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The controls on the composition of biodegraded oils in the deep subsurface—part 1: biodegradation rates in petroleum reservoirs

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Abstract

Biodegradation rates in oilfields have been assessed conservatively using whole oil-column minimum rate estimates, diffusion-controlled oil column compositional gradient modelling and mixed oil kinetic models. Biodegradation rate constants (first order) are around 10^{-6}–10^{-7} yr^{-1} for hydrocarbons in the degradation zones these corresponding well with zero order field-wide minimum rate estimates of about 10^{-8} kg hydrocarbons/kg oil/year for the whole oil column. With biodegradation induction times of around 1–2 Ma to perturb an entire oil column for light oil reservoirs and 10–20 Ma for heavy oil reservoir degradation the results indicate that where we see continuous gradients in the oil columns, degradation must have been occurring episodically for many millions of years. To remove the n-alkanes from an oil (i.e. about 10% of an oil) around ca 15 Ma is needed for a heavy oil (ca 5 Ma for a light N. Sea oil). The timescales of oilfield degradation and filling are thus very similar and consequently the degree of biodegradation will be substantially controlled by oilfield charge history. Assessment of mixed degraded/non-degraded oil occurrence provides an independent confirmation that these rates are realistic and that timescales of degradation and field charging are similar. The maximum effective rate constant of degradation, ultimately controlled by the limiting effect of diffusion of alkanes to the oil water contact (OWC) (ca 10^{-4} yr^{-1} for a 130 m thick oil column first order rate constant) is well above the estimated rate constants indicating oil biodegradation rate is not limited by electron donor supply (i.e. hydrocarbons) but by supply of nutrients or oxidants. This suggests that diffusive transport of nutrients and electron acceptors in the aquifer to the site of biodegradation may be adequate to maintain the low rate biosphere.

1. Introduction

In this paper we discuss our efforts at examining the controls on petroleum biodegradation in the subsurface and specifically in this article our assessment of biodegradation rates in deep reservoirs. In the absence of a clear understanding of biodegradation today we adopt several generic physical modelling approaches which are largely independent of the detailed chemical mechanisms involved.

Biodegradation of crude oil and natural gas in the reservoir is an important alteration process with major economic consequences and we briefly review as background the basic elements of our current understanding. Most of the world's petroleum is biodegraded (Roadifer, 1987). While the effects of biodegradation on the molecular composition and physical properties of crude oil and natural gases are empirically relatively well known (Evans et al., 1971; Hunt, 1979; Connan, 1984), the actual processes taking place during biodegradation of crude oil in deep reservoirs (below a few hundred meters) remain obscure, as do the rates of degradation, the oxidant and the nature of the reduced products in most cases.

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Oxidation of oil during biodegradation leads to a systematic decrease in paraffin content with increasing degradation and an increase in oil density, sulphur content, acidity, and viscosity (Connan, 1984) with huge negative economic consequences on oil production and refining operations. While the details and rates of the processes are still poorly understood, the central role of bacteria and archaea in subsurface petroleum degradation is accepted and the prediction of the degree of biodegradation of oil prior to drilling an exploration well is important for the assessment of the likely value of a prospective exploration target. Biodegradation is a biochemical process and geochemists have made substantial advances in their ability to describe empirically the geochemical sequences of subsurface oil degradation (Connan, 1984). In many cases however, geological factors such as oil mixing (Barnard and Bastow, 1991; Horstad and Larter, 1997) dominate final oil compositions and physical properties. It is this complex interplay of biological, chemical and physical mass transport process that makes biodegradation such an intriguing and puzzling process to simulate in a petroleum geological context.

Rates of aerobic biodegradation of hydrocarbons are often high enough to be observable on a short human timescale and thus aerobic processes dominated petroleum geological thinking about subsurface petroleum biodegradation for many years. While aerobically degraded oilfields are described in the literature (Winters and Williams, 1969; Evans et al., 1971; Hunt, 1979), even conservative mass balances of the volumes of water needed to transport sufficient oxygen present overwhelming problems geologically in most reservoirs (Horstad et al., 1992). Even where meteoric water has flushed basins it does not follow that oxygen was carried to the deep reservoirs. The difficulties are in A) maintaining oxygen levels deep into the subsurface after passing through soils and aquifers with reactive organic matter and pyrite and B) the very common observation that deep degraded oilfields in marine basins often contain saline water indicative of minimal flushing of deep aquifers with fresh water.

Russian workers have considered anaerobic hydrocarbon degradation in deep reservoirs as the primary process for many years (Kartsev et al., 1959) and the first bacteria isolated from oilfield waters by Bastin (1926) were anaerobes. Shallow subsurface waters or organic rich environments such as rice paddies are usually anaerobic and there is increasing evidence of the occurrence of viable anaerobic hydrocarbon degradation processes (e.g. Zengler et al., 1999; Wilkes et al., 2001; Widdel and Rabus, 2001). Though, to date, only one thermophilic anaerobic hydrocarbon degrader potentially capable of living in the deepest degraded reservoirs has been identified (Rueter et al., 1994), Connan and co-workers (Bernard and Connan, 1992; Magot and Connan, 1993; Magot et al., 1994; Connan et al., 1996) have convincingly demonstrated, with a large and pivotal body of work the common presence of diverse anaerobic organisms in oilfields. They concluded from lab and field studies that anaerobes were indeed responsible for most subsurface hydrocarbon degradation. Methanogenesis, an exclusively anaerobic process, during oil degradation in reservoirs is common (cf. Scott et al., 1994; Larter et al., 1999; Larter and Di Primio, in press) and is a likely fate for most carbon dioxide produced during biodegradation. These results, together with the availability of long periods of time for degradation to occur, makes it likely that anaerobic hydrocarbon degradation is the common process of biodegradation in most petroleum reservoirs.

While biodegradation of seeps can undoubtedly proceed aerobically at high rate of degradation, environmental and aquifer studies suggest that slow anaerobic processes dominate hydrocarbon degradation in the subsurface and involve multiple oxidant zones including, among others, iron reduction and methanogenesis (cf. Hunkeler et al., 1998; Bennett et al., 1993; Zengler et al., 1999). Water, itself is a very plausible reactant for the production of oxygenated organic compounds and free energy during hydrocarbon degradation in deep anoxic settings with a thermodynamic and microbiological basis for this conclusion (Helgeson et al., 1993; Zengler et al., 1999).

Reservoir temperature is the primary control on the degree, and hence by inference the rates of subsurface biodegradation with the probability of observing a given level of biodegradation increasing for decreasing reservoir temperatures below about 80 °C (Hunt, 1979; Connan, 1984; Pepper and Santiago, 2001). Thus we would infer that biodegradation rates decrease with increasing reservoir temperature to reach effectively zero at around 80 °C. This temperature may be lower in high salinity reservoirs (Bernard and Connan, 1992).

This zero degradation rate temperature (80 °C) corresponds in general to that temperature above which there appears to be an absence of significant microbial life in petroleum reservoirs (Bernard and Connan, 1992). While degradation level generally decreases with increasing reservoir temperature, at any temperature a wide range of commercially sensitive oil properties such as viscosity or API gravity (a gross proxy for oil composition whereby oil gravity decreases with increased biodegradation) can be found in subsiding basins such as the Viking Graben basin of the N. Sea. (c.f. Fig. 1). At 80 °C the probability of finding oils in reservoirs degraded to level 5 on the Peters and Moldowan (1993) scale is close to 0 while at 50 °C it is near 0.7 (Pepper and Santiago, 2001). A curious geological inference from the clear temperature related biodegradation trends and the observation that degraded oils are rarely found in still subsiding reservoirs above 80 °C is that

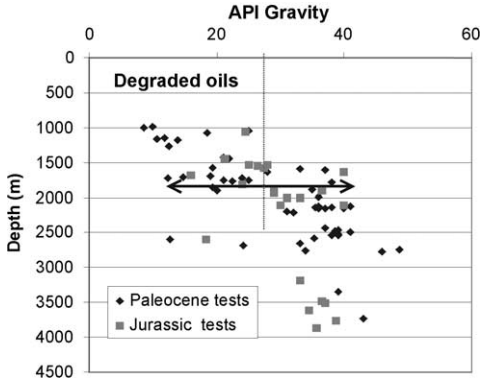

Fig. 1. Oil API gravity versus reservoir depth (mRKB) for the N. Sea. Paleocene and Jurassic reservoirs are differentiated by the symbols and biodegraded oils are typically found in reservoirs shallower than 2000 m. While low API heavily degraded oils are increasingly dominant in shallower reservoirs, at any depth, large variations in API gravity and viscosity are evident (see arrow) with high gravity non-degraded oils being found at the same depths as heavily degraded oils.

most biodegraded reservoirs in these basins must have been charged quite recently with degradation and charging occurring close to present depths of burial!

The 80 °C cutoff for biodegradation implies that the biodegradation rate of petroleum in reservoirs at temperatures above 80 °C is essentially zero with micro-organisms typically absent (Bernard and Connan, 1992). This temperature boundary may thus represent a fundamental limit to the crustal biosphere, (not merely the hydrocarbon degrading biosphere) which may be a realm where hyperthermophiles are typically absent. As microbial growth rate curves plotted as a function of temperature frequently show optimum growth rates within ca 5 °C or so of maximum growth temperature (Madigan et al., 2000) it seems very likely that the 80 °C biodegradation temperature limit is the death line for hydrocarbon degraders in basins and perhaps even the base of all life itself in deep oligotrophic sediments.

The pioneer work of Bastin (1926) and others in the last 75 years (cf. Bernard and Connan, 1992; Parkes et al., 1994; Fredericson et al., 1995; Pedersen, 2000) has led to the concept of the deep biosphere with suggestions that many micro-organisms found in deep sediments (>100 m) today evolved from organisms deposited at the time of sediment deposition (Fredericson et al., 1995). While there is abundant evidence for the presence of active bacteria deep (>1 km) in the Earth's crust (Parkes et al., 1994; Zobell, 1945; Pedersen, 2000) and a view among biologists and geochemists that life may occur even up to 150 °C (Parkes et al., 1994; Stetter, 1996) or beyond, there is a general view today among petroleum geoscientists that microbial oxidation of hydrocarbons (petroleum biodegradation) in oil reservoirs ceases around 75–80 °C (Connan, 1984; Barnard and Bastow, 1991; Bernard and Connan, 1992) in the zone of thermophilic organisms. Hyperthermophilic organisms grow optimally above 80 °C, often with no growth below 60 °C (Stetter et al., 1990).

Hyperthermophiles have been reported to operate at temperatures of up to 113 °C (Blöchl et al., 1997) with suggestions that the deep biosphere may extend even beyond these temperatures (Pedersen, 2000; Parkes et al., 1994; Stetter et al., 1990). While hyperthermophiles have been isolated from petroleum reservoirs (Stetter et al., 1993), they were probably introduced from surface fluid injection operations. Most reports of hyperthermophilic activity are limited to environments rich in reduced electron donors, electron acceptors and nutrients associated with shallow sediment or near surface hydrothermal activity (Stetter, 1996). Here, high levels of metabolic activity can be supported, conditions not likely to be found in deep nutrient depleted sediment pore environments. Wilhelms et al. (2001) concluded hyperthermophiles were not present naturally in petroleum reservoirs but are often introduced with seawater. The crustal biosphere is the realm of thermophiles!

Bernard and Connan (1992) concluded reservoirs are sterile above 80 °C and Wilhelms et al. (2000) suggest, that in inverted basins, non-biodegraded oils are common providing that the reservoirs were pasteurised by deep burial heating to a temperature above approximately 80–90 °C before final oil recharging. Even when such reservoirs are subsequently uplifted to much cooler regimes and filled with oil, degradation does not occur, suggesting that the sterilised sediments are not recolonised by bacteria.

To illustrate this, Table 1 shows pristane/n-heptadecane values for oils in Barents Sea, Wessex basin (uplifted basins) and Viking Graben, Tampen Spur areas of the N. Sea (subsiding basins) for reservoirs currently at 80 °C or below and for hotter reservoirs in the Tampen Spur area of the N. Sea. Also plotted are estimates of maximum reservoir temperatures based on vitrinite reflectance data (uplifted Barents Sea and Wessex basin) and current reservoir temperatures for the Viking Graben and Tampen Spur (subsiding basins). Fig. 2 compares current and paleotemperature indicators (vitrinite reflectance) from degraded North Sea (subsiding basins) and non-degraded Barents Sea (uplifted basins) reservoirs. Cross plotting present day reservoir temperature and the approximate reservoir Ro (determined from Ro trends of the various wells) for reservoir horizons with current temperatures of 40–90 °C, two distinct groups of oils are discernible: a) low API degraded oils (<29 API) are found in the N. Sea where the reservoirs are at maximum burial depth and b) high API (>32 API) non-degraded oils are found in the Barents Sea where the reservoir Ro suggests that the reservoir units have all experienced temperatures in excess of 80–90 °C (indicated by the shaded areas) prior to uplift.

Table 1
Summary geochemical data for petroleums from reservoirs in the Wessex, Barents Sea and N. Sea basins charged from Jurassic source rocks (after Wilhelms et al., 2001)

Province	#Samples	Average pr/nC_{17}	Stand. Dev. pr/nC_{17}	Max reservoir temp. (°C)	Current reservoir temp. (°C)
Wessex basin (reservoirs 500–1600 m)	3	0.5	0.07	90–100C	40–65C
Barents Sea basins (reservoirs < 2 km depth)	19	0.87	0.21	> 90C	45–80C
Barents Sea basins (reservoirs > 2 km depth)	10	0.89	0.16	> 90C	80–130C
Tampen Spur (reservoirs > 2 km depth)	70	0.67	0.14	80–130C	80–150C
Viking Graben/Tampen Spur (reservoirs < 2 km depth)	22	5.13	4.86	50–80C	50–80C

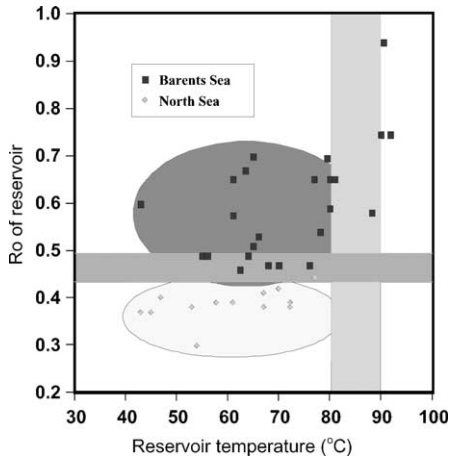

Fig. 2. Current reservoir temperature and reservoir vitrinite reflectance (Ro%), for reservoirs in the uplifted Barents Sea basins and the subsiding N. Sea basins. The horizontal shaded bar indicates reflectance levels equivalent to paleotemperatures of 80–90 °C, the vertical shaded bar the current 80–90 °C region.

In this similar set of petroleum systems, reservoirs which have never been heated to 80 °C show variable levels of degradation while those in inverted basins where reservoirs reached 80 °C or greater before final oil charge show little evidence of any biodegradation indicating degradation rates remain near zero presumably reflecting the absence of hydrocarbon degrading microbial life in these pasteurised sediments.

While these general temperature control considerations provide some empirical predictive capability, in reality, it is desirable to be able to model biodegradation in a deterministic way to achieve some understanding of key process variables and critical factors. One key variable in biodegradation level prediction is clearly the biodegradation rate in the subsurface—a parameter until recently not explored to our knowledge. We have thus sought to estimate rates by a variety of techniques that provide a basis for effective biodegradation modelling in a basin modelling environment.

Hydrocarbon biodegradation rates can be measured in the laboratory but this makes the assumption that rates are significant on human timescales. Anaerobic hexadecane degradation is slow on human timescales in the laboratory (Zengler et al., 1999) but it seems likely that the processes of hydrocarbon degradation in deep subsurface petroleum reservoirs are orders of magnitude slower still. This suggests direct comparison of deep biosphere processes with those occurring in nutrient rich surface or lab microcosm environments may not be appropriate.

Rates of biodegradation are assessed here by three approaches; 1) whole oil column minimum rate assessments, 2) diffusion related compositional gradients in biodegraded oil columns and 3) an approach based on examination of mixed degraded/non-degraded fresh oil occurrence.

2. Methods and materials

2.1. Whole oil column minimum rate assessments

The simplest approach to biodegradation rate assessment is to assume oil biodegradation occurs uniformly throughout a field's oil column and that degradation is a zero order process with respect to hydrocarbons (i.e. the rate controlling factor is not hydrocarbon supply), i.e. concentration of a reactive component such as an alkane at time t is given by $A_t = A_0 - k.t$ where A_0 represents concentration at time 0 and k is the rate constant. It turns out this model is reasonable as discussed below. We do not need to specify a mechanism (aerobic or anaerobic), simply the order of the reaction. If we then assume a timescale for oil charging to a reservoir, or in the case of very young oil reservoirs accept the age of the reservoir as the maximum time for degradation, then an assessment of the average minimum rate constant for degradation can be made. For example oils in Pleistocene reservoirs of the Gulf of Mexico can only have had less than ca 2 Ma to degrade the oil if we assume the degradation occurs in the reservoir.

2.2. Compositional diffusion gradients as a route to degradation rates

The geochemical study of a Chinese petroleum reservoir described here was carried out using procedures we have published previously (Karlsen and Larter, 1991; Larter and Aplin, 1995) and reported in Koopmans et al. (in press).

2.3. Numerical modelling of in-reservoir biodegradation

A vertical petroleum column was simulated by dividing it equally into 50 cells with a basal cell (2% of reservoir column height) in which degradation was simulated either as a first order reaction dependent on saturated hydrocarbon concentration or as a zero order reaction removing saturated hydrocarbons. The composition of the upper cell could be controlled to simulate filling of the reservoir with fresh oil. The charging and degradation of the petroleum column, with the associated movement of saturated hydrocarbons between the various cells in the petroleum column by diffusion along concentration gradients, was simulated numerically using a modification of the finite difference numerical solution of the classical advection diffusion equation as described by Muller (1999), this approach being typical of many chemical engineering diffusion/reaction models (Cussler, 1997). Degradation was assumed to occur at or near the oil–water contact in the example described because the gradients observed in the field suggested that this was the case. In a more general situation degradation may occur during filling at many sites synchronously within the reservoir or during the secondary migration process. In the example cited here we see evidence that clearly shows that degradation is occurring in-reservoir, supporting the calculation we describe. While we consider subsurface oil biodegradation to proceed anaerobically the actual mechanism is not important for the simulation.

The actual extent of zones of biodegradation in oil fields are poorly described but we have seen zones of biodegraded residual oil in several biodegraded oilfields which are up to 10% of petroleum column height where we suspect most biodegradation occurs (Horstad and Larter, 1997; Larter and di Primio, in press). Our choice of a reaction zone of 2% of the oil column is a conservative value chosen to maximise any apparent rate constant derived. Actual stoichiometry and reactions involved in subsurface biodegradation are poorly known and, depending on assumptions made, the saturated hydrocarbons may either be mineralised to carbon dioxide and water or transformed to unknown compounds. While well-established sequences of alkane removal are known (Connan, 1984), and aromatic species may also be removed penecontemporaneously, in this model we merely describe biodegradation in terms of removal of saturated hydrocarbons to provide a gross but conservative assessment of degradation rates. Saturated hydrocarbon concentrations were expressed as kg saturated hydrocarbons/kg oil.

Oil charging to the reservoir was simulated by adding "fresh oil" to the top cell in the model with an initial saturated hydrocarbon content equal to the current saturated hydrocarbon content of the top of the current reservoir petroleum column (reservoir top) and adjusting the length scale of the model to accommodate the new oil. The model was implemented in Modelmaker V4.0 (Cherwell Scientific Ltd) a flexible modelling environment which allows for a Runge–Kutta numerical solution to the finite difference advection–diffusion equation and allows for rescaling the model after each calculation step thus allowing simulation of simultaneous filling and biodegradation. While the model can also account for shrinkage of the petroleum column during degradation, investigations of the effects of this suggest it is a secondary effect and is ignored here as reaction stoichiometry is not known and thus accurate estimates of petroleum column shrinkage were not obtained. The evolution of the saturated hydrocarbon profile in the reservoir was followed both in terms of the concentration profiles of saturated hydrocarbons observed and the gradient in saturated hydrocarbons observed through the reservoir section. Gradients of hydrocarbon concentrations observed in models and observation of biodegraded reservoirs are not usually linear for a diffusion-dominated system with both filling with variable oil charge composition and simultaneous biodegradation. In our experience observed field gradients are close to linear in appearance and a linear fit of observed hydrocarbon concentrations throughout a reservoir is adequate for the discussions below. Thus actual gradients in concentration of saturated hydrocarbons are reported as linear fits to observed saturated hydrocarbon concentration gradients with depth.

Vertical saturated hydrocarbon content gradients in reservoirs were expressed as saturated hydrocarbon concentration change per meter (kg sats/kg oil/m). The Chinese oilfield studied has marked compositional gradients (0.0007 kg sats/kg oil/m). Visually obvious vertical compositional gradients within single contiguous oil columns have not been reported to date in others published studies of biodegraded petroleum columns. Usually the petroleum column in published studies appears "more or less" visually homogeneous, as in the Gullfaks field (Horstad et al., 1990). Simple empirical experiments with a spreadsheet suggested that saturated hydrocarbon concentration gradients in saturated hydrocarbon data on ca 100 m thick oil columns become visually detectable when the gradient exceeds 2% saturated hydrocarbons/100 m or 0.0002 kg saturated hydrocarbons/kg oil/m. We take 0.0002 kg saturated hydrocarbons/kg oil/m as a minimum detectable gra-

dient to assess minimum degradation rates for light oilfields though it is possible that no gradients exist in some oilfields as degradation may have ceased. We have seen vertical compositional gradients related to biodegradation in around ten different sandstone reservoirs from around the world including some N. Sea reservoirs (Bennett, Ross, Huang, Larter, unpublished results) and we have seen statistically testable gradients of up to 0.0006 kg saturated hydrocarbons/kg oil/m in one N. Sea well. Though we cannot prove degradation is active today in all these fields, large biodegradation related methane isotope variations in the gas caps of giant fields such as the Troll field suggest contemporaneous biodegradation is occurring today in the N. Sea (Horstad and Larter, 1997; Larter and di Primio, in press).

Diffusion coefficients of saturated hydrocarbons in oil were estimated using the relationships between oil viscosity and diffusion coefficient described by Reid et al. (1987). Diffusion coefficients for light oils have been reported by England et al. (1987) at around $0.5.10^{-9}m^2$ s^{-1} for alkanes in the C_{12} range. For heavy oils with subsurface viscosities estimated to be around 100 cP (Koopmans et al., 1999, in press) diffusion coefficients could be as low as 10^{-12} m^2 s^{-1} or as high as $0.5.10^{-10}$ m^2 s^{-1}. We use the higher value and assume it is an average value for the saturated hydrocarbon fraction. Taking a relatively high value for the diffusion coefficient tends to overestimate biodegradation rate constants and, as we suggest below, if biodegradation reaction rates are slow this will provide a conservative maximum estimate of such rates. Diffusion coefficients were scaled for porous media allowing for tortuosity effects as described by Dormieux and Lemarchard (2000).

Investigation of the effects of biodegradation on the compositional gradients in oilfields when both during filling and column shrinkage during biodegradation were simulated indicate that the values obtained for biodegradation rate constants with a static column (i.e. without change in oil column thickness with time) provide adequate estimates of degradation rates for a given column saturated hydrocarbon gradient. Thus all simulations reported show a static petroleum column thickness through time but the values obtained for degradation rates will be very similar to those involving more realistic filling, degradation scenarios.

2.4. Mixed oil studies as a surrogate route to biodegradation rates

Modelling studies of the evolution of *n*-alkane/unresolved hump ratios were carried out as follows. It is assumed that the UCM in biodegraded oils represents a largely non-degradable component when *n*-alkanes are still present in the mixture. The *n*-alkane/hump abundance ratios for oils are derived as peak heights of *n*-alkanes above the hump, ratioed to the height of the hump above the gas chromatographic baseline. The ratio '*n*-C_{20}/hump height at *n*-C_{20}' is arbitrarily defined as parameter L1. While other carbon numbers could just as easily be used, this carbon number is frequently near the hump maximum in many oils we see. A simple model is constructed which allows for charging of oils consisting of two components—a degradable *n*-alkane and a non-degradable hump component (cf. Rowland et al., 2001) in constant proportion defined from a non-degraded oil. L1 would typically be around ca 10–20 for non-degraded oil. In the reservoir, the *n*-alkane component is biodegraded (removed) using a zero order rate equation where the degradation rate of the alkanes (volume or mass of alkanes degraded in a given time derived from a rate constant times volume or mass of degradable oil) is given a value relative to the charge rate of oil to the reservoir (volume or mass of oil charged in unit time). As the *n*-alkanes degrade, the resistant hump simply accumulates in the reservoir. At any time the ratio of L1 can be calculated and the variation of L1 assessed in terms of the relative rate of biodegradation to the rate of charging of the reservoir and the effect of mixing of the fresh and degraded oils.

3. Results and discussion

3.1. Whole oil column minimum rate assessments

We assume oil biodegradation occurs uniformly throughout an oil column and that degradation is a zero order process with respect to hydrocarbons. If we then assume a timescale for oil charging to a reservoir, then an assessment of the average minimum rate constant for degradation can be made. Fig. 3 shows some average minimum whole oil column degradation rates made in this way for different levels of conversion of oil. Degradation actually occurs near oil-water-contacts (OWC's). Thus these field-wide rates are lower than the rates present in the volume of oil that is actually degrading (i.e. if only 1% of the volume of a field is actually degrading the actual rates in the degrading zone would be 100 times greater than the whole oil column rate, and so on) but this approach does provide general indications of minimum rates. For young oilfields in California and the Gulf of Mexico minimum effective field wide rates of around 10^{-7} kg saturated hydrocarbons/ kg oil/ year are implied whereas for N. Sea fields charged in the last 10 Ma, rates are approximately an order of magnitude lower.

3.2. Biodegradation rates from oilfield compositional gradients

This approach, to our knowledge, was first described by Larter et al. (2000) and the approach is reviewed here. Biodegradation rates in deep oilfield reservoirs

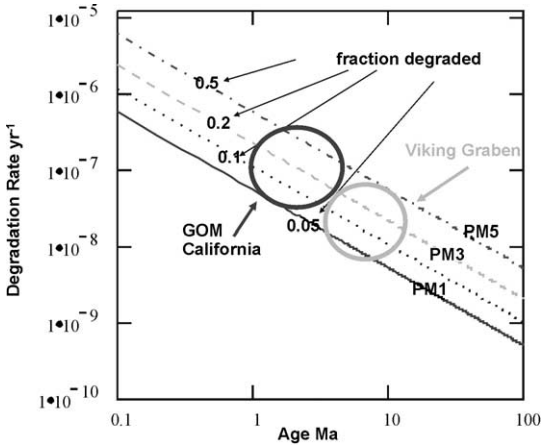

Fig. 3. Minimum degradation rates (kg hydrocarbons degraded/kg oil/year) on the *Y*-axis, assessed for oilfields from the USA and Europe assuming degradation uniformly throughout the oil column. The rates are plotted versus minimum oil residence times (*X* axis, Ma), for two sets of petroleum systems represented by the circles. Very recently charged oils in the Tertiary basins of California or of the Gulf of Mexico (GOM) may have oil residence times in reservoir of only a few Ma while oils in the Viking Graben, N. Sea may have minimum residence times of around 5–10 Ma. The contour lines represent the oil fractions degraded (0.1, 0.2 etc.), the approximate equivalent Peters and Moldowan scale levels of degradation being indicated by PM1, PM3 etc.

have not been reported previously though it seems reasonable to assume that they will be slower than near surface degradation rates derived from lab or bioremediation studies. The latter indicate that near surface anaerobic hydrocarbon degradation is typically occurring with rate constants of around 10^{-2} per year (cf. data from Zengler et al., 1999).

Compositional gradients in hydrocarbons in biodegraded petroleum columns will persist in a high permeability connected reservoir if the rate of diffusive mixing is similar to or lower than the rate at which the hydrocarbons are destroyed (or in the case of methanogenesis, produced). In reservoirs where diffusive mixing within the oil column is much more rapid than degradation of alkanes near the oil water contact, large measurable compositional gradients throughout the oil column will not be expected to develop and persist. Diffusion of hydrocarbons to the oil water contact zone will be the ultimate control on maximum degradation rate. The petroleum in parts of a heavy oil reservoir in the Liaohe Basin, China shows an unusually well developed vertical biodegradation gradient in core extract petroleums from several wells in an isolated fault block with progressive and systematic loss of alkanes over a 130 m vertical interval (Fig. 4a) towards the oil water contact (Koopmans et al., 1999, in press).

The heavy oils of the Liaohe basin study area in the vicinity of the Lengdong oilfield are reservoired in turbiditic sandstones of Eocene age at 1.8km depth, laterally intercepted by time-equivalent, mature, deep-water lacustrine source rocks down-dip. Reservoir temperatures are around 60–65 °C. The gross composition and some biomarker characteristics of the oils are described by Koopmans et al. (in press) and those conclusions are reviewed here. The oils are sourced from section 3 (Es3) and/or section 4 (Es4) of the lacustrine Eocene Shahejie Formation and were charged from Oligocene times on. The geological framework with deeply buried mature

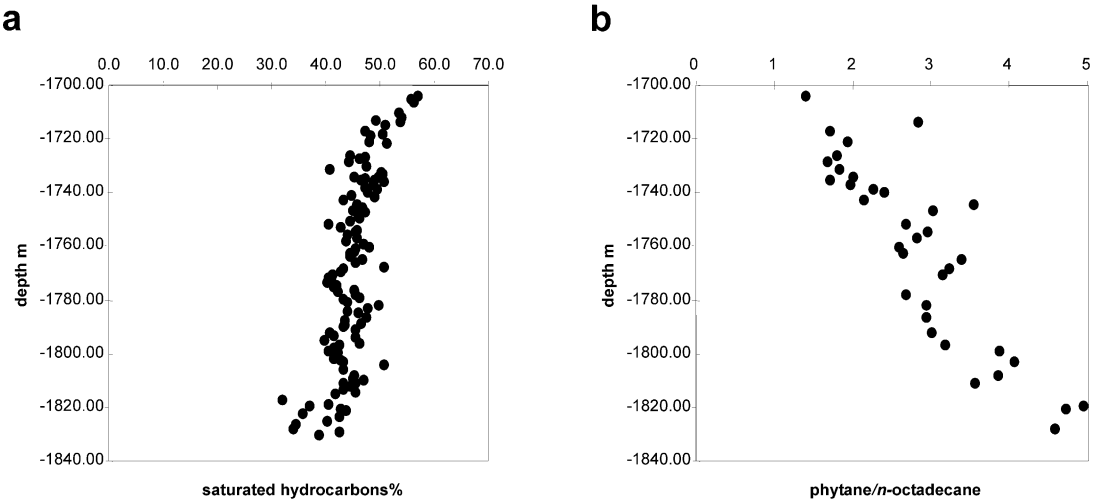

Fig. 4. The saturated hydrocarbon content (a) decreases while the phytane/*n*-octadecane ratio (b) increases towards the oil water contact for petroleum in a sandstone reservoir from the Liaohe Basin containing heavy oil (after Larter et al., 2000; Koopmans et al., 1999, in press). This reflects a vertical biodegradation gradient in the oil column produced by degradation near the oil water contact at ca 1830 m.

source rocks in these units close to the reservoir suggests that it is likely that both these units may have contributed to the reservoir charge with the Es3 charge dominant. The maturity of the oils is rather uniform with 0.46 ± 0.03 for S/(S + R) C_{29} steranes, and 0.35 ± 0.02 for $\beta\beta/(\alpha\alpha + \beta\beta)$ C_{29} steranes. Regionally, the Liaohe oils have been extensively and variably biodegraded with evidence of large scale mixing of fresh and degraded oils in the reservoirs (Koopmans et al., in press).

Though compositional gradients in heavy oilfields are sometimes related to gravitational compositional segregation (Khavari-Khorasani et al., 1998), this decrease in bulk saturated hydrocarbon content is also mirrored by systematic changes down reservoir in molecular parameters such as phytane/*n*-octadecane that unambiguously reflect the effects of biodegradation (Fig. 4b). Other molecular parameters support this interpretation and suggest the gradients are not simply the result of vertical mixing of fresh oil and a previously degraded oil charge. We interpret this systematic compositional gradient as evidence of in-reservoir degradation primarily near the oil water contact with diffusion of alkanes to the oil water contact. We have seen similar degradation related gradients in several reservoirs in Asia and Europe though not all biodegraded reservoirs show such profiles. Many fields do not show this systematic behaviour and elsewhere in this heavy oil province such systematic gradients are rarely seen. Nevertheless we can use this situation to derive a gross biodegradation rate for this oilfield compartment.

Attempting to derive rate constants for biodegradation using oilfields is potentially fraught with difficulty as there is no clear indication of when biodegradation started or what the starting concentration of alkanes was. Similarly we do not know whether the saturated hydrocarbon gradient is in a near steady state condition or not and we do not know whether the field was degrading as a static column or whether it was filling penecontemporaneously. The timescale (t) of response of a diffusion controlled fluid column of a given dimension (length) with a uniform diffusion coefficient to a compositional perturbation is proportional to the Fourier number:-

$$t = (\text{Length})^2/(\text{Diffusion coefficient}) \quad (1)$$

where t is time for a compositional perturbation to propagate through the column (Cussler, 1997). The timescale of response of an oil column to a compositional perturbation is of the order of 10% of this value (Schulte, 1980). Thick oil columns or more viscous oil columns with low diffusion coefficients will respond more slowly.

We refer to this time as the biodegradation column response induction time or the "Schulte time". Running the degradation model indicates that after this induction time, for low levels of biodegradation (a few% of alkanes removed), the saturated hydrocarbon gradient remains nearly constant. Thus, after the induction time, we can use the compositional gradient produced by biodegradation to assess the rate constant of degradation without knowing when degradation started. Biodegradation induction times of a million years or so will apply for a light oil column with several million years for a heavy oil reservoir.

Because the timescale of response of the oil column to degradation scales as the square of the oil column height [Eq. (1)], there is much less difference between degradation of a static thick oil column and a gradually filling one than might be expected and similar rates are inferred in our models. Fig. 5 shows a plot of geological time versus the alkane concentration gradient and the fraction of oil degraded for a series of numerical degradation experiments with first order rate constants for the Chinese example modelled with a continuous 130 m oil column. The oilfield saturated hydrocarbon gradient of 0.0007 kg saturated hydrocarbons/kg oil/meter is marked as a dashed horizontal line. A diffusion coefficient of $0.5.10^{-10}$ m^2 s^{-1} for alkane diffusion in heavy oil was used in the model and this was scaled for diffusion in porous media. This value (one order of magnitude less than a value for light oil; England et al., 1997) was assessed using correlations between oil viscosity and diffusion coefficients. Assuming degradation occurs at the base of the oil column in the basal cell of the model (2.6 m zone), the compositional profile and saturated hydrocarbon concentration gradients observed can be broadly matched with first order biodegradation rate constants around 10^{-6}–10^{-7} per year. These are similar orders of magnitude to those minimum whole field biodegradation rate estimates of degraded oil reservoirs (Fig. 2) rescaled for degradation in the basal 2% of the oil column (i.e. the rate in the basal cell is 50 times the whole field rate). At low degradation of saturated hydrocarbons, zero order rate constants are of similar magnitude with the units used. Surprisingly, with a diffusion coefficient of $0.5.10^{-9}$ m^2 s^{-1}, matching the maximum saturated hydrocarbon gradient (0.0006 kg saturated hydrocarbons/kg oil/meter) seen in a N. Sea oilfield of similar reservoir temperature with lighter oil indicates similar rate constants are involved there too. With induction times of around 1–2 Ma for light oil reservoirs and 5–10 Ma or more for heavy oil reservoir degradation this implies where we see continuous gradients throughout the oil columns that degradation must have been occurring on and off for many millions of years.

Degradation it seems, is a long slow process though it is likely that the average rates assessed here do not reflect the instantaneous maximum rates possibly occurring if the biota are operating in a feast and famine mode (Poindexter, 1981). In this situation the biota

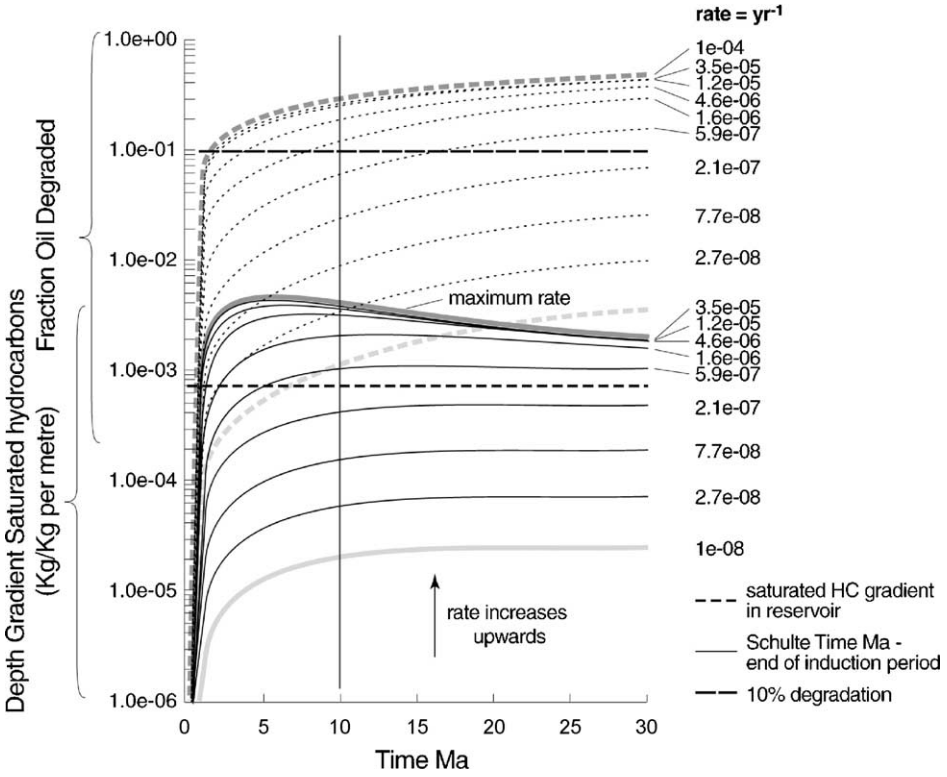

Fig. 5. Simulation of biodegradation in a Chinese oilfield petroleum column. The *X* axis represents time (years) with biodegradation starting at 0 and continuing for 30 Ma. Two sets of curves are shown. The lines in the lower half of the diagram show the linear gradient of saturated hydrocarbon concentrations through the whole oil column (kg/saturated hydrocarbons /kg oil/m) for a range of first order rate constants of from 10^{-8} to 10^{-4} per year. The lines in the upper half of the diagram show fraction of oil degraded as a function of time. A horizontal line represents the linear saturated hydrocarbon gradient through the oil column today.

would alternate between ''rapid'' growth and ''high'' degradation rates and probably long periods of dormancy. Smooth compositional gradients will be produced if the biodegradation events occur much more rapidly that the induction time of the petroleum column. The upper set of curves in Fig. 5 show the extent of oil degradation as a function of time and indicate that to remove significant quantities of alkanes from an oil (i.e. about 10%—or all the *n*-alkanes in a marine oil) around 15 Ma is needed for the Chinese oil (ca 5 Ma for a typical N. Sea oil reservoir). This indicates the timescales of oilfield degradation and filling are very similar and thus the degree of biodegradation observed will be substantially controlled by oilfield charge history and reservoir residence time.

Fig. 5 also indicates that the maximum rate constant of degradation supportable by diffusive supply of hydrocarbons to the oil water contact (ca 10^{-4} per year) is well above the observed degradation rate constant (10^{-7} per year) even with this order of magnitude level resolution. Actual oil biodegradation rate in this oilfield it seems is not limited by electron donor availability (hydrocarbon supply) but by some other controlling element, probably a nutrient. Alkane degradation kinetics are thus in fact zero order for oil! This modest result implies supply of nutrients or electron acceptor to the site of degradation is the limiting factor, not hydrocarbon supply, and thus diffusion of nutrients in the water leg may be adequate to supply the degradation zone (diffusion coefficients of ions in water are of similar magnitudes or greater than the rates of alkane diffusion in oils). This suggests biodegradation in some oil reservoirs may be isochemical (i.e. involving only mass transport of hydrocarbons, nutrients and oxidant within the reservoir). The system may operate even if closed at reservoir scale and water flow may not be needed though undoubtedly it would help, as it would aid mineral dissolution and nutrient supply!

Reservoir topology in general will be important with regard to rate and location of degradation. The ratio between the areas of degradation at oil–water contacts to reservoir volume should ultimately control overall rate of degradation-physics rather than chemistry! The arguments above however indicate that supply of hydrocarbons is not rate limiting in subsurface biodegradation. As in many fields there is no aqueous

geochemical evidence for extensive water flow in the aquifer (e.g. waters are more saline than seawater), it thus is likely that the volume of the aquifer will control nutrients and electron acceptors accessible by diffusion to organisms living near the oil water contact. Aquifer volume relative to oil leg volume may therefore be a key variable in controlling biodegradation rate and extent (Connan, 1984; Horstad et al., 1989). Field examples indicate that where reservoirs are filled by oil down to an under-seal (a shale for example) that oils are frequently not degraded even when nearby oil columns with water-legs are biodegraded.

With first order alkane degradation rate constant of around 10^{-6} yr^{-1}, net hydrocarbon removal rates in the reservoir degradation zone are on the order of 10^{-6} mmol oil/L/day in the degradation zone, comparable with many reported aquifer organic matter respiration rates such as those reported for the Middendorf and other aquifers by Murphy and Schramke (1998) and Chapelle and Lovley (1990), even though these are affected by meteoric water invasion and may not be directly comparable. The inferred rates are also much slower than inferred anaerobic lab alkane degradation rates (Connan et al., 1996; Zengler et al., 1999). This may explain why true simulation of deep biodegradation has and may well remain elusive and emphasises the need for long time period approaches to studying biodegradation in the lab (J. Connan, pers. comm.).

3.3. Rates assessed from mixed oil occurrence (MOO)

Many oils in biodegraded oil provinces have multiple levels of degradation. This is indicated with *n*-alkanes often coexisting with oils that show extreme levels of degradation. These mixed oils may occur as frequently as 50% or more of a province's oils. This mixed signature contains information on the relative time scales of *n*-alkane degradation and fresh oil charging.

Non-degraded N. Sea oils typically have values of L1 of >10 (parameter L1 as defined in experimental section) and oils with few *n*-alkanes left have values with $L1 << 0.1$. Mixed oils have intermediate values of L1. This approach is simple, but useful, in that it allows assessment of the timescale of degradation in terms of the timescale of filling. Running simple charge and simultaneous degradation models as described in the experimental section indicate that mixed oils with *n*-alkane/hump ratios near 1 are common where the charge and degradation rates are similar. Oil charge rates will be primarily controlled by source rock heating rates and as these are well known, filling timescales can be defined. Typically oil-expelling source rocks mature over a 50 °C window (100–150 °C). With typical heating rates of around 3–5 °C/Ma for source basins, a charge timescale for an oilfield will be on the order of 10–15 Ma. If degradation rates are 10 times the charge rate only degraded hump dominated oils with $L1 < 0.1$ are seen even if continuous new charge is present. If the degradation rate is ten times lower than the charge rate non-degraded looking oils dominate with high values of L1.

As mixed oils are common in our experience (some N. Sea fields contain 50% obviously mixed oils—c.f. Horstad and Larter, 1997) this suggests the average rates of charge and degradation and thus the timescales of oil biodegradation and field filling are very similar. Thus degradation timescales are around 5–15 Ma for typical oilfields. These timescales are those also indicated by the diffusive gradient method for *n*-alkane removal (Fig. 5) and so we conclude that biodegradation is a slow process in reservoirs with many millions of years typically needed for *n*-alkane removal.

Under stressed, nutrient limited conditions in an oil reservoir with these low inferred reaction rates, it is unlikely that the temperature extremes survived by organisms in nutrient rich hydrothermal environments are relevant. This is so even though the empirical upper temperature limit of ca 80 °C (Connan, 1984) observed for petroleum biodegradation in deep reservoirs is considerably lower than temperatures quoted for the denaturation and decomposition of many bacterial and archaeal proteins and nucleic acids (Blochl et al., 1997; Stetter, 1996; Daniel and Cowan, 2000). Equally, Helgeson's theoretically predicted stabilities of proteins suggest that life may be possible at higher temperatures still (Helgeson et al., 2000) and thus the 80 °C limit of biodegradation ("the Connan limit") is not one controlled by macromolecule stability. One of the many mechanisms that are believed to contribute to the unexpected thermal stability of hyperthermophilic *Archaea* and *Bacteria* is rapid re-synthesis of temperature sensitive cell components (Daniel and Cowan, 2000; Stetter, 1999). In a system such as an oil reservoir where low hydrocarbon degradation rates appear to be the norm, controlled by supply of limiting nutrients or oxidants, the high metabolic rates required to replenish rapidly degrading chemicals are unlikely to be sustainable. This failure of rapid cell repair mechanisms, rather than protein or nucleic acid stability per se, is a more plausible cause of the cessation of bacterial activity in deep sediments. It's not the heat that kills them, it's heat under malnourished conditions!

4. Conclusions

Biodegradation rate constants (first order) in oilfields are around 10^{-6}–10^{-7} per year in the degradation zones these corresponding well with field-wide minimum rate estimates (zero order) of ca 10^{-8} kg hydrocarbons/kg oil/year for the whole oil column. These low rates give estimates of the time to remove ca 10% of the alkanes of oil as around 5–15 Ma depending on initial oil gravity,

oil column height and diffusion coefficients. At low conversions of saturated hydrocarbons, with the units used, zero and first order rate constants are of similar magnitude. With induction times of around 1–2 Ma for light oil reservoirs and 5–15 Ma for heavy oil reservoir degradation the results indicate that where we see continuous gradients in the oil columns that degradation must have been occurring for many millions of years and indicate that to remove the *n*-alkanes from an oil (i.e. about 10% of an oil) around 15 Ma is needed (ca 5 Ma for a light N. Sea oil). This indicates the timescales of oilfield degradation and filling are very similar and that degree of biodegradation will be substantially controlled by oilfield charge history. Assessment of mixed oil occurrence provides an independent confirmation that these rates and timescales are realistic.

The maximum effective rate constant of degradation, ultimately controlled by the limit of diffusion of alkanes to the oil-water contact (ca 10^{-4} per year for a 130 m thick oil column) is well above the observed rate constants indicating that the oil biodegradation rate is not limited by electron donors (hydrocarbons) but by supply of nutrients or oxidants. With a first order alkane degradation rate constant of around 10^{-6} yr^{-1}, net hydrocarbon removal rates in the reservoir are on the order of 10^{-6} mmol oil/L/day in the degradation zone, comparable with many reported aquifer respiration rates. These slow rates of degradation in nutrient-depleted reservoirs are inferred to be inadequate to support the rapid resynthesis of key biochemicals necessary to support the activity of microorganisms at temperatures above 80 °C. Observations of non-degraded oils in reservoirs heated to greater than 80 °C prior to oil charging suggest that the effective base of the oil degrading biosphere is accurately indicated by the base of the zone of biodegraded oils in most basins, or around 80 °C as indicated by the work of Bernard and Connan (1992). We suggest that low metabolic rates rather than biomacromolecule stability are the primary control on the base of the petroleum biodegrading biosphere. We can conjecture that this will be the same for all life in the oligotrophic deep crust. Heterotrophic life IN earth ceases at 80 °C!

With similar time scales of oil charging and biodegradation, the dominant control on bulk and molecular composition of biodegraded crude oils is in-reservoir or in-carrier oil mixing between degraded and fresh oils. This explains why, so frequently, geochemical biodegradation level schemes fail to work clearly even when only one oil charge *appears* to be present based on the proportions of resolved to unresolved gc components. The timescales of biodegradation and field charging and mixing are similar and an early highly degraded oil residue in a reservoir can dominate the physical properties of oils even with abundant late fresh oil charge. We will discuss this elsewhere.

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