Review

Applications of petroleum geochemistry to exploration and reservoir management ☆

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Abstract

Petroleum geochemistry improves exploration efficiency by accounting for many of the variables that control the volumes of crude oil and natural gas available for entrapment, including source-rock distribution, richness and quality, thermal maturity, and the timing of generation-migration-accumulation relative to trap formation. It is most powerful when used with other disciplines, such as seismic sequence stratigraphy and reservoir characterization. Four key technology milestones form the basis for most modern applications of geochemistry to exploration. These are the concepts and applications of (1) petroleum systems and exploration risk, (2) biomarkers, stable isotopes, and multivariate statistics for genetic oil-oil and oil-source rock correlation, (3) calibrated three-dimensional thermal and fluid-flow modeling, and (4) controls on petroleum composition by secondary processes. Petroleum geochemistry offers rapid, low-cost evaluation tools to aid in understanding development and production problems. Some technology milestones in reservoir geochemistry include (1) assessment of vertical and lateral fluid continuity, (2) determination of proportions of commingled production from multiple zones and leaky casing, (3) prediction of oil quality in reservoir zones, and (4) prediction of gas/oil and oil/water contact locations. As described in the conclusions, future research will continue a trend toward *predictive* geochemistry. Examples of predictive tools that draw major research support include piston-core surveys to assess deepwater petroleum systems prior to drilling and three-dimensional basin modeling to predict the regional timing of generation, migration, and accumulation of petroleum. Among other research objectives, models are needed to better predict the distribution and quality of petroleum in reservoirs. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Petroleum geochemistry is an established science that improves exploration and production efficiency. The purpose of this review paper is to provide an historical background for petroleum geochemistry since about 1980, and to shed light on current geochemical research. Hydrocarbon gases are not discussed. To simplify the discussion, we describe a few key technology milestones for exploration and reservoir management, supplemented by some of our own and other work that further illustrates applications of petroleum geochemistry. We recognize that there is room for debate on what constitutes a significant technology milestone and that each advance rests upon previous work. Not all of this supporting work is cited because of limited space. In some cases, we reference a later publication because it is more definitive than earlier work by the same author.

Several key books also represent technology milestones because they educate industry and academia

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about the competitive edge provided by petroleum geochemistry and help to assure its continued use. Some of these books include Tissot and Welte (1984), Waples and Machihara (1991), Bordenave (1993), Peters and Moldowan (1993), Hunt (1996), and Welte et al. (1997).

2. Historical background

In recent years, petroleum geochemistry has been characterized as a mature science (e.g. Miller, 1995). This is somewhat misleading because among geologists and industry management, the term mature is associated with extensively explored basins with little further potential. Petroleum geochemistry is mature in the sense that powerful theories and tools were developed to characterize source rocks and to understand the origin, migration, and accumulation of petroleum, and these have been remarkably successful. About three-fourths and two-thirds of the worldwide conventional oil and gas resources, respectively, have been discovered (USGS, 2000). Geochemistry continues to play a critical role in finding the remaining resources that are becoming more difficult to locate and produce. However, petroleum geochemistry is not a completely mature *predictive* science. Many enigmas remain, and their solutions could yield tremendous competitive advantages in exploration and production. For example, new developments in reservoir geochemistry could significantly improve exploitation of so-called unrecoverable petroleum in established reservoirs.

Geochemistry increases exploration efficiency by accounting for many of the variables that control the volumes of petroleum available for entrapment (charge), including source rock quality and richness, thermal maturity, and the timing of generation-migration-accumulation relative to trap formation (e.g. Murris, 1984; Hunt, 1996, pp. 604–614). It is most powerful when used with other disciplines, such as seismic sequence stratigraphy and reservoir characterization (e.g. Kaufman et al., 1990; Isaksen and Bohacs, 1995). Including geochemistry in prospect appraisal improves exploration efficiency. Fig. 1 shows that forecasting efficiency initially based only on structural and reservoir data (e.g. geophysics) approximately doubles when geochemical charge and retention parameters are included in prospect evaluation. Costly exploration failures, such as the No. 1 Mukluk OCS Y-0334 well in Alaska (~$140 million in 1983 dollars; Weimer, 1987), are painful reminders that large structures indicated by seismic data may lack oil and gas due to geochemical charge limitations.

Many development and production problems can be understood using rapid, inexpensive petroleum geochemical methods. For example, geochemical analysis of reservoir fluids improves evaluation of reservoir continuity and compartments that contain bypassed petroleum,
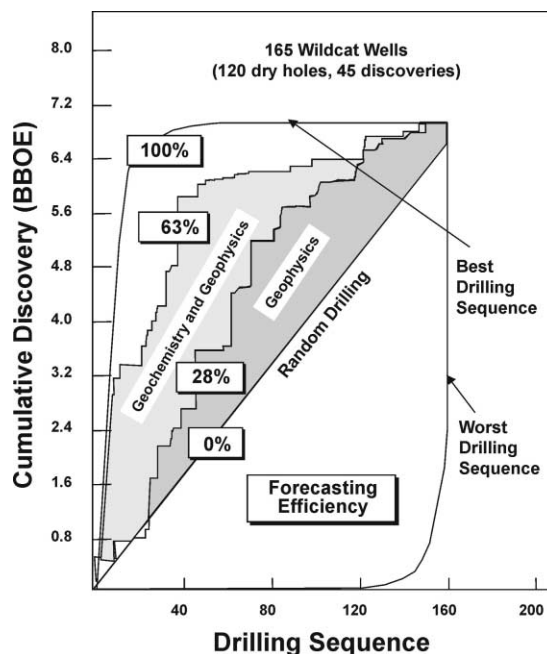

Fig. 1. Petroleum geochemistry improves forecasting efficiency (FE; modified from Murris, 1984). The figure shows results for 165 petroleum prospects evaluated prior to drilling. Vertical axis = cumulative discovered volumes in place (billions of barrels), horizontal axis = well sequence number. The upper curve is the theoretical best possible ranking of prospects (100% FE) compared to actual outcomes. Random drilling would lead to a discovery sequence along the diagonal line (0% FE). Ranking based on trap size from structural and reservoir data gave the lower stepped curve (28% FE). Actual ranking based on complete prospect evaluation, including geochemistry, gave the upper stepped curve (63% FE). AAPG© 1984; reprinted by permission of the AAPG whose permission is required for further use.

pipeline leaks and oil spills, leaky casing, nonproductive zones, and the relative proportions of commingled production from multiple zones for production allocation calculations (e.g. Kaufman et al., 1990).

3. Geochemistry applied to exploration

Four technology milestones form the basis for most modern applications of geochemistry to petroleum exploration. These are the concepts and applications of (1) petroleum systems and exploration risk, (2) biomarkers, isotopes, and multivariate statistics for genetic oil–oil and oil–source rock correlation, (3) calibrated three-dimensional (3D) basin modeling, and (4) controls on petroleum occurrence and composition related to secondary processes.

Traditional exploration focuses on subsurface traps and the play concept in sedimentary basins described according to tectonic style. A play consists of prospects

and fields with similar geology (e.g. reservoir, cap rock, trap type). Plays use the characteristics of discovered accumulations to predict similar, undiscovered accumulations. Focus by interpreters on a particular play type, as in anticline or pinnacle reef trends, may limit creative ideas on other potential play types. Furthermore, although generalizations can be made about field size, heat flow, and trap retention for basins of a given tectonic style, source-rock richness and volumes are only weakly related to tectonic style, and tectonic classifications are of little value to forecast petroleum volumes (Demaison and Huizinga, 1994). The key elements needed to forecast petroleum volumes, such as source, reservoir, and seal rock, as well as adequate generation, migration, and accumulation factors, were incorporated into the petroleum system concept, as discussed below.

3.1. Petroleum systems and exploration risk

A petroleum system encompasses a pod of active or once-active source rock, all related oil and gas, and all geologic elements and processes that are essential for petroleum accumulations to exist (Perrodon, 1992; Magoon and Dow, 1994). The principal objective of the petroleum system approach is to show the geographic boundaries of oil and gas occurrence. A valuable by-product of this approach is identification of limits in our knowledge of the generation, migration, and accumulation of petroleum in each study area. This facilitates the identification of new plays and allows us to more readily identify the additional data, training, and skills needed to properly allocate resources. For example, geochemical confirmation of a petroleum system by oil-to-oil correlation allows us to focus on defining migration pathways with the expectation that we can find traps that have not yet been identified (e.g. Terken and Frewin, 2000).

The petroleum system folio sheet consists of five charts that define a systematic method to assess the regional, stratigraphic, and temporal distributions of petroleum (Fig. 2). The figure describes the hypothetical Deer-Boar (.) petroleum system, where the name includes the source rock (Deer Shale), the major reservoir rock (Boar Sandstone), and a symbol expressing the level of certainty in the genetic relationship between the source and the trapped petroleum (Magoon and Dow, 1994). The symbols (?), (.), and (!) indicate speculative, hypothetical, and known genetic relationships, respectively. The first chart on the folio sheet is a cross section showing the extent of the petroleum system at the critical moment, i.e. a snapshot in time that best depicts the generation-migration-accumulation of petroleum. This chart is useful because the present-day distribution of discovered petroleum can obscure important information needed to understand a petroleum system and to predict the location of undiscovered

reserves. A map shows the extent of the Deer-Boar(.) petroleum system, including the pod of active source rock and the discovered petroleum accumulations at the critical moment. A table of accumulations for the Deer-Boar(.) petroleum system relates oil and gas fields to their key geochemical and reserves characteristics. The burial history chart shows the critical moment and the timing of oil generation. The petroleum system events or timing-risk chart shows timing of the elements and processes in the petroleum system.

Geochemistry is the key to petroleum systems because it is required to:

- establish the genetic link between petroleum and the pod of active source rock (oil–source rock correlation),
- map the geographic extent of the petroleum systems and of the pod of source rock (e.g. for volumetric calculations of yield), and
- assess the timing of generation-migration-accumulation relative to trap formation.

Maps of the extent of the active source-rock pod and estimates of generated volumes of petroleum require input from multiple disciplines, including geochemistry, seismic sequence stratigraphy, and well log analysis (e.g. Creaney et al., 1994; Demaison and Huizinga, 1994). Some geochemical innovations that contribute to constructing these maps include Rock-Eval pyrolysis and geochemical logs (Espitalié et al., 1984. 1987; Peters and Cassa, 1994), $\Delta \log R$ (Passey et al., 1990), and calibrated basin modeling (Welte et al., 1997), including custom kerogen kinetic measurements (Braun et al., 1991). For example, the $\Delta \log R$ method allows prediction of total organic carbon (TOC) profiles in wells that lack measured TOC by using the separation between scaled transit-time and resistivity curves from conventional well logs (Creaney and Passey, 1993). Predictions of TOC from $\Delta \log R$ must be calibrated using wells where measured TOC values are available in representative lithologies.

3.1.1. Piston-core studies

Piston-core seep surveys and related technologies are rapidly growing research topics because they provide information on the geographic extent of petroleum systems prior to drilling (e.g. Brooks et al., 1986). Seeps provide information on the quality, thermal maturity, age, and distribution of the underlying source rock. In marine settings, core sites are chosen based on seismic evidence for leakage and subsurface disturbance of unconsolidated sediments by rising petroleum (e.g. Haskell et al., 1999). Target core sites are best located where faults link the source or reservoir rock to the seabed, as commonly occurs in tectonically active areas, such as the Gulf of Mexico or Niger Delta. Ideal faults
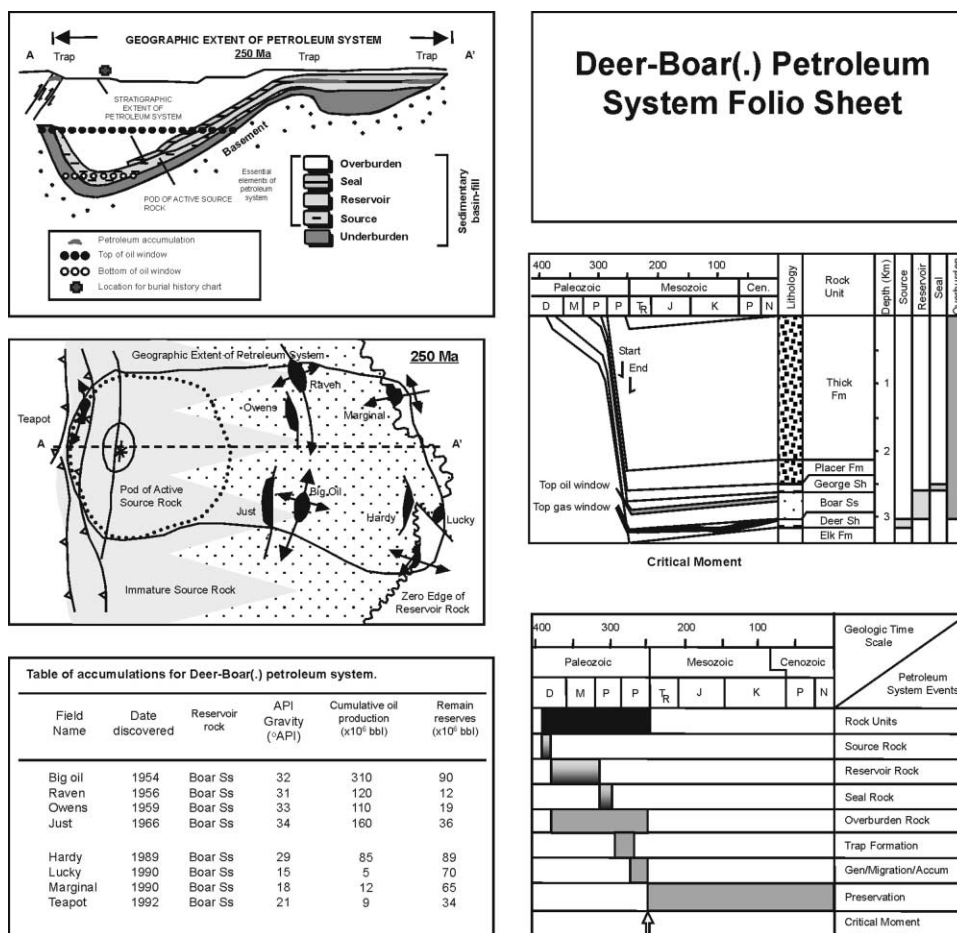
Fig. 2. Folio sheet for the hypothetical Deer-Boar petroleum system contains five charts that define a systematic method to assess the regional, stratigraphic, and temporal distributions of petroleum (modified from Magoon and Dow, 1994). AAPG© 1994; reprinted by permission of the AAPG whose permission is required for further use.

are those associated with: (1) seismic amplitude anomalies and/or bottom-simulating reflectors associated with gas hydrates (Kvenvolden and Lorenson, 2001), (2) seabed leakage features, such as carbonate accumulations and mud-gas mounds or pits, and (3) thermogenic gas chimneys (MacDonald, 1998). Core sites can be positioned using differential global positioning satellite technology (Cameron et al., 1999).

Interpretation of piston core data is complex because of variable biodegradation of the seep oil and mixing with recent organic matter near the sediment–water interface.

Analyses focus on sediment below the top meter of core, thus minimizing the effects of bioturbation, anthropogenic pollution, and diffusion of gases from the water column. Screening methods identify samples that provide the least ambiguous data for interpretation. For example, Table 1 shows four criteria used to classify the quality of piston-cored seep samples. The unresolved

Table 1
Examples of criteria used to classify piston core samples. UCM = unresolved complex mixture (hump) on whole-oil gas chromatogram, TSF = fluorescence response, C_{2+} = ethane, propane, butanes, and pentanes

Parameter	No seep	Oil seep	Gas Seep
UCM (ppm)	< 30	> 30	< 30
n-Alkanes (ppm)	< 1500	> 1500	< 1500
TSF (fluor. units)	< 4000	> 4000	< 4000
C_{2+} (ppm)	< 1	> 1	> 1

complex mixture, n-alkanes, and C_{2+} gases are measured using gas chromatography. Total scanning fluorescence (TSF) provides a rapid, semi-quantitative measure of petroleum aromatic hydrocarbons that is insensitive to all but severe biodegradation (Brooks et al., 1986). Migrated oil has higher concentrations of

larger aromatic compounds containing three or more benzene rings and fluoresces at longer wavelengths. Extracts containing gas or condensate fluoresce at shorter wavelengths. Many oil seeps can be further classified based on weak to strong gas chromatographic fingerprint intensity. For example, a strong chromatographic response for oil consists of a large unresolved complex mixture (UCM) and an *n*-alkane distribution similar to that of thermally mature crude oil that covers a broad range of carbon numbers with little preference for odd- or even-numbered homologs. A weak chromatographic response for oil shows a small UCM and a limited *n*-alkane distribution like thermally immature recent organic matter with a preference for odd- or (less commonly) even-numbered *n*-alkanes. Symbols designating the different classes of piston core samples can be plotted on bathymetric maps to assist geologic interpretation.

Assignment of seep samples to a particular petroleum system requires geochemical oil-oil or oil-source rock correlation as discussed below. For seep samples, special care must be taken to avoid the use of correlation parameters affected by interfering materials from the associated sediment. Wenger et al. (1994) used maps of oil or seep types to delineate the complex regional distributions of petroleum systems in the Gulf of Mexico by age of the source rock and by chemical composition of the generated products. These maps can be used to predict the geochemical character of petroleum that might be discovered by drilling in selected areas.

3.2. Oil–oil and oil–source rock correlation

Correlations are geochemical comparisons among oils or between oils and extracts from prospective source rocks, and are used to determine whether a genetic relationship exists (Peters and Moldowan, 1993; Waples and Curiale, 1999). Oil–source rock correlation is based on the concept that certain compositional parameters of migrated oil do not differ significantly from those of bitumen remaining in the source rock. In this multi-parameter approach, independent measurements of biomarker, stable carbon isotope, and other genetic parameters support the inferred correlation. The approach commonly relies heavily on gas chromatography–mass spectrometry (GC–MS) of biomarkers (Seifert and Moldowan, 1978, 1981; Mackenzie, 1984). Biomarkers are complex organic compounds that occur in sediments, rocks, and crude oils, and that show little or no change in structure from their parent organic molecules in living organisms (Peters and Moldowan, 1993). Biomarkers in seep or oil samples can be used to indirectly predict source-rock quality, even when source-rock samples are not available for direct comparison (e.g. Dahl et al., 1994).

Several key geochemical advances that facilitate the successful correlation of oils and source rocks include innovations in GC–MS, metastable-reaction monitoring-GC–MS, and GCMSMS (e.g. Gallegos, 1976; Warburton and Zumberge, 1982) and compound-specific isotope analysis (CSIA, e.g. Hayes et al., 1990). Correlations are also facilitated by better integration of geochemistry with source-rock sequence stratigraphy (e.g. Isaksen and Bohacs, 1995) and increased research on age-related biomarkers and isotopes (e.g. Chung et al., 1992, Moldowan et al., 1994; Holba et al., 1998; Andrusevich et al., 2000). The use of multivariate statistics improves evaluation of large, complex data sets (chemometrics, e.g. Peters et al., 1986; Zumberge, 1987).

Recent work on the Mahakam Delta in Indonesia is an example of how the combined use of geochemistry, multivariate statistics, and sequence stratigraphy resulted in a new and successful model for exploration in a mature basin. This new geochemical-stratigraphic model for the Mahakam Delta is based largely on oil–oil and oil–source rock correlation. The model upgrades the potential of the outer shelf, where it influenced drilling that resulted in significant deepwater oil discoveries (Peters et al., 2000; Payenberg and Miall, 2001; Snedden et al., 2001). The model predicts distinct oil accumulations that originated from local kitchens (regions of petroleum generation) between anticlinal trends aligned parallel to the coast. Multivariate statistical analysis of source-related biomarker and isotope data for sixty-one crude oil samples confirms that oils from Mahakam Delta anticlinal trends differ genetically (Fig. 3). Waxy oils occur onshore and originated near the peak of the oil-generative window from Middle-Upper Miocene coals and shales deposited in coastal plain highstand systems tract environments. Less waxy oils occur offshore and originated in the early oil window from Middle-Upper Miocene coaly rocks deposited in deepwater lowstand systems-track environments. A small group of nonwaxy oils occurs mainly onshore and originated at low thermal maturity from Middle Miocene marine shales deposited near times of maximum flooding. Based on statistical analysis described below, the waxy, less waxy, and nonwaxy oil groups are designated highstand, lowstand, and transgressive oil groups, respectively.

The 61 oil samples were used as a training set to construct a K-Nearest Neighbor (KNN) statistical model of oil families. This KNN model was used to establish genetic oil-to-source rock correlations based on the geochemical compositions of extracts from organic-rich source rock candidates. The systems tract (e.g. highstand, lowstand, transgressive) and geologic age for each source-rock sample, and, by infererence, the related oils, was determined using biostratigraphic and seismic sequence stratigraphic data (Fig. 4). Classification using KNN compares the *n*-dimensional distance between all samples where *n* is the total number of genetic geochemical variables. The three (or more) training set oils most similar to each source-rock extract were determined in order to predict the group to which each extract belongs.
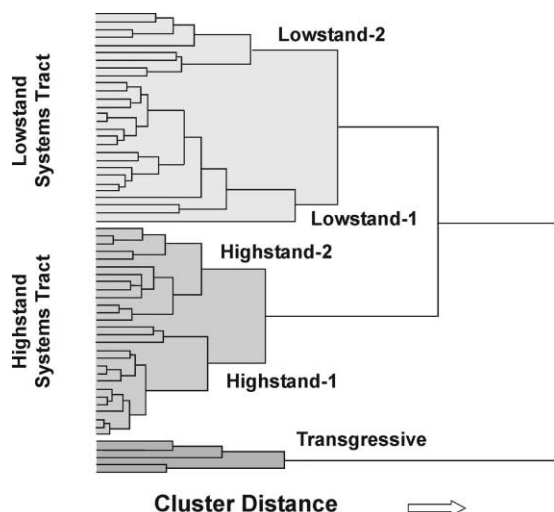
Fig. 3. Hierarchical cluster analysis dendrogram based on multivariate statistical analysis of fifteen source-related geochemical parameters for sixty-one crude oils from the Mahakam Delta (Peters et al., 2000). Cluster distance measures genetic similarity as indicated by the horizontal distance from any two samples on the left to their branch point on the right. AAPG© 2000; reprinted by permission of the AAPG whose permission is required for further use.

The older model downgraded the potential for commercial deepwater petroleum accumulations on the outer shelf and failed to explain discoveries in this area (Burrus et al., 1992; Duval et al., 1992). According to the older model, middle Miocene coaly source rocks occur only in updip shelfal areas and all oils in the area are genetically related to this source. Furthermore, this model predicted that age-equivalent rocks in deepwater have low petroleum potential due to oxidation of coaly source material during transport across the shelf break, deep burial (~6 km) and high maturity of the source intervals, and diagenetic cementation of reservoirs at great depth.

In the new model, the Middle Miocene source-rock interval in deepwater is not buried as deeply as previously believed, and is now within the oil window based on regional seismic reinterpretation and thermal modeling using source-specific kerogen kinetics (Peters et al., 2000). During lowstand system-tract time, downdip depocenters received terrigenous organic matter by a process similar to that responsible for gravity-flow sandstones on the outer shelf and slope. Oxidation of this organic matter was minimized due to proximity of the shelf break to the depocenters. Because few downdip wells penetrate marine sections in the offshore Mahakam Delta, the best evidence for terrigenous-rich deepwater source rocks comes from observations of updip erosion and transport of terrigenous organic matter. For example, cores of Middle Miocene channel and incised-valley fills show high organic carbon and hydrogen index values. Extracts from these lowstand rocks have significant marine character and show genetic affinities to the less waxy oils.

After the source rock for petroleum is established by oil-source rock correlation, it is possible to make predictions of the timing of generation and the volumes
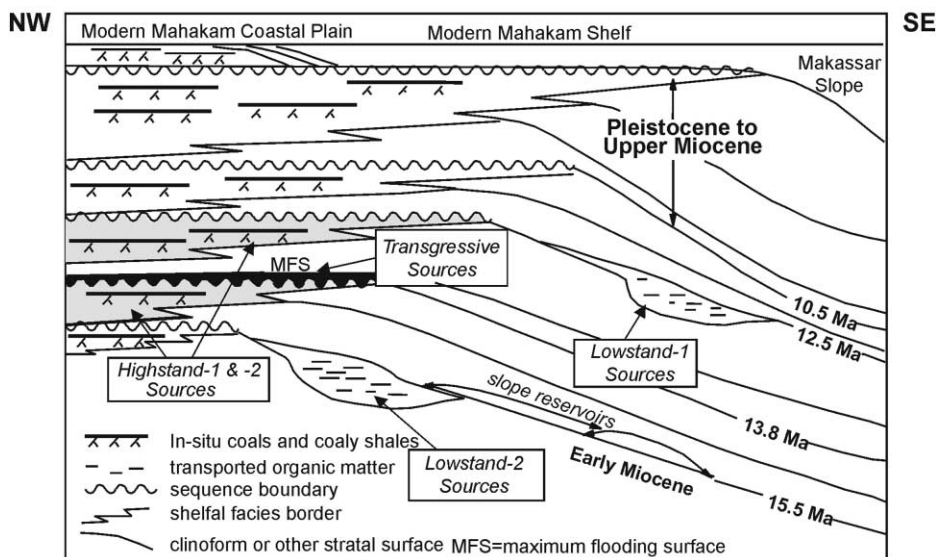

Fig. 4. Schematic of the geochemical-stratigraphic model and predicted distribution of source rocks near the Mahakam Delta based on oil-source rock correlation (Peters et al., 2000). Faults are not shown. HST, LST, TST = highstand, lowstand, and transgressive systems tracts, respectively. MFS = maximum flooding surface. NW–SE refers to X–X′ in Fig. 5. AAPG© 1984; reprinted by permission of the AAPG whose permission is required for further use.

and character of trapped petroleum using calibrated basin models. Although many examples are in the literature (e.g. Welte et al., 1997), our discussion again focuses on the deepwater Mahakam Delta (below).

3.3. 3D-basin modeling

Calibrated 3D-basin models attempt to reconstruct the history of sedimentary basins and predict how the processes of generation, expulsion, migration, trapping, and preservation control the volumetrics, quality, and distribution of petroleum (Waples, 1994b; Welte et al., 1997). Basin modeling includes thermal and fluid-flow modeling. Thermal modeling deals with maturation of thermal indicators (e.g. vitrinite reflectance), and with petroleum generation and cracking (Waples, 1994a). For accurate simulations, basin models require input on the timing of geological events with respect to the source, carrier, reservoir, and overburden rock, including

deposition, nondeposition, uplift, and erosion. Also required are data on the material properties and the distribution of these rocks and their thermal history. Important material parameters include the kinetics and type of organic matter in the source rock, detailed lithologies and their thermal properties, porosity, and permeability. The results of these calculations must be calibrated against measured thermal maturity parameters from wells, such as vitrinite reflectance (e.g. Taylor et al., 1998), to test sensitivity of the input data (Poelchau et al., 1997, and references therein).

Peters et al. (2000) includes an example of 3D-basin modeling applied to the Mahakam Delta. A map generated from the model shows the present-day extent of kerogen fractional conversion for the lower Middle Miocene source-rock interval based on custom measured kinetics for the lowstand source rock (Fig. 5). The older model predicted only gas or no petroleum at all in deepwater because of little or no source rock beyond the
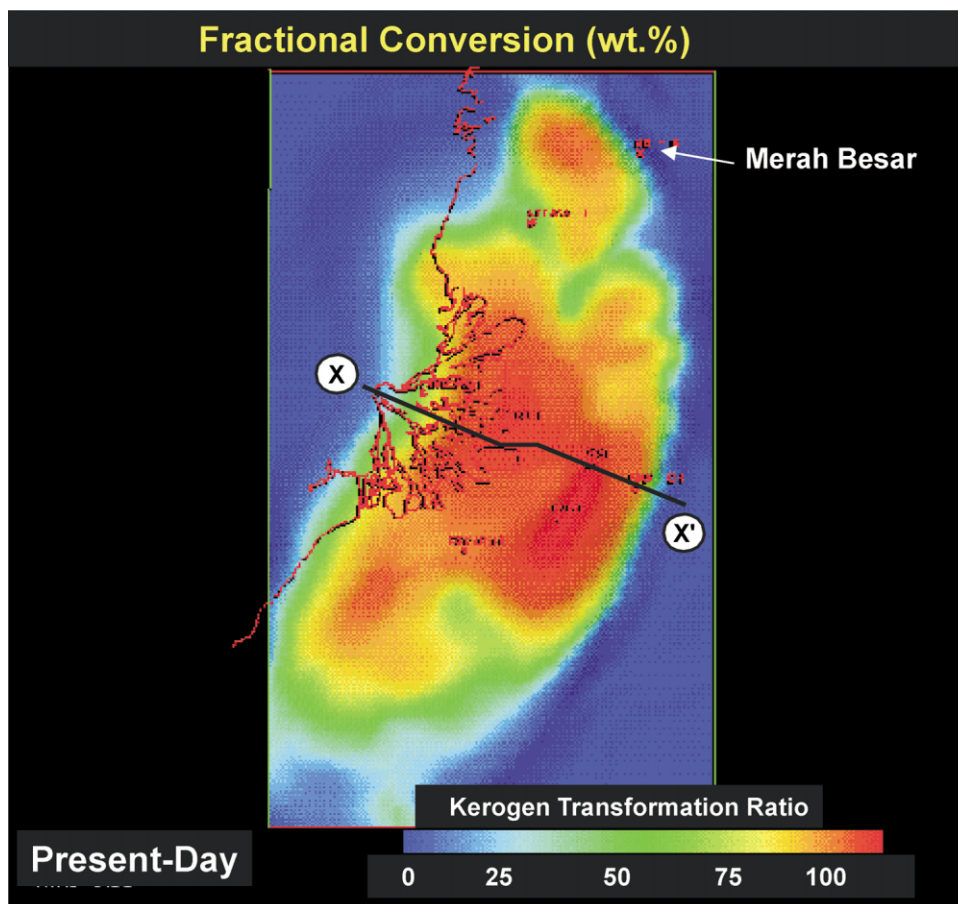

Fig. 5. Map shows the calculated present-day extent of kerogen fractional conversion for the lower Middle Miocene source interval (16.3–16.5 Ma), offshore Mahakam Delta (Peters et al., 2000). The map is based on 3D-basin modeling using custom measured kinetics for the lowstand source rock that correlates geochemically with the lowstand oil group (Fig. 4). AAPG© 2000; reprinted by permission of the AAPG whose permission is required for further use.

shelf break, deep burial, and high thermal maturity, as discussed above. However, the 3D-basin model using measured source-rock kinetics correctly predicted oil rather than gas at recent discoveries, such as the Merah Besar field.

3.4. Secondary processes affecting petroleum

Various physicochemical processes can alter the composition of petroleum after it has been generated from the source rock and trapped in the reservoir. For example, oils from deep reservoirs tend to have higher API gravity due to thermal cracking, while oils from shallow reservoirs commonly show lower API gravity due to biodegradation by microbes. In general, biodegraded oils are less desirable because they are difficult to produce and they pose problems for refineries, such as high sulfur and metal content. More risk is associated with exploration and development opportunities where secondary processes might adversely affect the quality of petroleum. In addition, contamination of petroleum can occur during migration, drilling, and sampling or handling.

3.4.1. Thermal alteration

Kerogen is a complex mixture of macromolecules in sedimentary rocks that is still insufficiently characterized to allow us to construct accurate fundamental predictive models of thermal cracking to generate petroleum (Xiao, 2001, and references therein). For this reason, most current thermal models assume first-order or multiple first-order kinetic reactions to describe primary cracking of kerogen and secondary cracking of petroleum (e.g. Ungerer et al., 1988; Burnham and Braun, 1990; Horsfield et al., 1992; Behar et al., 1997). Kinetic parameters are measured using open or closed pyrolysis, and the models are calibrated using field data (e.g. Tang and Stauffer, 1994; Curry, 1995; Lewan, 1997; Welte et al., 1997). The importance of minerals, transition metal catalysis, and water in petroleum generation is poorly understood (Goldstein, 1983; Mango et al., 1994; Seewald, 1994; Lewan, 1997).

At high temperatures, crude oil cracks to light oil, condensate, and finally gas and pyrobitumen in reservoirs buried below the oil deadline, where liquid petroleum (C_6+) no longer exists (Hunt, 1996). Although most models of oil-to-gas cracking assume multiple first-order parallel reactions (however, see Dominé et al., 1998), the kinetic parameters determined by different workers vary widely (Waples, 2000 and references therein). Therefore, predictive temperatures for the oil deadline remain uncertain (e.g. Quigley and Mackenzie, 1988; Ungerer et al., 1988; Hayes, 1991; McNeil and BeMent, 1996). For example, the thermal stability of hydrocarbons (Mango, 1991) and the occurrence of oils at high reservoir temperatures (Horsfield et al., 1992; Price, 1993; Pepper and Dodd, 1995) suggest that liquid

components may be preserved at higher temperatures than previously thought. Using the kinetic parameters of Waples (2000), the maximum temperature where oil is preserved varies from 170 °C at geologically slow heating rates to over 200 °C at geologically fast heating rates. Thermochemical sulfate reduction (discussed below) can lower the temperatures required for oil destruction (Orr, 1974).

Diamondoids ($C_{4n+6}H_{4n+12}$) are small, thermally stable fragments of diamond in petroleum. They consist of pseudo-homologous series, and include adamantane, dia-, tria-, tetra- and pentamantane ($n = 1$–5, respectively), plus various alkylated series. Diamondoids can be used directly to determine the extent of oil-to-gas cracking in reservoirs, and offer a means to recognize mixtures of high- and low-maturity oils (Dahl et al., 1999). Detection of mixed oils is important because it can result in new exploration play concepts.

Pyrobitumens consist of solid organic materials derived by thermal alteration of oil or bitumen, which are insoluble in organic solvents. Pyrobitumen can cause production problems by decreasing the permeability and porosity in deep reservoir rocks. Huc et al. (2000) studied a sandstone reservoir in Oman, where up to 40% of the reservoir porosity was filled by pyrobitumen. They used microscopy, Rock-Eval pyrolysis, elemental analysis, ^{13}C NMR, extraction, and stable isotopes to explain the properties and occurrence of the pyrobitumen. This included identifying the main events and their timing leading to pyrobitumen formation, and recognizing that heavily biodegraded oil was thermally altered.
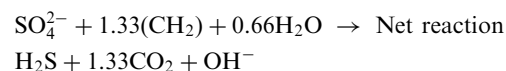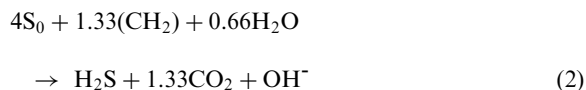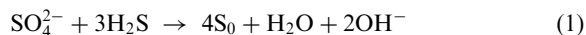
3.4.2. Deasphalting

Deasphalting is the process where asphaltenes precipitate from crude oil, leaving oil with higher API gravity. Laboratory or refinery deasphalting is used to remove complex components from oil by adding light hydrocarbons, such as pentane or hexane. Deasphalting of petroleum can occur with increasing thermal maturation or when methane and other gases that escape from deep reservoirs enter a shallower oil reservoir (Evans et al., 1971). Deasphalting was thought to occur in Devonian reefs from the Western Canada basin, where porosity is partly plugged by solid bitumen (Bailey et al., 1974), and it may account for many tar mats at the base of reservoirs in the North Sea (Dahl and Speers, 1986; Wilhelms and Larter, 1994).

3.4.3. Thermochemical sulfate reduction

Thermochemical sulfate reduction (TSR) is the abiological reduction of sulfate by hydrocarbons in reservoirs close to anhydrite at high temperatures (e.g. Worden et al., 1995). TSR occurs in the Smackover Trend in the Gulf of Mexico (Claypool and Mancini, 1989), the Western Canada basin (Krouse et al., 1989), and the Big Horn basin in Wyoming (Orr, 1974). Other

examples of TSR occur in the Permian Zechstein Formation in northwestern Germany (Orr, 1977), the Aquitaine basin in France (Connan and Lacrampe-Couloume, 1993), and Abu Dhabi (Worden et al., 1995). The following is a simplified TSR reaction scheme (Orr, 1974).

$$SO_4^{2-} + 3H_2S \ \rightarrow \ 4S_0 + H_2O + 2OH^- \qquad (1)$$

$$4S_0 + 1.33(CH_2) + 0.66H_2O$$

$$\rightarrow \ H_2S + 1.33CO_2 + OH^- \qquad (2)$$

$$SO_4^{2-} + 1.33(CH_2) + 0.66H_2O \ \rightarrow \ \text{Net reaction}$$
$$H_2S + 1.33CO_2 + OH^-$$

In the above equations, (CH₂) represents reactive organic matter. Some types of organic matter are more susceptible to TSR than others. For example, the C_2–C_5 hydrocarbon gases are more reactive than methane. Many sour gas reservoirs lack C_2–C_5 hydrocarbons but contain methane, H_2S, and other nonhydrocarbon gases, such as carbon dioxide. As discussed later, the relative rates of reaction of higher molecular-weight hydrocarbons also vary. Because the oxidation state of sulfur ranges from $+6$ to -2 during the reduction of sulfate to sulfide, S_0 in reactions (1) and (2) includes elemental sulfur and other sulfur intermediates, such as polysulfides and thiosulfates (Steinfatt and Hoffmann, 1993; Goldstein and Aizenshtat, 1994). Anhydrite is an effective seal rock that is generally the source of the sulfate. Because anhydrite is not particularly soluble, reaction (1) is considered to be the rate-determining step.

The minimum temperature to initiate TSR was controversial for many years. Some authors proposed temperatures as low as 80 °C (Orr, 1977), while others argued that it was unlikely to occur below 200 °C (e.g. Trudinger et al., 1985), partly because of disputes over the meaning of laboratory data (Goldhaber and Orr, 1995). Recent work suggests that TSR begins in the range 127–140 °C, depending on the hydrocarbons in the reservoir, and that higher temperatures are required to initiate TSR for methane than for heavier hydrocarbons (Machel et al., 1995; Worden et al., 1995; Rooney, 1995).

While TSR is commonly associated with gas accumulations, the lower temperature range for TSR corresponds to that for generation of light oils and condensates. TSR can modify the compositions of these fluids. Various parameters distinguish the effects of TSR from those of thermal maturity on the composition of liquid hydrocarbons (Table 2).

With increasing thermal maturation of crude oil, saturated hydrocarbons increase relative to aromatics (e.g. Tissot and Welte, 1984, p.187). The opposite trend occurs during TSR due to the greater reactivity of saturated compared to aromatic hydrocarbons (Fig. 6). While both TSR and thermal maturation increase saturated hydrocarbon $\delta^{13}C$ (Table 2), Claypool and Mancini (1989) noted that condensates affected by TSR had more positive values. Compound-specific isotopic analysis (CSIA) of the gasoline-range hydrocarbons in oils ($\sim C_6$ and C_7 hydrocarbons) shows greater isotopic shifts for *n*-alkanes and branched alkanes than for monoaromatic compounds, such as benzene and toluene, indicating that the saturated compounds are more reactive (Rooney, 1995).

Without TSR, the main controls on aromatic sulfur compounds in oils are source-rock depositional environment and thermal maturity (Ho et al., 1974; Hughes, 1984). However, the concentration of aromatic sulfur compounds increases with H_2S content during TSR because these compounds are formed as by-products (Orr, 1974). This results in a slight increase or even a decrease in API gravity with increasing maturity (Claypool and Mancini, 1989; Manzano et al., 1997). Because anhydrite is the source of sulfur in the neo-formed sulfur compounds, the $\delta^{34}S$ values of whole oils increase toward the $\delta^{34}S$ of the anhydrite with increasing TSR (Fig. 7; Orr, 1974; Manzano et al., 1997).

CSIA of gasoline-range hydrocarbons is a sensitive method to detect TSR in condensates (Rooney, 1995; Whiticar and Snowdon, 1999). The change in $\delta^{13}C$ due to TSR appears to correlate with both molecular structure and reservoir temperature. Rooney (1995) showed substantial isotopic shifts in the $\delta^{13}C$ of some gasoline-range hydrocarbons in TSR-affected oils relative to the maximum shifts caused by thermal maturation alone. Variations in $\delta^{13}C$ also depended on the types of hydrocarbons. The *n*-alkane and branched hydrocarbons in TSR-affected oils vary in $\delta^{13}C$ by up to 22‰, whereas monoaromatics, such as toluene, show much smaller shifts in the range 3–6‰. Oils not affected by TSR show a maximum increase of 2–3‰ for each molecular species with increasing maturation, whereas much larger shifts occur with increasing reservoir temperature among TSR-affected oils. TSR may accelerate the destruction of some hydrocarbons compared to thermal cracking, with the remaining hydrocarbons becoming enriched in ^{13}C due to higher fractional conversion for each compound. This was supported by much lower concentrations of branched and normal alkanes with increasing reservoir temperature in TSR-affected relative to other oils (Rooney, 1995).

Changes in the composition of gasoline-range hydrocarbons caused by TSR can complicate correlation of condensates. For example, TSR affects the Mango parameters (ten Haven, 1996) as exemplified for crude oils generated from the Upper Devonian Duvernay Formation in Western Canada (Fig. 8). Mango (1987, 1990)

Table 2
Comparison of geochemical changes in liquid hydrocarbons due to increasing thermochemical sulfate reduction or increasing thermal maturation. Stable carbon isotope ratios are presented as delta-values ($\delta^{13}C$) representing the deviation in parts per thousand (‰ or per mil) from a standard

| Parameter	Increasing TSR	Increasing maturity
Saturate/aromatic	Decrease	Increase
Organosulfur compounds	Increase	Decrease
API gravity	Slight increase or decrease	Increase
$\delta^{34}S$ of sulfur compounds	Approaches $CaSO_4$	Little change
$\delta^{13}C$ of saturates	Increase	Increase
$\delta^{13}C$ (CSIA) of gasoline range	Normal/branched alkanes increase up to 20‰, cyclics and aromatic less	2–3‰ for all compounds
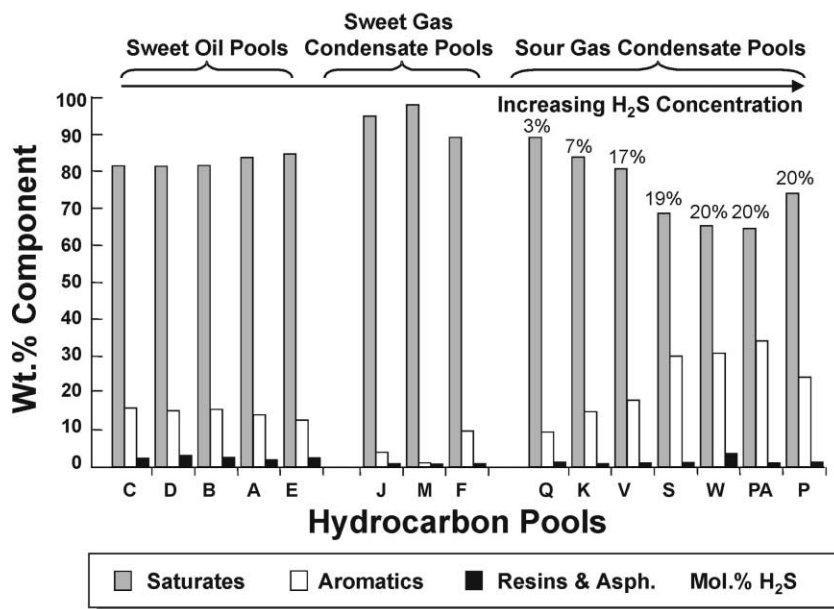
Fig. 6. Gross composition of oils and condensates from Nisku Formation reservoirs in the Brazeau River area of west central Alberta. Pools with higher H_2S (more affected by TSR) have less saturated and more aromatic hydrocarbons than the sweet oil and gas pools (modified from Manzano et al., 1997).

hypothesized that steady-state catalytic isomerization involving metal catalysts controls preferential ring opening of cyclopropane (3-ring) intermediates to form the isoheptanes. Based on this kinetic model (van Duin and Larter, 1997), 2-methylhexane + 2,3-dimethylpentane should co-vary with 3-methylhexane + 2,4-dimethylpentane depending on temperature, as in Fig. 8. Mid-mature Duvernay oils plot in a narrow band just below the $K_1 = 1$ line in the figure. Higher maturity Duvernay oils from the Brazeau River field that are unaffected by TSR plot along a trend similar to the mid-mature oils. Oils that are associated with H_2S plot above the $K_1 = 1$ line. The Peco sample has the highest concentration of H_2S, appears to be most affected by TSR based on CSIA data, and plots farthest from the $K_1 = 1$ Line. Data from other oil families suggest a tendency

for all TSR-affected oils to plot above the $K_1 = 1$ line (Fowler, unpublished results).

3.4.4. Biodegradation

Biodegradation, the alteration of crude oils by microbes (e.g. Milner et al., 1977; Connan, 1984; Palmer, 1993; Blanc and Connan, 1994), is an important process: the amount of biodegraded oil worldwide may exceed that of conventional oil (e.g. Tissot and Welte, 1984; pp. 480–481). Most surface and subsurface biodegradation has been assumed to be due to aerobic activity (e.g. Connan, 1984; Palmer, 19930). For example, Connan et al. (1997) found that deep reservoirs (> 60 °C), contain only anaerobic bacteria and the oils are at most only mildly biodegraded. They concluded that aerobic biodegradation is a dominant process in shallow
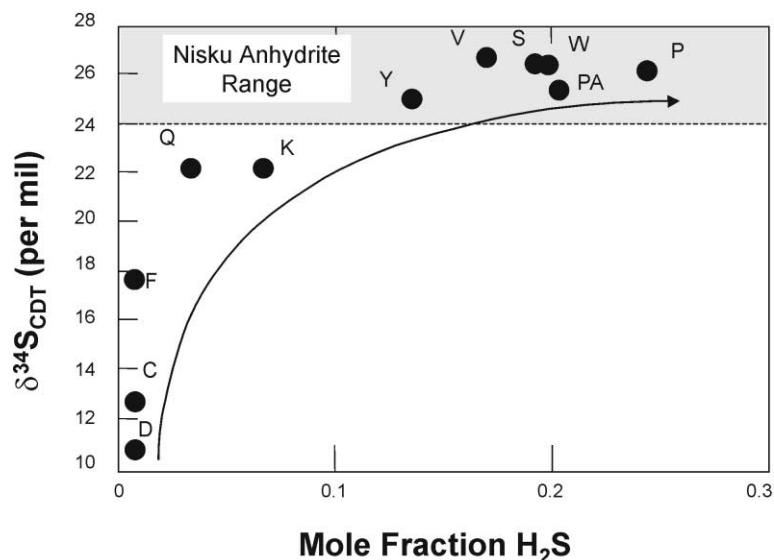
Fig. 7. Variation of $\delta^{34}S$ in crude oils versus hydrogen sulfide concentration for Nisku Formation reservoirs in the Brazeau River area of west central Alberta. The $\delta^{34}S$ of the samples increased from about 10.8–26.3‰ relative to Canyon Diablo Troilite standard (CDT), approaching the $\delta^{34}S$ values of Upper Devonian anhydrite (24–28‰) with increasing H_2S (modified from Manzano et al., 1997).
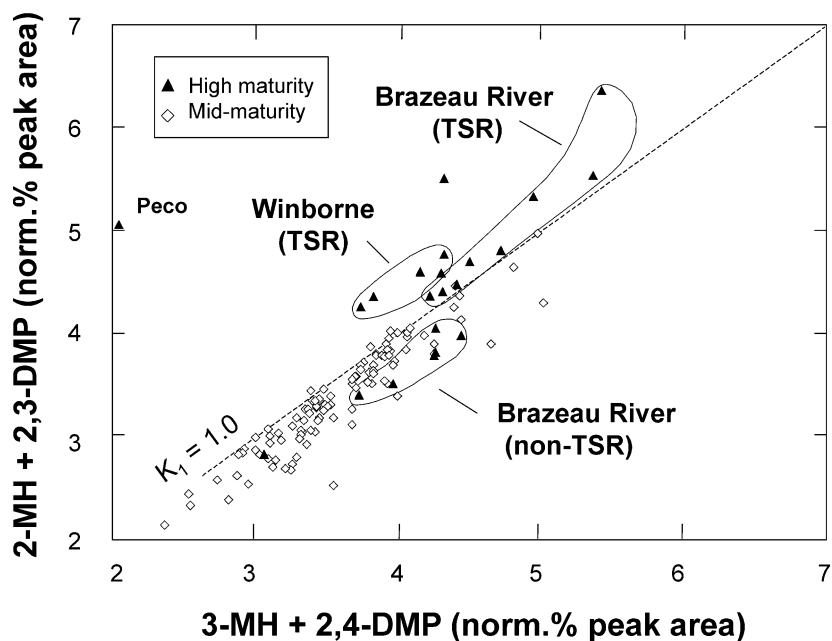

Fig. 8. Plot of 3-methylhexane + 2,4-dimethylpentane versus 2-methylhexane + 2,3-dimethylpentane (Mango parameters) for petroleum generated from the Upper Devonian Duvernay Formation in Alberta. High-maturity, non-TSR light oils and condensates from the Brazeau River area plot near mid-mature oils below the $K_1 = 1$ line. Condensates affected by TSR and light oils from the Winborne field that are associated with high H_2S plot above the $K_1 = 1$ line. Peco condensate was severely altered by TSR and plots far from the other samples (M.G. Fowler, unpublished).

reservoirs, and accounts for many tar sands. Nonetheless, it is difficult to explain how biodegraded accumulations the size of the Alberta tar sands (~269.8 billion m³) could be degraded solely by aerobic

microbes, when small plumes of organic contaminants are sufficient to remove oxygen from near surface groundwater (e.g. Baedecker et al., 1993). It is possible that water may dissociate to provide some oxygen in

deep, nutrient-depleted reservoirs where metabolic rates are low (Larter et al., 2000). Furthermore, recent work suggests that anaerobic biodegradation may be more important than previously thought (e.g. Coates et al., 1996; Caldwell et al., 1998; Zengler et al., 1999).

While aerobic and anaerobic biodegradation mechanisms are still not fully understood, the following conditions appear to be necessary for biodegradation of large volumes of oil at the pool or field scale (Connan, 1984; Palmer, 1993; Blanc and Connan, 1994).

1. The reservoir temperature must be less than about 60–80 °C, which corresponds to depths shallower than about 2000 m under typical geothermal gradients. Biodegradation occurs at higher temperatures, but the rate decreases significantly.
2. There must be sufficient access to nutrients and electron acceptors (e.g. molecular oxygen, nitrates, and phosphates), most likely through circulation of meteoric water into deeper portions of the basin.
3. The reservoir must lack H_2S for aerobic microbes or contain no more than about 5% H_2S for anaerobic sulfate reducers to be active.
4. Salinity of the formation water must be less than about 100–150 parts per thousand.

Thus, biodegradation is observed to be most active in cool, shallower reservoirs flushed by nutrient-rich water. As a consequence, in rare cases where deep reservoirs contain biodegraded oil, the oil was probably biodegraded prior to deep burial.

The rate of biodegradation is not well known. Empirical evidence from surface or near-surface oil spills suggests that biodegradation occurs relatively quickly in environments that are at least partially aerobic with plentiful nutrients (Jobson et al., 1972), while degradation of oil in deep reservoirs is very slow (Larter et al., 2000).

The effects of biodegradation on the physical properties and molecular composition of petroleum are well known (e.g. Volkman et al., 1983; Connan, 1984; Palmer, 1993; Peters and Moldowan, 1993; Peters et al., 1996). With increasing biodegradation, oils become more viscous, richer in sulfur, resins, asphaltenes, and metals (e.g. Ni and V), and have lower API gravities, making them less desirable as refinery feedstocks. The first indications of oil biodegradation normally occur among the light hydrocarbons, where normal alkanes and aromatics are removed first, the latter by water washing as well as microbial action (e.g. Palmer, 1983). Oils that are more biodegraded show changes in the C_{15+} saturated hydrocarbon fraction gas chromatograms. As n-alkanes and acyclic isoprenoids are removed by microbial action, the elevated chromatographic baseline consisting of complex unresolved compounds becomes more pro-

minent. Discrete peaks protruding above the elevated baseline are the more resistant compounds, such as hopanes. Bragg et al. (1994) measured the extent of degradation of hydrocarbons spilled from the *Exxon Valdez* by comparing their abundance to that of hopane. In the initial stages, it is possible to measure the extent of biodegradation among genetically related oils by using the pristane/nC_{17} and pristane/hopane ratios. Brooks et al. (1988b) used these ratios to show greater biodegradation in coarser- compared to finer-grained reservoir lithologies in a heavy oil accumulation (Figs. 9 and 10), although McCaffrey et al. (1996) show that lithology is not the only variable controlling extent of biodegradation. In more severely biodegraded samples, the extent of biodegradation is shown by the progressive removal of specific compound classes, as discussed below.

The susceptibility of saturated hydrocarbon classes to increasing biodegradation is generally thought to be
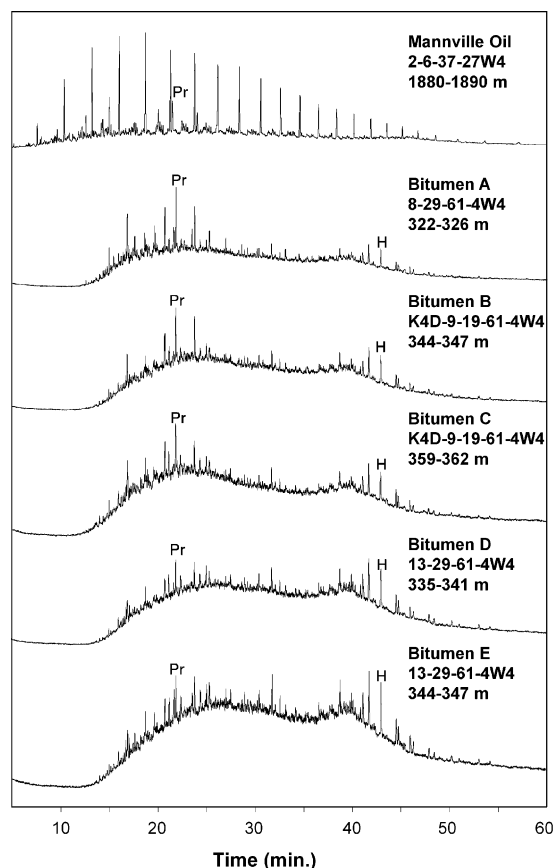

Fig. 9. Saturate gas chromatogram of Mannville formation conventional oil (top) and biodegraded heavy oil (bitumen) samples from the Mannville formation, Fort Kent thermal project of the Cold Lake deposit, Alberta. Pr = pristane, H = 17α(H)-hopane.
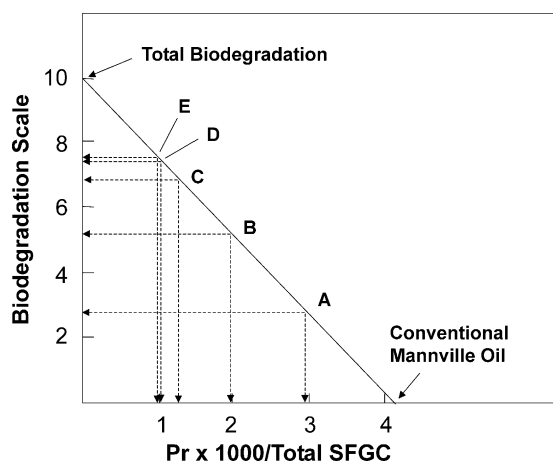
Fig. 10. Pristane×1000/total signal from saturate fraction gas chromatogram (SFGC) versus 0–10 biodegradation scale for six oils (conventional Mannville oil plus biodegraded oils A–E, Fig. 9) from Fort Kent property (Brooks et al., 1988b). Pristane/total SFGC of zero is a value of 10 on the biodegradation scale (i.e. all pristane was catabolized). Pristane/total SFGC of 4.1 is a value of 0 on the biodegradation scale, corresponding to conventional Mannville oil. Oils in coarser-grained lithologies (e.g. E) show more extensive biodegradation. Engineers used this relationship to determine the best strategy to extract bitumen from the property.

n-alkanes > n-alkylcyclohexanes > acyclic isoprenoids > regular steranes > hopanes > rearranged steranes > tricyclic terpanes (Volkman et al., 1984). The sequences of biodegradation and TSR susceptibility are similar because both are oxidation processes. Peters and Moldowan (1993) developed a quasi-stepwise biodegradation scale (levels 1–10), where details of the degradation sequence can vary because of many factors that affect which microbes occur and what compounds are preferentially catabolized.

Fisher et al. (1998) and Trolio et al. (1999) provide examples of biodegraded oils with emphasis on aromatic compounds, such as alkylnaphthalenes and alkylbiphenyls. For example, 4-ethylbiphenyl increases relative to 2- and 3-ethylbiphenyls at Peters and Moldowan (1993) biodegradation level 3-4 and it is the only isomer remaining in Gippsland basin oils biodegraded to level 4-5 (Trolio et al., 1999). The removal sequence for some other aromatic hydrocarbons in biodegraded Dead Sea asphalts is as follows: alkylbenzenes, naphthalenes, benzothiophenes, phenanthrenes, and dibenzothiophenes (Connan et al., 1992). Biodegradation of aromatic steroids was reported by Wardroper et al. (1984). Until that time no biodegradation of triaromatic or ring-C monoaromatic steroids had been reported (Connan, 1984), attesting to their microbial resistance. Triaromatic steroids are generally more resistant to biodegradation than rearranged steranes or tricyclic terpanes (Peters and Moldowan, 1993).

In some severely biodegraded oils microbial alteration of hopanes produces 25-norhopanes, while in other equally degraded oils, 25-norhopanes are absent (Peters and Moldowan, 1993, pp. 258–262; Peters et al., 1996). Hopanes are usually degraded without the formation of 25-norhopanes in the Athabasca tar sands (Brooks et al., 1988a). However, 25-norhopanes occur in one suite of samples in close proximity to significant subsurface water flow, thus possibly allowing different groups of (possibly aerobic) microbes to carry out the degradation (Brooks et al., 1988a). Bost et al. (2001) showed that 25-norhopanes share a common degradation mechanism with regular hopanes in aerobic environments.

Recent papers show the potential of computational chemistry to predict the response of compounds in petroleum to temperature, pressure, and secondary processes in the subsurface (e.g. Peters et al., 1996; Peters, 2000; van Duin and Larter, 2001; Xiao, 2001). For example, Peters et al. (1996) used molecular mechanics and quantum structure activity relationships to investigate the formation of 25-norhopanes. They showed that C-25 demethylation by microbes occurs preferentially among low molecular-weight hopanes (e.g., C_{31}), while higher homologs are progressively more resistant, and that this demethylation is stereoselective. The 22S epimers of the C_{31} and C_{32} hopanes are preferentially demethylated compared to 22R, while the opposite applies to C_{34} and C_{35}. Geometry-optimized structures of the C_{31}–C_{35} hopane 22S and 22R epimers from molecular mechanics force-field calculations result in distinct scorpion- versus rail-shaped conformations, respectively. Because 22S epimers of the extended hopanes tend to favor the scorpion conformation, which folds the side chain back toward the C-25 position, longer side chains appear to increasingly hinder C-25 from microbial attack.

In many cases, heavy oil is a mixture of biodegraded and nonbiodegraded crude oils, indicating a complex filling history. Geochemistry can be used with other methods (e.g. fluid inclusions, thermal modeling, seismic) to describe the filling history of these reservoirs. For example, most fields in the Jeanne d'Arc basin, offshore eastern Canada, have stacked reservoirs that were connected by faults at various times in the past. API gravity generally increases with depth and nearly all reservoirs shallower than 2000 m (<80 °C) contain biodegraded oil. Many shallow oils are undergoing biodegradation today. Some reservoirs toward the basin center at depths over 2000 m contain mixtures of biodegraded and nonbiodegraded oils, where present-day temperatures are too high for biodegradation. For example, saturate gas chromatograms and gross compositions of liquids collected from three drill stem tests in three separate Cretaceous reservoirs show mixing of biodegraded and nonbiodegraded oil in the Mara M-54 well (Fig. 11) (Von der Dick et al., 1989; Fowler et al.,

1998b; Shimeld and Moir, 2001). Biomarker and other data indicate that the two deeper reservoirs in the well originally received a pulse of lower maturity crude oil than that in the shallowest reservoir. Gross compositional data indicate that the two deeper oils are also more biodegraded, although *n*-alkanes remain. This low maturity oil (~25°API) was biodegraded when the two deeper reservoirs were less than 1000 m deep (Shimeld and Moir, 2001). Upon further burial, these reservoirs received a second pulse of more mature oil. More of this high-maturity oil occurs in the DST-2 (drill stem test) than the DST-1 reservoir based on the lower API gravity and the gross composition of DST-1. Because of the greater depth of the reservoirs when the second pulse of oil arrived, these oils were not significantly biodegraded. The shallowest reservoir (DST-3) did not receive the original oil pulse and hence contains only oil from the second pulse. The higher maturity of this oil is evident from biomarker parameters (Fig. 11). Because this reservoir is shallow (<2000 m), the oil is biodegraded.

A scenario similar to that at the Mara M-54 well is thought to occur nearby at the larger Hebron accumulation. Optical fluorescence indicates three populations of oil inclusions in the Ben Nevis formation in the Hebron area. The first oil to be entrapped had intermediate gravity (~25–30°API) and was followed by a second, higher gravity oil (~35–45°API). Both oils were subsequently biodegraded to generate a heavy oil (15–20°API). Detailed Late Cretaceous-Cenozoic biostratigraphy, apatite fission track data, and thermal modeling support this scenario of two phases of oil generation and migration separated by uplift, erosion, and biodegradation. 3D-seismic analysis revealed a Late Cretaceous surface with features suggesting subaerial exposure. This facilitated a risk assessment model for biodegradation in the Jeanne d'Arc basin (Shimeld and Moir, 2001).

Some crude oils produced from Tertiary reservoirs in the North Sea contain 25-norhopanes despite relatively low levels of biodegradation. Rather than invoking two pulses of oil as described above for the Jeanne d'Arc basin, Mason et al. (1995) suggested that different parts of the oil column were biodegraded to varying degrees. Based on geochemical analysis of DST samples from different intervals, the produced oil was thought to represent the entire oil column, rather than oil from individual DST zones.

3.4.5. Primary and secondary migration

Petroleum accumulations generally occur in reservoir rocks that are some distance from the source rock. Primary migration is the expulsion of petroleum from the fine-grained source rock into rocks with higher porosity and permeability. Some workers advocate models based on diffusion through a continuous 3D-kerogen network (Stainforth and Reinders, 1990), while most assume a relationship between petroleum saturation and relative
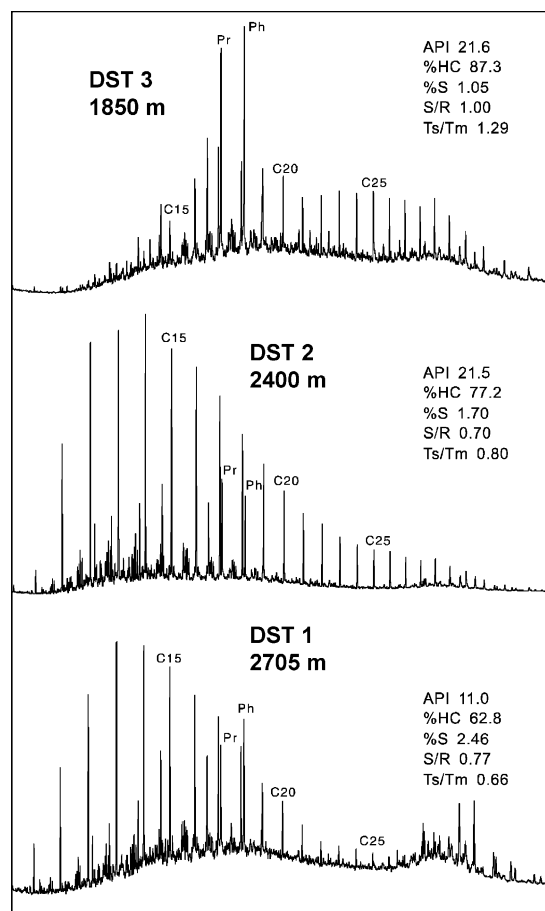

Fig. 11. Saturate gas chromatogram of three oils from Mara M-54 well, Jeanne d'Arc basin, offshore eastern Canada. %HC = weight percent saturated and aromatic hydrocarbons, %S = wt.% sulfur, S/R = C_{29} 5α(H),14α(H),17α(H) 20S/20R steranes, Ts/Tm = 18α(H)-trisnorneohopane/17α(H)-trisnorhopane.

permeabilities to oil, gas, and water (Welte, 1987; Doligez et al., 1986). Although controversial, key factors in expulsion include the amount and type of organic matter in the source rock, its relative permeability for petroleum, the viscosity of the generated petroleum, and the minimum amount needed to saturate the pore space (Palciauskas, 1985; Rudkiewicz and Behar, 1994; Pepper and Corvi, 1995). Hydrous pyrolysis is a laboratory simulation of petroleum generation than may be useful to evaluate natural expulsion (Lewan, 1994).

Secondary migration is a controversial process that involves the movement of petroleum within permeable carrier beds to the reservoir (Wendebourg and Harbaugh, 1997, and references therein). It occurs over distances from a few kilometers to hundreds of kilometers, although typically it is on the order of tens of kilometers. Although rates of secondary migration are likely to be highly variable (England et al., 1991), laboratory

experiments suggest that they are rapid on a geologic time scale (e.g. Dembicki and Anderson, 1989).

Petroleum composition can be altered by secondary migration due to differences in pressure, volume and temperature (Glaso, 1980) or geochromatography (Bonilla and Engel, 1986; Kroos et al., 1991). There is considerable evidence for compound class fractionation during primary migration, such as preferential loss of NSO-compounds (nitrogen-sulfur-oxygen) from source-rock bitumen to expelled oil (Hunt, 1996, and references therein). However, geochromatographic fractionation of similar compounds during secondary migration is more difficult to verify (Kroos et al., 1991), partly because of potential mixing of migrated petroleum with other components along the migration pathway.

Physical processes can also fractionate petroleum during migration. As petroleum migrates upward, temperature and pressure decrease. If the bubble point is reached, a single phase fractionates into liquid and gas phases that can migrate separately. Partitioning of petroleum between these phases depends on the vapor-equilibrium constants for each component (Thompson, 1987). This can result in reservoirs filled with petroleum from a common source, but with different gross compositions. The effects of evaporative or phase fractionation were described based mostly on laboratory experiments (e.g. Thompson, 1987; Larter and Mills, 1991; van Graas et al., 2000). The process leads to oils deficient in light ends and enriched in aromatics, as exemplified by many U.S. Gulf Coast oils (Thompson, 1987, 1988).

3.4.6. Migration distance and reservoir filling history

For petroleum exploration, it is desirable to know the distance, direction, and timing of secondary migration. Some indication of distance and direction can be obtained once an oil-source correlation has been made (e.g. Fig. 2) and the maturity of oil and regional maturity of the source rock is known. For example, Upper Cretaceous oils in the Western Canada basin are thought to have migrated up to 400 km from their source rocks in the Rocky Mountain foothills of Alberta to reservoirs in southwest Saskatchewan based on this concept (Allan and Creaney, 1991). These large distances are not unusual for foreland basin settings, while shorter distances with a relatively large vertical component are more common in rift basins (Hunt, 1996, pp. 281–287).

Using the above approach, Horstad et al. (1995) generated a migration/fill scenario for the Tampen Spur area in the North Sea. Various techniques, including gas chromatography, GCMS, and stable carbon isotopes, identified several petroleum populations within the study area. For example, biomarker maturity parameters for the Snorre field, such as C_{30} diahopane/(C_{30} diahopane + C_{29}-moretane), show that reservoirs in the northern part of the field filled with higher maturity oil

than those in the southern part. Horstad et al. (1995) combined this result with gas-to-oil ratios (GOR) and the locations of oil-water contacts to conclude that the Snorre field received oil from at least two fill points. A similar study for the Beryl Complex is discussed below.

A multiple source-rock model combined with detailed compositional studies of oils and gases improved understanding of the reservoir filling history and continuity in the Beryl Complex in the South Viking Graben in the North Sea, United Kingdom (Walters et al., 1999). The two primary source rocks in the area are the Kimmeridge Clay and Heather formations. The study confirmed that the Kimmeridge Clay contains Type II and IIS kerogen, where early expulsion may occur as low as ~90 °C with peak expulsion at ~120 °C. The Heather formation has lower generative potential and contains Type II/III kerogen. Thermal modeling shows that expulsion from the Heather Formation requires higher temperatures than are necessary for the Kimmeridge Clay, i.e. initial and peak expulsion at ~120 °C and ~140–150 °C, respectively.

Light hydrocarbon and biomarker data from oil samples provide evidence for the charging history of the Beryl Complex (Fig. 12). Multivariate analysis of these data shows that most of the variance is described by the first principal components represented by these two different molecular-weight fractions. The data indicate that oils from the East Flank originated mainly by single migration events because the source of the light hydrocarbons and biomarkers is consistent with a single maturity phase of generation. Oils from Bravo and western satellite fields received two oil pulses: mature oil from the Kimmeridge Clay and Heather formations, and highly mature light oil, mostly from the Heather.

Migration timing and pathways were inferred based on the filling histories derived from the multiple-source model (Fig. 13). The first pulse of oil (white arrows) came from the Frigg kitchen and filled structures west of the central ridge along the East Flank. The second pulse (hatched arrows) came from the same direction, but recharged the Bravo and western satellite fields with highly mature oil. The third pulse (black arrows) is low-maturity oil from Kimmeridge clay in the Beryl kitchen. These oils migrated to fill the Lewis reservoirs along the eastern edge of the East flank. None of these oils migrated across the structural high. Oils from local sources of low maturity Kimmeridge Clay on the East flank (S33) and within the central trough migrated short distances into adjacent reservoirs.

Benzocarbazoles can be used to measure the distance of secondary oil migration. The benzocarbazole ratio, {benzo[a]/(benzo[a] + benzo[c]carbazole)}, and concentrations of these pyrrolic nitrogen compounds decrease with oil migration distance in the North Sea and Western Canada basin (Fig. 14). Larter et al. (1996) believed that this was most likely due to different
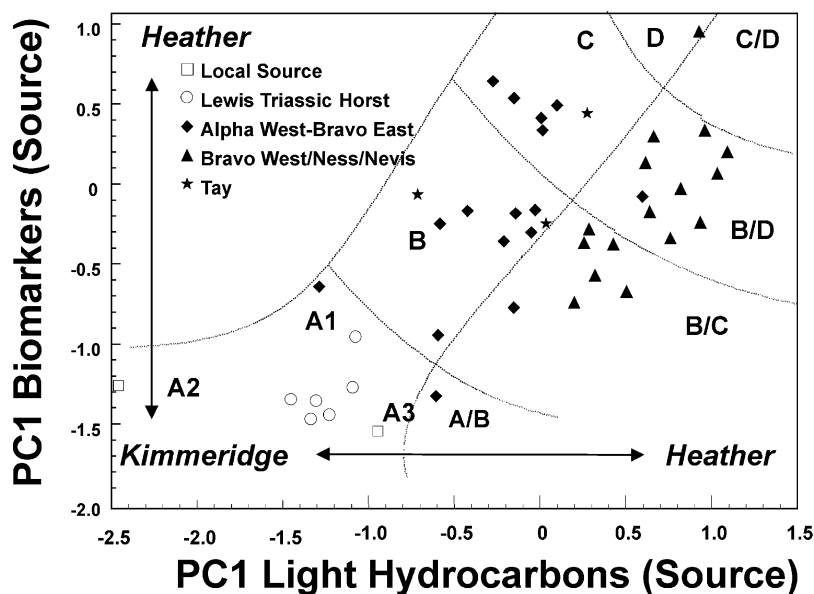
Fig. 12. Principal component plot of light hydrocarbon and biomarker data provides evidence for the filling history of the Beryl Complex, North Sea (C.C. Walters, 2001, personal communication). Labels in fields separated by dashed lines refer to oil families (e.g. A, B, C, D), subfamilies (e.g. A1, A2, A3), or mixtures (e.g. A/B, B/D).

adsorption characteristics of benzocarbazoles on mineral surfaces, but more recent molecular dynamics studies suggest that oil-water partitioning may be more important (van Duin and Larter, 2001). Terken and Frewin (2000) used benzocarbazole, seismic, and thermal modeling data to help focus exploration along selected migration paths in Oman. Li et al. (1997) and Clegg et al. (1998) caution that varying source input or thermal maturity along the migration pathway could cause effects similar to migration on benzocarbazole distributions. Therefore, source and maturity must be constrained by other geochemical data before using benzocarbazoles for migration studies. For example, changes in lithology and geometry of migration conduits along migration pathways affect the apparent migration distance of oils of similar maturity and source along the Rimbey-Meadowbrook Trend (Li et al., 1998).

Fowler et al. (1998a) explained API variations in an Ordovician oil field in the southwest Saskatchewan portion of the Williston basin based on variable migration distances. All of the oils in Red River reservoirs within the Upper Ordovician Yeoman Formation in the Midale area have a kukersite-type source similar to that in close stratigraphic proximity to the reservoirs. Despite this and the limited geographic extent of the field (~100 km^2), these crude oils show a wide range of API gravity (26–42°API), which reflects a comparably broad range of maturity as indicated by gross composition, gasoline-range hydrocarbons, and biomarker data (Fig. 15). Oils with intermediate maturity appear to be

mixtures of the high- and low-maturity end members. Based on a maturity map of the kukersite source rocks in the Yeoman formation, the low-maturity oils originated locally, while the high-maturity oils migrated 50 km or more from the south. Analyses of benzocarbazoles (Fig. 16) and optical fluorescence of fluid inclusions trapped in diagenetic cements in the Yeoman formation source rocks and carrier beds support this hypothesis. Mixing of the oils is thought to occur during migration because of the close proximity of the carrier beds to the source rocks.

Phenols can also be used to estimate relative migration distances. Taylor et al. (1997) observed a systematic decrease in the total C_0–C_3 alkylphenol concentrations in four North Sea oils with increasing migration distance, but little effect on the relative distributions of the phenols. Galimberti et al. (2000) observed some variations within the distributions of phenols and used a molecular migration index (MMI, o-creosol/phenol ratio) to infer a migration trend for some North Sea oils.

Analysis of petroleum in fluid inclusions is another method to elucidate complex filling and migration histories. Oil inclusions formed in different authigenic silicate phases during subsidence of the reservoir in the Ula Field from the North Sea showed different geochemical characteristics (Karlsen et al., 1993; Nedkvitne et al., 1993). These results suggest an initial pulse of oil to the reservoir that was diluted by later oil from a different source rock. George et al. (1997) showed that source and maturity-related geochemical characteristics of DST
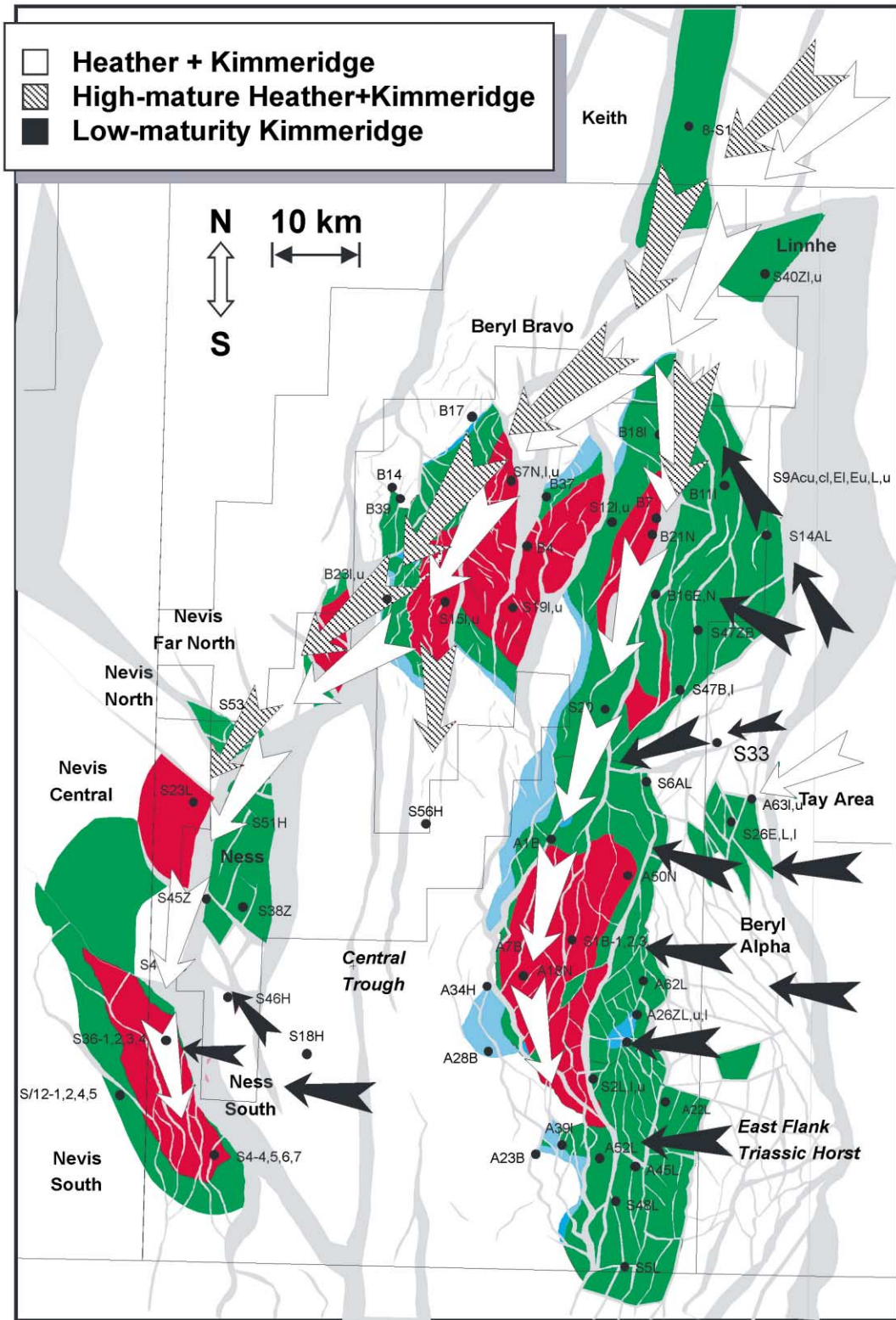
Fig. 13. Migration and timing pathways for the Beryl complex, indicated by arrows, were derived from the multiple source model (C.C. Walters, 2001, personal communication). Red = gas, green = oil, gray = faults, blue = water.
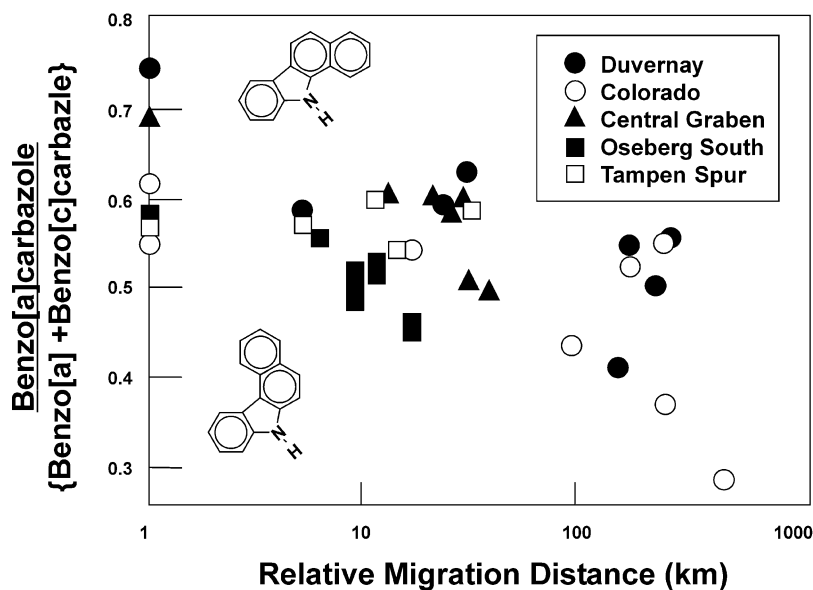
Fig. 14. The benzocarbazole[a]/[a + c] ratio for oils from five petroleum systems in western Canada and the North Sea versus estimates of secondary migration distance to the reservoir relative to a reference oil nearest the source rock. The reference oil is given an arbitrary migration distance of 1 km. Structures for benzo[a]carbazole (top) and benzo[c]carbazole (bottom) are shown. Modified and reprinted with permission from Nature (Larter et al., 1996) Copyright 1996 Macmillan Magazines Limited.

oils and oils in fluid inclusions from a sandstone reservoir differed, implying at least two different petroleum pulses to the structure. Because no chromatographic techniques are suitable to analyze the small quantities of extract from single fluid inclusions, Jones and Macleod (2000) developed a crush-leach methodology that minimizes contributions of petroleum other than that in the inclusions.

3.5. Sample contamination

Contamination can occur naturally during petroleum migration, or during drilling, collection, or handling of the samples. For example, biomarker analyses of light oils and condensates can be unreliable due to migration contamination. The high maturity of many condensates results in mainly gasoline-range components with few biomarkers. Condensates may extract biomarkers from less mature carrier or reservoir rocks during migration (Peters and Moldowan, 1993). Because indigenous biomarkers are already low in condensates, contaminating biomarkers may adversely affect various interpretations, including correlation, source organic matter input, and thermal maturity. For example, Curiale et al. (2000) noted that classical biomarker parameters indicated unreasonably low thermal maturity for a suite of light oils from Brunei. They concluded that biomarker parameters reflected the present-day maturity of the reservoirs rather than that of the source rock(s) for the oils due to migration-contamination, where the oils acted as solvents to extract low-maturity biomarkers during

migration. They relied on bulk parameters and abundant components (e.g. n-alkanes and acyclic isoprenoids) that were not readily overprinted by contaminating compounds to determine characteristics of the source rock.

Oil-based muds (OBM) are commonly used to enhance borehole stability, reduce drilling time, and cut drilling costs. Diesel is commonly used as the base oil. More recently, other more environmentally friendly materials have been used, including Biovert, an emulsion of water and highly paraffinic, low aromatic mineral oil. OBM has a major effect on analyses of drill cuttings, but can also affect core and DST oil samples. This problem increases as more organic materials are used during drilling, particularly in offshore areas where drilling is especially costly.

Intervals affected by OBM are usually apparent on Rock-Eval pyrolysis and TOC logs of well cuttings, based on high S1 and production index [PI = S1/(S1 + S2)] values (e.g. Fig. 17). Extraction of samples contaminated by OBM commonly gives a saturate gas chromatogram with a hump of unresolved compounds corresponding to the distillation cut of the base oil. For example, samples contaminated by Biovert show a hump in the C_{13}–C_{16} n-alkane region (Fig. 18a). Biomarkers commonly elute from gas chromatographic columns long after the base oil, resulting in little interference. However, interpretations of thick intervals affected by OBM may be complex because OBM can act as a solvent during mud circulation, thus homogenizing biomarkers over the open-hole section of the well.
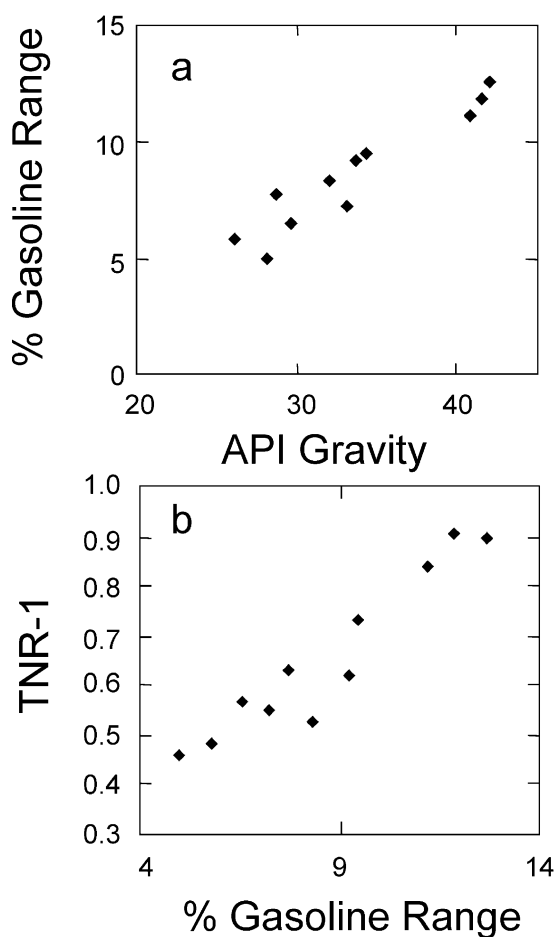
Fig. 15. Plots of (a) API gravity versus %gasoline-range hydrocarbons, and (b) %gasoline-range hydrocarbons versus TNR-1 (trimethylnaphthalene ratio) for Yeoman formation oils in the Midale area of southwest Saskatchewan, Canada. %gasoline range = C_6 and C_7 relative to total integrated hydrocarbons from gas chromatography; TNR-1 = 2,3,6-TMN/ (1,4,6-TMN + 1,3,5-TMN) (Alexander et al., 1985). The plots indicate that there are two oil end members, both having the same source: lighter, more mature ($\sim 42°$ API) and heavier, less mature oils ($\sim 26°$ API). Most oils have intermediate gravity or maturity and are thought to be mixtures (Fowler et al., 1998a).
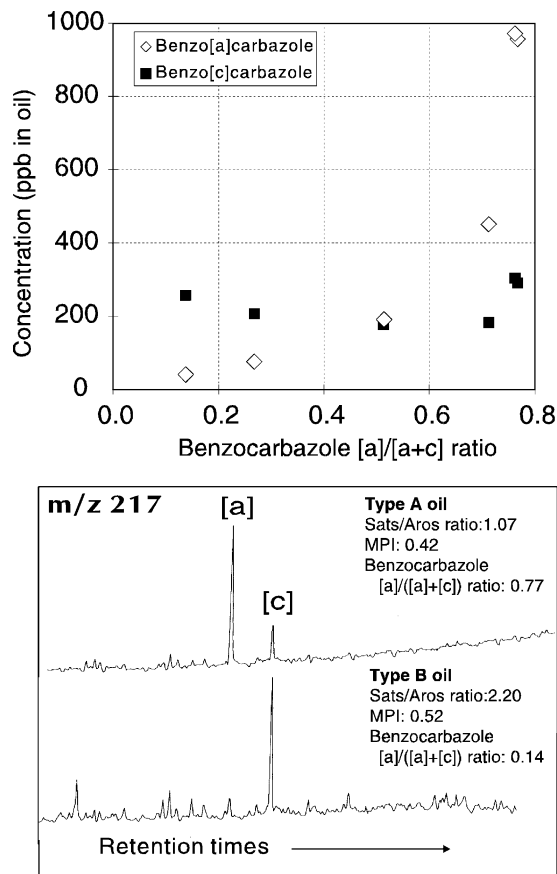

Fig. 16. Benzocarbazole data for low-maturity oil that was locally generated (Type A) and high-maturity oil that underwent long-distance migration (Type B) show that the concentration of benzocarbazoles and the benzocarbazole[a]/[a + c] ratio are lower in the Type B oils (Fowler et al., 1998a). Larter et al. (1996) also found lower benzocarbazoles and benzocarbazole[a]/[a + c] ratios in oils that had migrated long distances in western Canada and the North Sea (Fig. 14).

Occasionally, DST oil samples are affected by OBM. The saturate gas chromatogram of 14° API gravity oil from DST 1 in the Springdale M-29 well, Jeanne d'Arc basin is dominated by light hydrocarbons (Fig. 18b) and resembles that for extracts from cuttings contaminated by Biovert (Fig. 18a). This well was drilled with Biovert OBM, which acted as a solvent, enabling some of the biodegraded oil to be obtained as a DST sample.

Common organic drilling additives include lignite, asphalt, rubber, walnut hulls, diesel, and paint. An extreme case of contamination by asphaltic material occurred during the drilling of Lancaster F-70, a well in

the Flemish Pass, offshore Canada. A lubricant called Superlube was used in the lower part of this well. Superlube is gilsonite, a heavy, low-mature oil generated from Green River lacustrine source rocks (Uinta basin, Utah), that was used with a light base oil as a solvent. Over the depth range where this material was employed, cuttings samples resembled road asphalt. Extracts of these cuttings gave biomarker distributions that were characteristic of the Green River lacustrine palaeoenvironment, an unlikely depositional analog for any rocks in the Flemish Pass area (Fowler, 1993).

Geochemical differences between oil samples (e.g. DST and RFT samples) and reservoir core extracts from the same horizon are common (Larter and Aplin, 1995, and references therein). These differences commonly are not caused by contamination, but simply reflect different gross compositions, where core extracts are enriched in
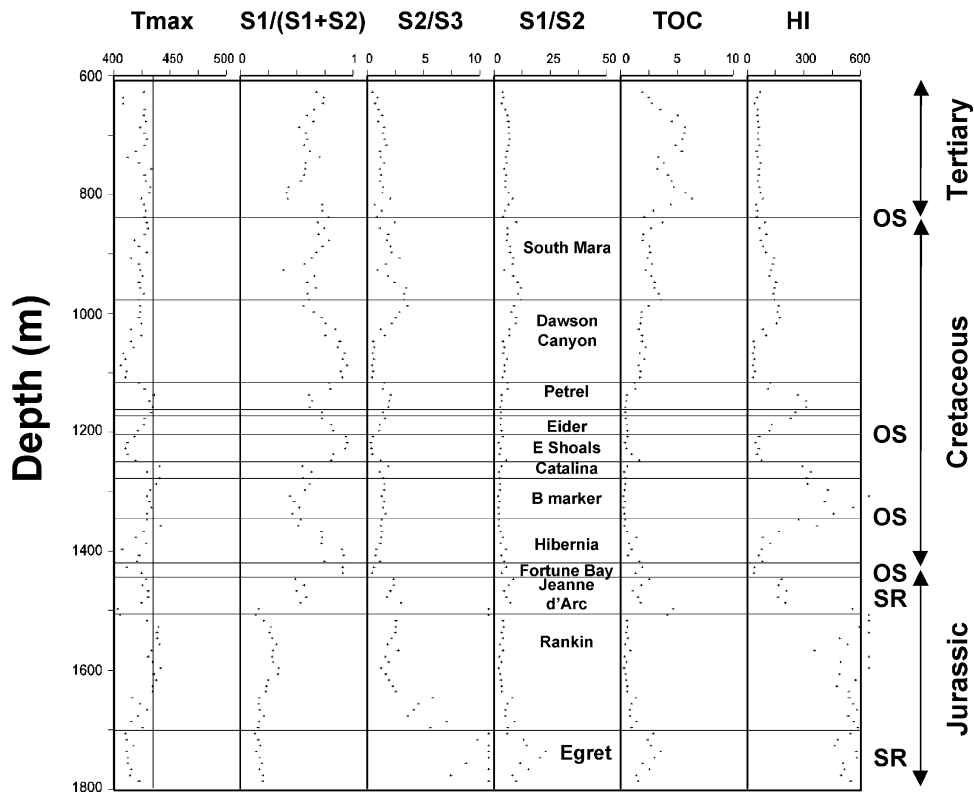
Fig. 17. Rock-Eval/TOC log based on cuttings samples from the South Brook N-30 well, drilled in the Jeanne d'Arc basin, Canada, using Biovert OBM. Contamination by the base oil caused high S1/(S1 + S2) values throughout the section. Elevated TOC, HI and S2/S3 values near 1500 m and from 1700 m to TD are due to Upper Jurassic Jeanne d'Arc and Egret source rocks, respectively. SR = source rock, OS = oil stain.

NSO-compounds compared to oil samples. However, Bayliss (1998) also noted differences in biomarker ratios between core extracts and DST oil samples, apparently caused by mobilization of materials in the cores that are not present in the oils.

4. Geochemistry applied to reservoir management

The amount of petroleum that can be recovered from reservoirs ranges from 10% to 80%, but the global average may be as low as 20% (Miller, 1995, and references therein). Petroleum geochemistry offers rapid, low-cost assessment of reservoir-related issues that can increase recoveries of the vast amounts of petroleum abandoned in reservoirs as unrecoverable. Geochemistry is particularly useful to complement information from reservoir engineering and has become more reliable as a result of improved chromatographic and statistical methods. However, the fundamental gas chromatographic pattern recognition or fingerprinting approach remains the same. Some technology milestones in reservoir geochemistry are listed below.

- vertical and lateral fluid continuity (Slentz, 1981; Ross and Ames, 1988; Halpern, 1995)
- proportions of commingled production from multiple zones and leaky casing (Kaufman et al., 1990)
- oil quality in different reservoir zones and heavy oil accumulations (Karlsen and Larter, 1990; Baskin and Jones, 1993; BeMent et al., 1996; McCaffrey et al., 1996; Guthrie et al., 1998; Jarvie et al., 2001)
- gas/oil and oil/water contacts (Baskin et al., 1995)

The following discussion provides some examples of how petroleum geochemistry contributes to the solution of reservoir problems.

4.1. Reservoir continuity

Different fluid compositions within a field imply compartmentalization. These differences can be studied in screening mode (e.g. fluid inclusions; Barclay et al., 2000) or using more detailed gas chromatographic fingerprint methods (e.g. Kaufman et al., 1990; Halpern, 1995). Identifying these compartments and their distribution can help to guide the development of reservoirs, because it allows more accurate estimates of
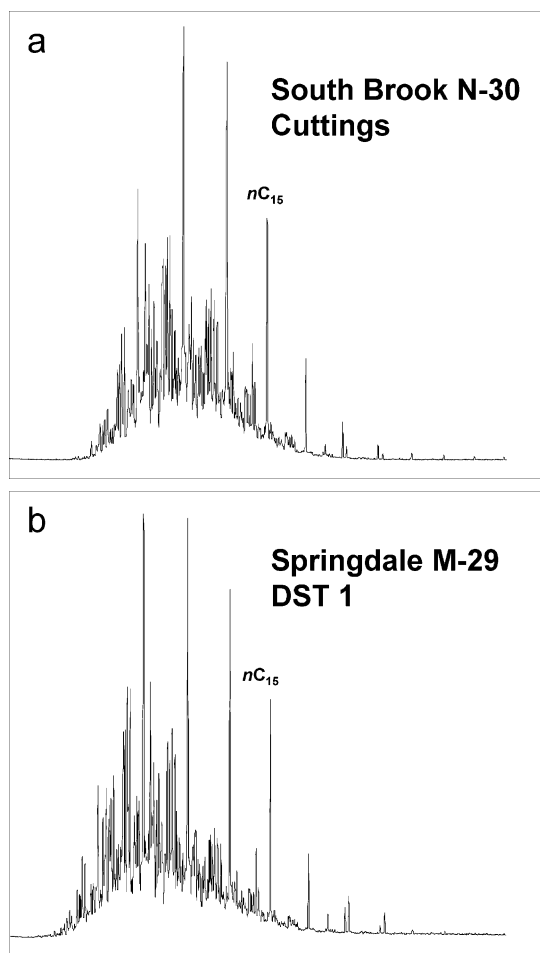
Fig. 18. Saturate gas chromatogram from the extract of a cuttings sample (from the South Brook N-30 well) that was contaminated during drilling by Biovert OBM (a) and Springdale M-29 DST 1 oil, Jeanne d'Arc basin, offshore eastern Canada (b).

reserves, better production strategies, and a baseline for evaluation of future production problems. For example, geochemical analyses of petroleum from different portions of reservoirs can be used to identify bypassed reserves near previously discovered accumulations. Use of existing platforms, pipelines, and/or refineries in the area might then make such new reserves economic. Enhanced understanding of migration directions can improve ranking of exploration or development targets.

Halpern (1995) proposed five C_7 gas chromatographic correlation ratios and eight C_7 process (transformation) ratios that can be used to study reservoir continuity and alteration processes (Table 3). To distinguish small numbers of samples, these correlation and process ratios can be plotted using polar coordinates on C_7 oil correlation or C_7 oil transformation star diagrams, respectively. For more than about one or two dozen samples,

dendrograms (e.g. Fig. 3) are more convenient to visually distinguish groups.

Halpern (1995) used C_7 correlation and star diagrams to determine the source of casing leakage in several Arabian fields and to correlate oils and condensates in Saudi Arabia and the Red Sea. Wever (2000) used Halpern ratios and star diagrams to differentiate oils and condensates from Egyptian basins in the Gulf of Suez, the Western Desert, and the Nile Delta.

Halpern ratios and star diagrams provide a framework to investigate correlations and reservoir alteration processes, but should not be used alone. Supporting evidence might include biomarker and isotopic data, as well as a consistent geologic model. For example, Carrigan et al. (1998) used Halpern ratios and stable carbon isotopic data to show systematic differences among condensates from the Devonian Jauf reservoir in the giant Ghawar Field, Saudi Arabia. Although all of the condensates originated from the basal organic-rich hot shale of the Qusaiba Member in the Silurian Qalibah Formation, the data show distinct north-south trends indicating at least six compartments within the reservoir that do not allow mixing of the trapped hydrocarbons. The geochemical differences between condensates in these compartments indicate distinct migration pathways into the reservoir that drained different areas of the source kitchen. Early identification of these compartments assists design of efficient production strategies.

We studied DST samples from the Sable Island E-48 well from the Scotian Shelf, offshore Eastern Canada, where fifteen zones were tested in the depth range 1460–2285 m. Using the Halpern correlation parameters, most of the DST samples cluster tightly within a narrow band (Fig. 19) that includes both degraded and nondegraded fluids. DST 1 and 9 define a second petroleum group. Numerically, the ratios are not very different; however, the variance is clearly evident when plotted on the star diagram. DST 1 and 9 correlate well, even though DST 1 lost appreciable volatile hydrocarbons during sampling and/or storage.

DST 2, 10, and 11 appear to be mixtures of the two end-member fluid groups based on the correlation parameters. By taking the averaged, normalized values for each Halpern correlation ratio, the percent contribution of each end-member to the mixed samples was estimated by minimizing the combined error. Following this procedure, DST samples with intermediate compositions can be expressed as DST 11 = 67%, DST 10 = 38%, and DST 2 = 23% of the end-member composition defined by DST 1 and 9.

4.2. Commingled production

Kaufman et al. (1990) used gas chromatography and matrix mathematics to deconvolute mixtures of oils

Table 3
Halpern (1995) C_7 ratios used for polar plots (star diagrams) to differentiate oils

Name	Ratio	ΔBP (°C)	ΔSolubility (ppm)	Process
TR1	Toluene/X	22.8	496	**Water washing**
TR2	n-C_7/X	10.6	−21.8	
TR3	3-Methylhexane/X	4.0	−21.4	
TR4	2-Methylhexane/X	2.2	−21.5	
TR5	P2/X	(3.2)	(−21.4)	Evaporation
TR6	1-*cis*-2-Dimethylcyclcopentane/X	11.7	−11.0	
TR7	1-*trans*-3-Dimethylcyclcopentane/X	3.0	−4.0	
TR8	P2/P3	(6)	(−2.4)	
C1	2,2-Dimethylpentane/P3	(−5.8)	(−0.6)	
C2	2,3-Dimethylpentane/P3	(4.8)	(0.3)	
C3	2,4-Dimethylpentane/P3	(−4.5)	(−0.6)	Correlation
C4	3,3-Dimethylpentane/P3	(1.1)	(0.9)	
C5	3-Ethylpentane/P3	(8.5)	(−2.0)	

X = 1,1-dimethylcyclopentane, boiling point = 87.8 °C, solubility = 24 ppm; P2 = 2-methylhexane + 3-methylhexane, boiling point = 91 °C, solubility = 2.6 ppm; P3 = 2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 3,3-dimethylpentane + 3-ethylpentane, boiling point = 85 °C, solubility = 5 ppm; ΔBP = boiling point of numerator; −boiling point of denominator (°C) ΔSolubility = solubility of numerator −solubility of denominator (ppm in distilled water); ( ) Average value for mixtures
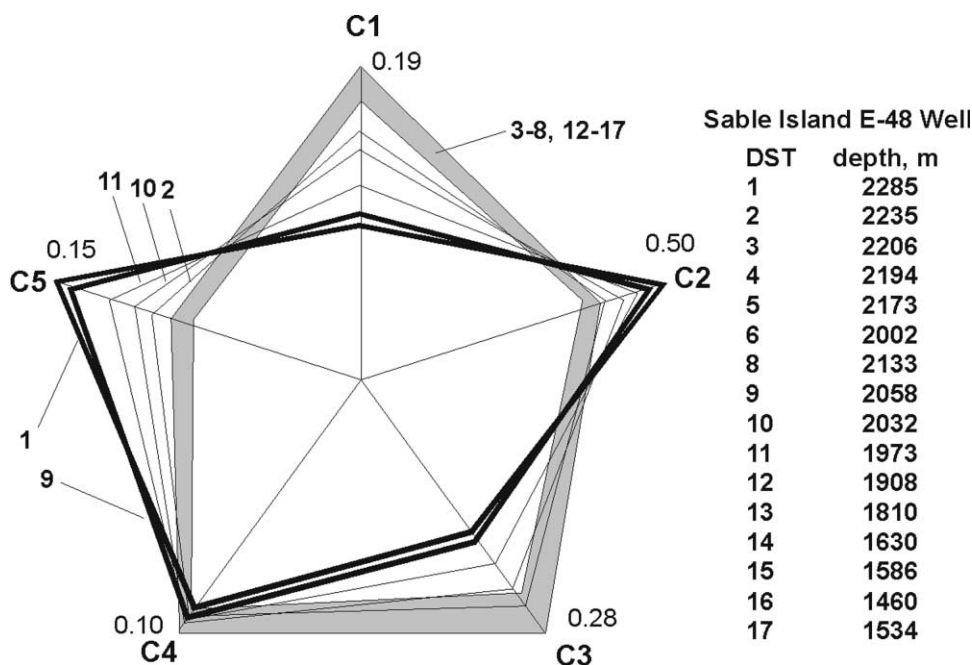

Fig. 19. Halpern C_7 oil correlation star diagram for DST samples from the Sable Island E-48 well, Scotian Shelf, Canada. The numbers at the end of each axis are endpoint values for individual ratios. Two end-member oil groups are apparent. One group includes DST samples from depths of 1460-1908 m and 2133-2206 m (DST 3-8 and 12–17, gray area). The other end member consists of DST 1 and 9. DST 2, 10, and 11 consist of mixtures of the two end-member fluids.

caused by leakage of production string in a dual producing well from the Gulf of Mexico. They selected several pairs of gas chromatographic peaks that maximized the differences among analyzed samples. The peaks in each pair had similar chromatographic elution times so as to minimize differences caused by secondary effects, such as preferential evaporation of light versus heavy compounds after collection. Because of natural variations in petroleum composition, the specific peaks selected for one study commonly differ from those used for another.
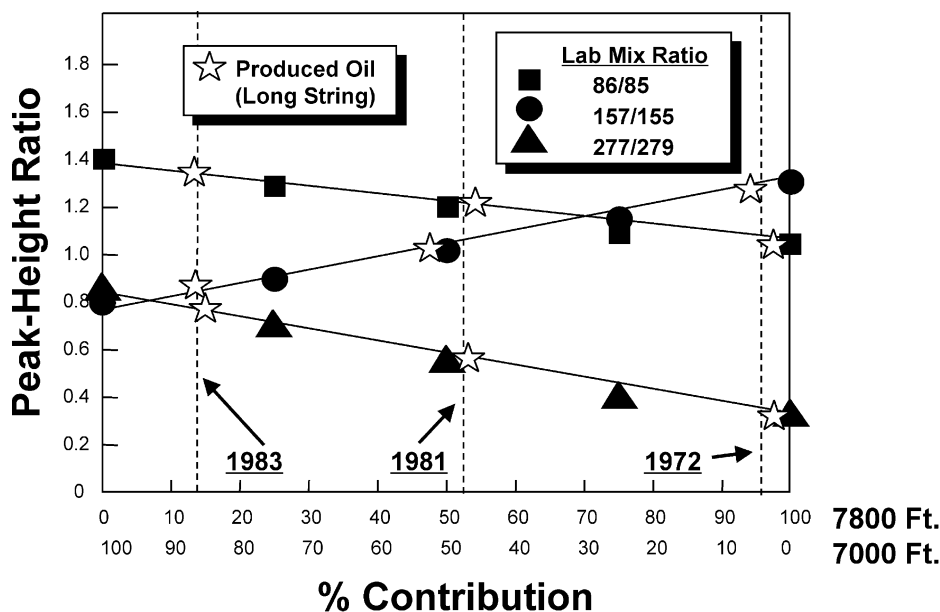
Fig. 20. Calibration of three gas chromatographic peak-height ratios indicates the degree of mixing of two end-member crude oils caused by leakage in a dual producing well in the Gulf of Mexico. In 1967, prior to leakage, oils from the 7800 and 7000-ft sandstone reservoirs had distinct ratios indicated by the solid symbols at the far right and left, respectively. Laboratory mixtures of these oils gave values for each ratio indicated by the solid symbols that are connected by lines. Oil samples collected from the 7800-ft sandstone after 1967 (open symbols) yield distinct values for these chromatographic peak-height ratios, indicating little or no leakage in 1972, a 50:50 mixture in 1981, and a 13:87 mixture in 1983 dominated by 7000-ft oil (see also Fig. 21). Modified from Kaufman et al. (1990) and reproduced with the permission of the Gulf Coast Section Society of Economic Paleontologists and Mineralogists Foundation.

Identification of the compounds represented by the peaks is less important than their use as a pattern recognition tool. The resulting gas chromatographic peak-height ratios, with precision in the range 1–3%, were calibrated using laboratory mixtures of oils from the 7000 and 7800-ft sandstone reservoirs collected in 1967 prior to suspected leakage (Fig. 20, black symbols). For simplicity, the figure shows only three of the sixteen peak-height ratios used. The fit of data for stored oils obtained after leakage indicates relative contributions from each reservoir interval through the production history (star symbols). Mixing of oil from the different tubing strings became more severe with time (Fig. 21). An estimated 500,000 barrels of oil thought to come from the 7800-ft sandstone actually came from 7000-ft sandstone. The change in the estimated reserves for the two reservoirs affected locations of development wells.

4.3. Oil quality prediction

Reliable oil quality prediction in different reservoir zones, such as estimates of oil API gravity, viscosity, and wax and sulfur contents, can dramatically affect the economics of oil field development. Sidewall cores offer several advantages over drill stem tests and other fluid samples for this analysis because they are generally less expensive and more numerous and they sample discrete

depths rather than intervals. Unfortunately, sidewall cores usually contain insufficient extractable oil to measure gravity or viscosity directly. Downhole tests are commonly too costly to develop vertical profiles of oil quality in stacked reservoirs. However, simple, inexpensive techniques, such as thermal extraction gas chromatography (Jarvie et al., 2001) and Iatroscan (Karlsen and Larter, 1990) can be used to assess oil properties through direct analyses of reservoir rock samples. Thermal extraction is achieved by thermal vaporization of petroleum from rock directly into a gas chromatograph. The resulting chromatograms can be used for various purposes; such as to identify bypassed pay zones or the presence of high-molecular weight waxes that might clog production equipment. Iatroscan (thin-layer chromatography/flame ionization detection) is a rapid screening tool that separates petroleum in small rock samples into fractions of various polarities. Iatroscan can used to distinguish petroleum populations in reservoirs prior to more detailed geochemical work and to predict barriers to reservoir continuity, such as carbonate-cemented horizons or asphaltic-rich zones.

Other micro-techniques offer inexpensive and accurate prediction of oil quality in potential reservoir zones (e.g. BeMent et al., 1996; Guthrie et al., 1998). For example, Guthrie et al. (1998) determined saturated and aromatic hydrocarbons, aromatics, resins, and asphaltenes
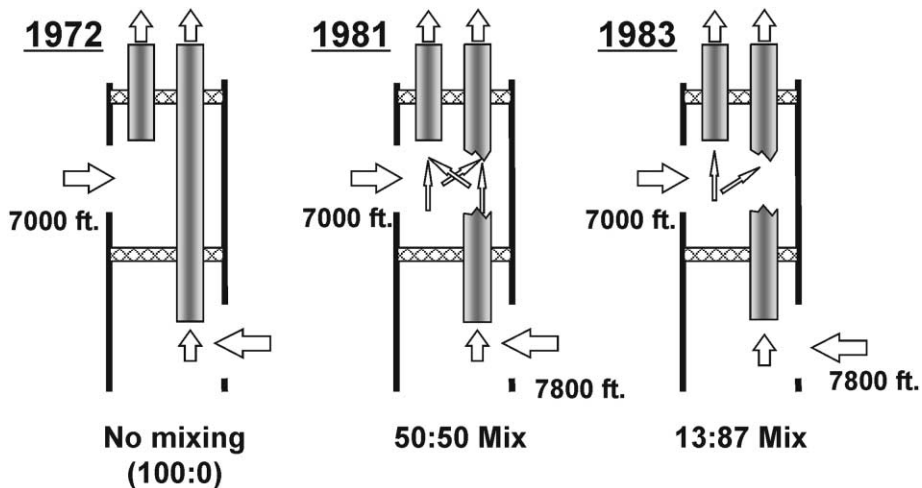
Fig. 21. Schematic production history in the Gulf of Mexico well based on geochemical deconvolution of mixed oils from storage. Modified from Kaufman et al. (1990) and reproduced with the permission of the Gulf Coast Section Society of Economic Paleontologists and Mineralogists Foundation.
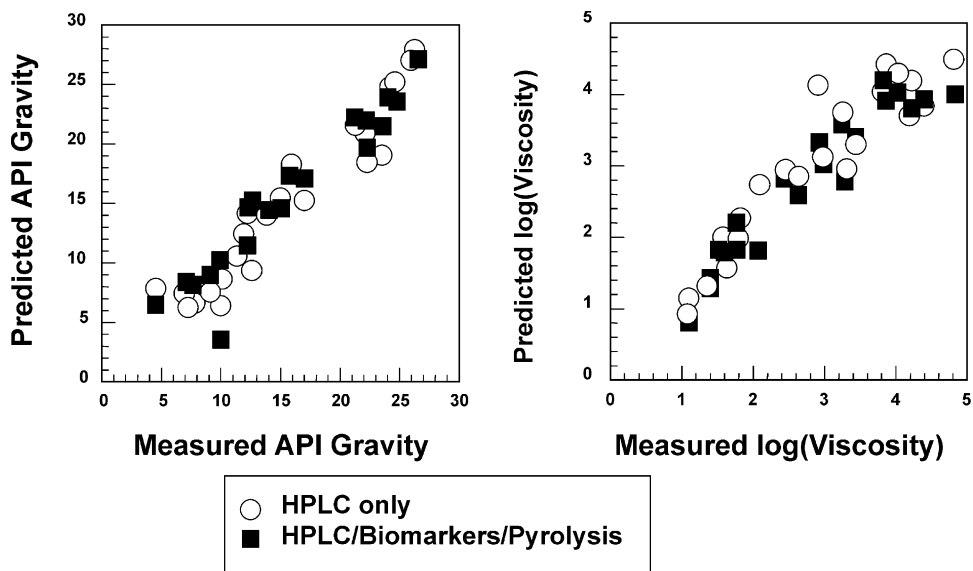

Fig. 22. Comparison of measured and predicted API gravity (left) and viscosity (right) for the Cerro Negro Field, Venezuela (modified from Guthrie et al., 1998). Two linear regression models were generated to predict the oil properties from sidewall core samples based on: (1) HPLC, and (2) HPLC, biomarker, and pyrolysis-FID data, for a set of calibration oils with measured gravities and viscosities.

by high-performance liquid chromatography (HPLC) for crude oils from Venezuela and used them to generate a calibration to predict API gravity, sulfur, and viscosity from sidewall core extracts. Multivariate linear regression showed that the HPLC calibration works as well as more expensive and time-consuming analyses based on combined HPLC, biomarker, and pyrolysis data (Fig. 22). The biomarker parameters included the same demethylated hopane ratios used by McCaffrey et al.

(1996). The pyrolysis data included digitized S1 and S2 peaks, where S1 consists of volatile petroleum (<400 °C), while S2 consists of a mixture of the volatilized high-molecular-weight compounds and cracked components (>400 °C). A similar pyrolysis approach was used to estimate the API gravity of oil in ditch cuttings and core samples (Mommessin et al., 1981). Guthrie et al. (1998) used their data to generate oil quality profiles for wells that penetrated stacked
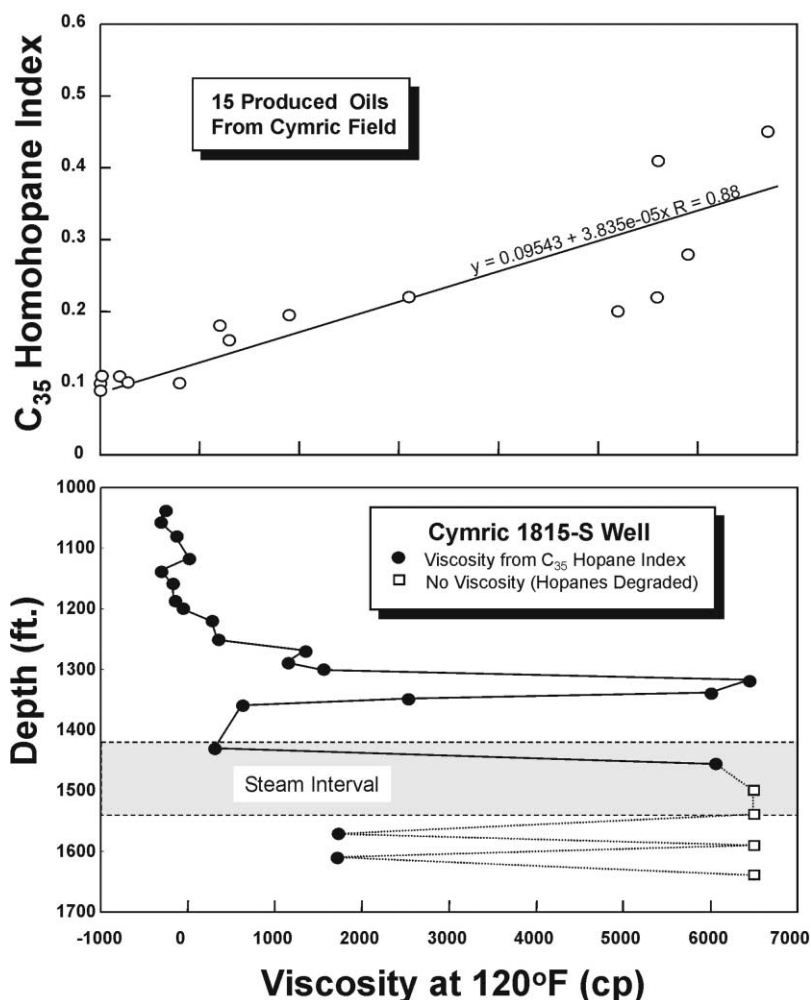
Fig. 23. Calibration of viscosity (centipoise) versus homohopane index [C_{35}/(C_{31} to C_{35}) homohopanes] for fifteen produced oils from the Cymric field (top) was used to predict viscosity of oil from measured homohopane indices of sidewall core extracts (bottom; modified from McCaffrey et al., 1996). The data predict that "huff-and-puff" production will be dominated by the lower viscosity oil from the top part of the steamed interval, as confirmed by production allocation calculations using the method of Kaufman et al. (1990) as discussed in the text. AAPG© 1996; reprinted by permission of the AAPG whose permission is required for further use.

reservoirs in the Cerro Negro area. The downhole profiles show significant vertical variations in oil quality, which can be correlated laterally using similar data in adjacent wells. Bypassed zones of higher oil quality can be identified and targeted for exploitation, which might include horizontal drilling.

McCaffrey et al. (1996) calibrated relationships between oil quality and biomarker biodegradation parameters for produced oils from the Cymric field in California to make quantitative predictions of the lateral and vertical changes in oil viscosity and gravity from sidewall core extracts (Fig. 23). Compositional variations were also used to allocate production to discrete zones. They used these data to optimize (1) placement of new wells, (2) placement of completion

intervals, (3) thickness of steam injection intervals, and (4) spacing between injection intervals in the same well.

5. Conclusions

The new millennium is an especially appropriate time to review developments in petroleum geochemistry since 1980 and to suggest future research directions. The reorganization of the petroleum industry and academia that began in the 1980s reflects a general trend since World War II from growth toward steady state funding of science. This trend promoted the reallocation of funds from mature to developing research areas and from pure research by individuals toward applied

research by interdisciplinary teams with clearly defined goals. Petroleum geochemistry has evolved systematically since 1980. Most research shifted from empirical observations for better understanding geochemical processes toward *predictive* modeling for improving exploration and production efficiencies. This trend is likely to continue because we now understand the major mechanisms for the origin, migration, and accumulation of petroleum. Empirical observations of these processes are still important, but are now used mainly to calibrate predictive models.

Two examples of predictive geochemistry described in this paper include (1) piston-coring and associated technologies to improve pre-drill assessment of petroleum systems in deepwater exploration settings, and (2) 3D-basin modeling to predict the timing of generation, volume, migration path, and accumulation of petroleum. These research areas are among the most active in petroleum geochemistry for obvious reasons: the predictions can be calibrated, visualized in three-dimensions to directly assist exploration, and tested by drilling. In 1980, calibrated basin modeling was a novelty in the field of petroleum geochemistry. Today, basin modelers commonly account for a major proportion of the geochemists in petroleum companies that conduct research.

What are the future research directions in petroleum geochemistry? One approach to answering this question is to highlight topics for which there is currently significant controversy, particularly those that might contribute to better *predictive* modeling. Some of these topics are itemized as questions below (see also Peters and Isaksen, 2000), but we acknowledge that this list could certainly be expanded by others.

- What is the best method to optimize statistical ranges of input data to basin models in order to assess output sensitivity? For example, how can we account for the effects of uncertainty in heat flow, surface temperature, thermal conductivity, timing and quantity of erosion, cracking kinetics, and other variables on simulated parameters, such as vitrinite reflectance, pressure, and oil or gas volumes? This question is linked to the need to reduce computation times for basin models, because as computation time increases, our ability to optimize input data and assess sensitivity decreases.
- Can geochemical properties derived from laboratory experiments be extrapolated more confidently to geologic time and temperature conditions (e.g. kinetics, generative yield, and chemical composition)?
- Can basin models be improved to better handle tectonic complexity, such as salt movement or thrust faulting, tectonic fracturing, and fluid flow through fracture permeability?

- Can we improve estimates of the timing and efficiency of petroleum expulsion from source rocks? Are expulsion efficiencies best estimated from the amounts of petroleum remaining in mature source rocks or from experimental simulations, such as hydrous pyrolysis? Can we better predict petroleum losses during secondary migration?
- How do we better quantify and calibrate seal and fault properties with respect to retention of hydrocarbons? Can basin modeling packages be implemented to predict faults, their permeability, and the consequent effects on fluid flow?
- Can we better quantify the controls on petroleum preservation? For example, can computational chemistry yield more reliable estimates of the stability of petroleum to biodegradation and thermal maturation under reservoir conditions? Can better constraints on kinetics and the complex structures of kerogen and petroleum improve predictions of the maximum depths where petroleum remains thermally stable? Can basin modeling account for the destruction of petroleum by thermochemical sulfate reduction and biodegradation?
- What controls the formation and three-dimensional distributions of the various solid bitumens in reservoirs? Can these controls be used to develop accurate predictive models to improve reservoir exploitation?
- Can the properties of reservoir cap rocks be better predicted by using geochemical, pressure-volume-temperature, and seismic data? Can models be improved to more accurately predict the loss of petroleum through cap rocks not yet penetrated by drilling? Are gas accumulations depleted by diffusion over geologically short time scales and can these times be predicted?
- Can geochemistry be used to improve recovery of the vast quantities of residual petroleum in reservoirs depleted by conventional means?

As exploration and production become more difficult in the twenty-first century, petroleum geochemistry will continue to evolve and those research topics with clear potential to improve forecasting efficiency will gain support. The continuing challenge in modern petroleum geochemistry is to make it an even more reliable *predictive* science.

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