined, but contribution from Tertiary deltaic shales, with terrestrial organic matter which generate high amounts of gas is considered (Requejo & Halpern, 1990; Comet et al., 1991).

The estimated depth at which two phases begin to separate is called the migration bubble point, which can be used to predict the type of accumulation. Accumulations deeper than the migration bubble point are expected to have single-phase petroleum, whereas two phase accumulations occur in shallower traps. This type of assessment was successfully applied in the Ardjuna depression, offshore Java, where the oils are also sourced by Tertiary deltaic sequence (Noble et al., 1991).

In contrast to variations observed in natural systems, oil and gas mixtures pressurized at different conditions during PVT simulation experiments revealed compositional modifications during pressure release that also affect compounds of higher molecular weight. The preliminary results, based on a single set of experiments, suggest significant modifications in naphthalenes, phenanthrenes and sterane carbon number distributions, selectively partitioning the lower homologues into the vapour phase due to the higher fugacity of



(modified from Thompson, 1987)

Figure 12 – Plot of the ratios toluene/*n*-heptane (Aromaticity) vs. *n*-heptane methylcyclohexane (Parafinicity) representing alteration vectors of four types: (A) evaporative fractionation; (B) maturation; (C) extraction of light aromatics by water; and (D) biodegradation. Unaltered pristine oils of normal maturity are represented by group 10. Fluid compositions 1-5 represent experimentally generated by removal of saturared gas. Vectors 6-7 and 8-9 represent evaporative fractionation of oils and condensates in four basins (Zechstein, North Slope, Williston and Coastal California). Groups 11 and 12 represent high maturity oils (modified from Thompson, 1987).

those components (Larter & Mills, 1991). However, the authors agree that further evaluation is required and that sampling procedures may have affected the results.

Entrainment of extraneous compounds

Entrainment of extraneous compounds from shallower sediments during prolonged migration though carrier beds in contact with extremely organic-rich immature source beds or coals is an additional for compositional changes.

Two instances of entrainment have been reported. Assimilation of thermally unstable 17β(H), 21β(H) hopanes from immature younger strata was demonstrated for oils migrating through coal horizons in the Gippsland Basin, Australia (Philp & Gilbert, 1982). Entrainment of immature components (dammarenes and diasterenes) was also reported by Bac et al. (1990) in oils recovered from a structurally complex and extremely faulted area of the San Joaquin Basin, California. In addition, carboxylic acids were suggested to indicate oil migration in the Mahakam Delta, attributable to both entrainment of these compounds and to fractionation between short and long chain acids (Jaffé et al., 1988, 1990).

MULTIPLE SOURCES

Petroleum dissimilarities can also be associated with contributions from different sources and with maturity variations. In order to understand these variations, a clear distinction between source rock maturity input and in-reservoir maturation is necessary.

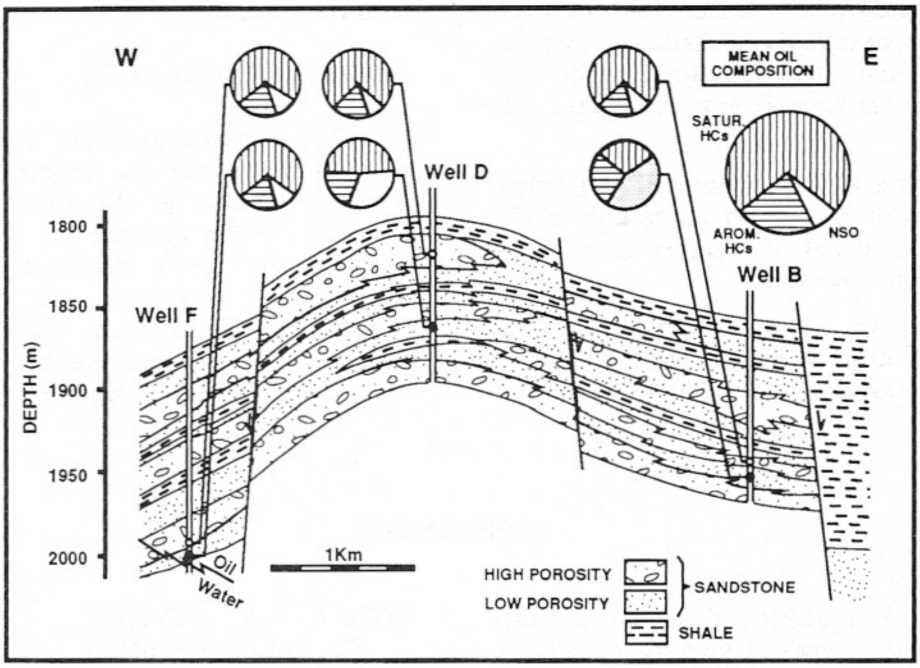
Heterogeneities in oil composition within a reservoir have also been attributed to successive stages of trap filling. Such step-wise pooling may occur on episodes of increasing burial and maturation of source rocks in combination with low rates of in-reservoir mixing, which retains the compositional variation inherited from the filling process. Lateral differences are better preserved than vertical variations, which tend to homogenize faster. According to England et al. (1987), vertical equilibrium by diffusion, thermally induced concentrations or gravitational segregation occurs over 1 m.y., provided the reservoir it not tectonically affected.

Compositional dissimilarities on an oil field scale have been observed in the North Sea by: (i) the screening of compound classes variations (Karlsen & Larter, 1989), (ii) the use of maturity dependent parameters (England, 1990), and (iii) the integration of maturity and biodegradation controls (Horstad et al., 1990). The integrated study of drill stem test and residual oil samples with porosity/permeability variations, associated with maturity parameters in oil fields from Germany clearly indicated the reservoir filling direction (Leythaeuser & Rückheim, 1989; Hillebrand & Leythaeuser, 1991). In those cases, as with examples from the North Sea, the direction of reservoir filling is indicated by the occurrence of more mature and late migrated oil in the area of the reservoir which is closest to the source rock (Fig. 13). Biomarker parameters dependent on source and maturity were also used to clarify the migration history of petroleum in the stacked reservoirs of two wells in the Jeanne d'Arc Basin, offshore eastern Canada (Fowler & Brooks, 1990). The results suggest contribution from a second source rock, which is dominated by terrestrially-derived organic matter, and reveal the most likely migration pathway.

Evaluations of petroleum compositional heterogeneities on a regional scale help the understanding of the distribution of the accumulations within the basin. In the Alaska North Slope, biomarker distributions and concentrations within several reservoirs suggest maturity trends that are related to contributions from shallow and more immature source rocks (Rullkötter et al., 1984; Mackenzie et al., 1985), and demonstrate the importance of integrated qualitative and quantitative information. In the Potiguar Basin, Brazil, trends in source- and maturity-dependent biomarker parameters helped understand the amount of oil mixing and the history of migration and reservoir filling (Trindade et al., 1992).

CONCLUDING REMARKS

Depletion trends associated with the short scale process of petroleum primary migration have been demonstrated for a series of compounds and compound classes, but no fractionation has been confirmed. However, evaluation of depletion trends for steranes and terpanes, two of the most important classes of biomarkers, has not



(modified from Leythaeuser and Rückheim, 1989)

Figure 13 – Cross-section illustrating the structural and facies relationship of the reservoir rocks of an oil field. Variation of gross composition of extracted oils with porosity of the reservoir beds in comparison with the mean composition of reservoir oils is exemplified. High porosity sandstones have higher percentages of saturates and lower relative concentrations of NSO compounds (modified from Leythaeuser & Rückheim, 1989).

been attempted yet.

Previous studies demonstrate that proposed compositional modifications during secondary migration of petroleum remain conjectural and that several other process can interfere with and produce results similar to effects promoted solely by migration. Also, there is some uncertainty with the assumptions that have been made. Despite the valuable information that they provide, experimental results cannot be applied without restrictions to natural systems, because they were performed under conditions that drastically reduce the geological time and scale of processes.

Several mechanism have been proposed to affect petroleum composition during secondary migration, including geochromatography, losses into solution and phase changes. However, they have been examined in individual situations and not integrated. In addition, the extent to which these mechanisms are active in petroleum fractionation during secondary migration, and mainly their role in biomarker distributions and concentrations, remains unclear.

The study of organic geochemistry of reservoirs has become more important in recent years. Detailed oil field evaluation of petroleum compositional heterogeneities which reveal maturity variations and contributions from several sources has proven useful in clarifying the history of migration and reservoir filling, by revealing mixing of oils with different degrees of maturity. However, systematic evaluation of biomarker compositions and concentrations on a regional scale are not common because samples suitable to this approach are seldom available.

Therefore, there is need of further study of well-constrained geological settings, which meet critical conditions, to evaluate the geochemical effects associated with petroleum migration phenomena. The sedimentary basins discussed here represent a new and important case history for this type of study. Thus, the present thesis intends to fill some fundamental gaps in knowledge of petroleum migration and its effects, including:

- An investigation of the effects of primary migration on sterane and terpane compositions in interbedded source rock and reservoir sequences;
- Exploration of the comparative roles of

geochromatography, losses into solution and phase changes in possible petroleum compositional fractionation associated with long distance lateral secondary migration;

- Clarification of the history of migration and reservoir filling on a regional scale by the assessment of compositional variability of mixed oils;
- Study of the isotopic composition of individual biomarkers of migrated mixed oils that may constitute a novel approach to the problem.

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