

The Kudu wells: Results of a biomarker study related to burial history modelling

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The extractable hydrocarbon content of a shale sample taken from the source rocks overlying the gas-bearing sands in the Kudu 9A-2 well is concluded to be an indigenous bitumen. Ratios of homologous series of total aromatic and saturated hydrocarbons support the high maturity levels and the source quality, determined from optical and pyrolysis analysis, but conflict with maturity levels derived from sterane and terpane isomerisation ratios. These biomarkerratios suggest generation at lower maturation levels. The conflicting maturity levels are resolved by a geohistory model which predicts early generation and expulsion from a wet-gas or oil-prone source. Early hydrocarbons were generated from the originally higher quality source rock and were possibly isolated from further hydrocarbon input in silty microreservoirs. The biomarker ratios were thus shielded from further change, although the light and medium gravity total hydrocarbon ratios continued to alter until the present due to increasing maturity, mediated possibly by clay catalysis.

Introduction

The objectives of this paper are to document the extractable hydrocarbon content of a sample of shale from the Kudu 9A-2 well and to determine whether the bitumen is indigenous, migrated or a contaminant. The implications of the extract data on the source quality, maturity and burial history are then compared with those described previously on the basis of routine pyrolysis and optical work.

Location and setting

The Kudu 9A-2 and 9A-3 wells were drilled during 1987 and 1988, 170 km due west of the Orange River mouth, in the southern section of the Namibian offshore (Fig. 1). Both these wells intersected three source intervals, viz: a thick (~140-150 m) early Aptian interval between horizons P and P1 (upper source), thought

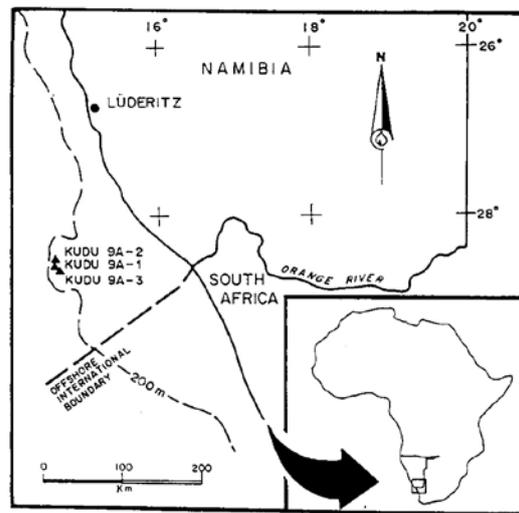


Figure 1: Location map showing the positions of the Kudu 9A boreholes, offshore Namibia

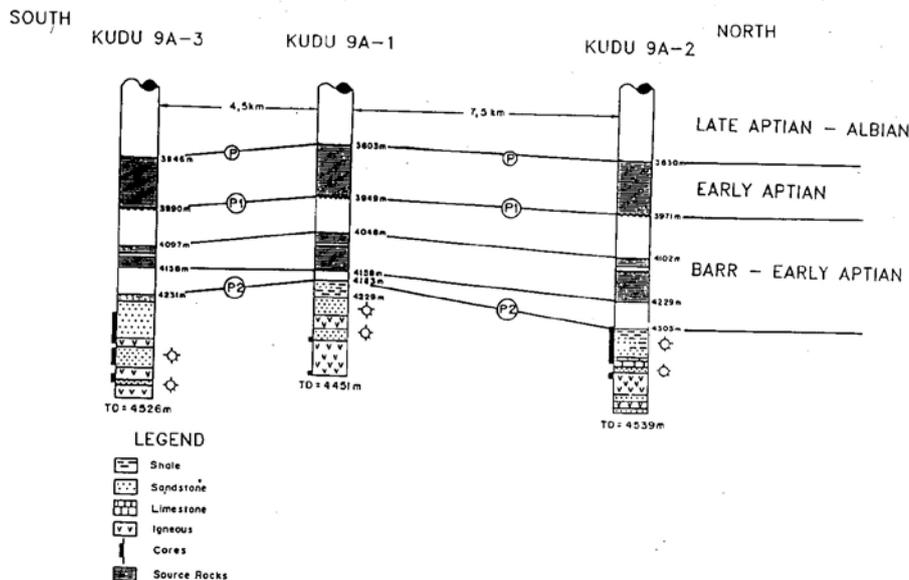


Figure 2: Cross section through the Kudu 9A boreholes showing the Barremian to early-Aptian source rocks intersected between horizons P and P2.

to be the equivalent of the early Aptian source in the Bredasdorp Basin (Davies, 1990), and two thinner (~30 m, ~60 m) Barremian to early-Aptian intervals between horizons P2 and P1 (lower source). The precise depths and thicknesses in each well can be derived from Figure 2. These dark grey shales were deposited in an upper slope or outer shelf environment under poorly oxygenated conditions (McMillan, 1990) and directly overlie volcanics, shallow marine shelly sands and sands interpreted as aeolian in origin (Wickens and McLachlan, 1990). Detailed discussion of age and environment may be found in the previous two references as well as in Benson (1990) and Marot (1990).

Previous Work

Sample processing

The processing, the analysis of the samples by optical and pyrolysis methods, and the methods of interpretation are dealt with in detail in Davies and Van der Spuy (1990) and will not be discussed here. However, as the original and present-day state of the source rocks is of key importance to this paper, aspects of their quality and maturity are summarised below.

Maturity

Rock Eval Tmax and vitrinite reflectance values, the interpreted source intervals and the positions of the oil and wet gas generation windows determined for Kudu 9A-2 are shown in Figure 3. The source intervals are presently overmature for oil generation and, with V_{RO} values greater than 1.3% and Tmax values greater than 450°C, these intervals are presently in the gas window.

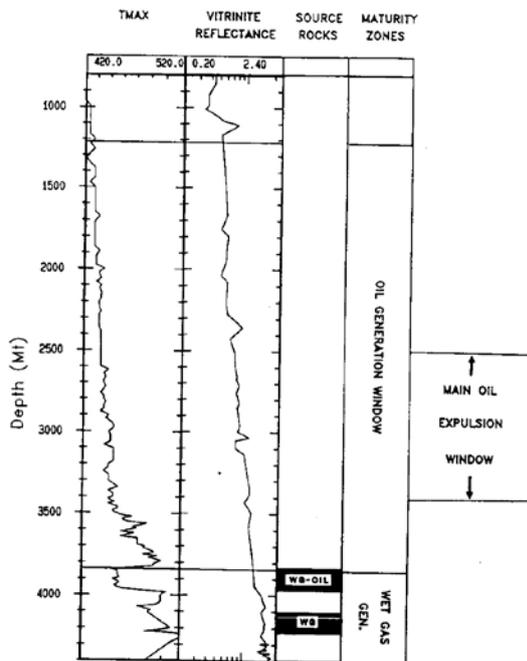


Figure 3: Tmax (°C) and vitrinite reflectance (%) curves for the Kudu 9A-2 borehole. The source-rock positions and interpreted generation windows are also shown

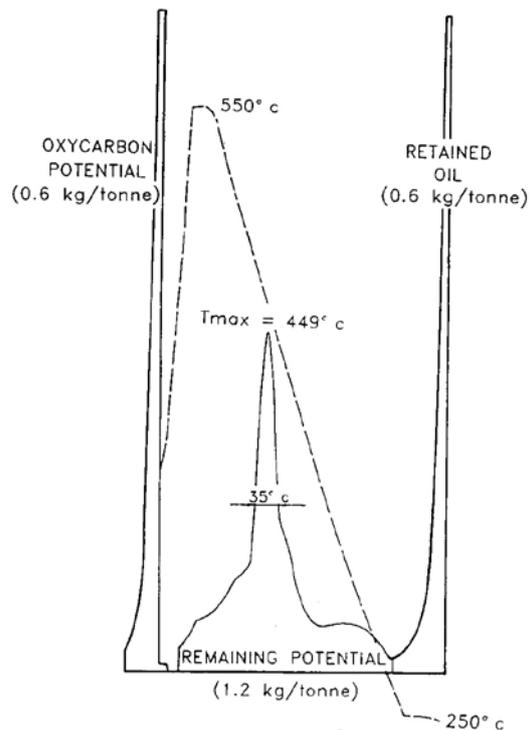


Figure 4: A RockEval pyrolysis chart for a sample from the upper source-rock interval (3872 m) in Kudu 9A-2. Note the narrow remaining potential (S2) peak

The upper interval also highlights the reduced Tmax values which are typically found (Espitalie, 1986) in good-quality source rocks.

The estimation of the present maturity level is furthermore supported by spore fluorescence colour and the Wetness Index curve.

Quality

Due to the high maturity level the source intervals are currently only capable of generating minor amounts of gas. However, comparison of the chemical and optical parameters with those of other source intervals from the southern offshore (which also have predominantly amorphous organic matter), provide evidence that the original quality of the upper interval was at least wet-gas to oil-prone. The upper source interval was interpreted (Davies and Van der Spuy, 1990) to have originally had a generative potential of up to 11 kg/tonne and should have expelled oil.

The lower two intervals were originally capable of generating wet gas but in smaller quantities. A typical Rock-Eval pyrolysis chart for a sample from the upper interval is shown in Figure 4. The narrow S2 peak indicates a limited range of activation energies, described by Burnham (pers. comm.) as being typical of originally oil-prone kerogens.

Recent extract and biomarker work, performed on samples of the Kudu 9A-2 shales, confirmed the earlier findings regarding source quality. The biomarker data

also shed further light on the conclusions regarding the maturity and therefore on the timing of generation which took place mostly in the late Cretaceous but also in the mid Tertiary.

Extract Data

Introduction

Oil-like hydrocarbons, commonly found in source rocks, are assumed to be unexpelled remnants of the oil generated therein (Tissot and Welte, 1984). Such bitumen traces were solvent extracted from two shale samples (3870 m and 4170 m) from the Kudu 9A-2 well for capillary Gas Chromatography (GC) studies.

The shale samples are considered to be representative of the upper source interval (between horizons P and P1) and the lower source intervals (between horizons P1 and P2) as shown on Figure 2. One of the samples was further analysed by GC-Mass Spectrometry (GC-MS) and the characteristic fragmentation ions of steranes and triterpanes (m/z 217 and m/z 191 respectively) were monitored.

In addition to these two samples a further sample, from a well in the Bredasdorp Basin, was also solvent extracted and studied by gas chromatography. This sample is from a wet-gas to oil-prone source rock of similar potential to that proposed for the upper Kudu interval (Davies and Van der Spuy, 1988) and is the highest maturity sample of that shale which is available for comparison.

The bitumens in each of the three samples are considered to be indigenous for four reasons. Firstly the production index data (Table 1) all lie within the range of mature, non-impregnated source rocks (Miles, 1989 and Tissot and Welte, 1984). Secondly the samples were all selected from the centre of the source intervals at least 30 metres from the edge of the shale where the effects of capillary impregnation are minimised. Thirdly none of the samples displayed any fluorescence under ultraviolet light and fourthly none of the samples was selected from intervals with anomalously high ditch gas.

Experimental

Routine sample processing and analysis methods were carried out to industry-wide standards, as described in Davies and Van der Spuy (1988).

Shale extractions were carried out for 8 hours on finely ground samples in glass Soxhlets using chloroform. The extracted organic matter (EOM) was treated with excess n-pentane to precipitate the asphaltenes and centrifuged at high speed to enhance their separation from the other fractions. The resulting deasphalted bitumen was injected onto a silica gel/alumina LPLC column to separate it into its constituent fractions.

The total saturates were eluted from the column using n-hexane, the total aromatics using benzene and the res-

ins using a 4:3 v/v mixture of benzene and methanol.

GC analyses were carried out on a Varian 3300 instrument using the split/splitless injection technique and the resulting hydrocarbons detected using a flame ionisation detector. The fused silica WCOT capillary column (25 m x 0.25 mm i.d.) was coated with a micron film of OV101. The GC oven programme conditions were 80-280°C at a temperature ramp rate of 2.5°C/minute. The detector output was directed to a MIAD PC running the DAPA programme (for data capture and processing) using a scan rate of 500 m seconds.

The saturated hydrocarbon fractions were further processed for GC-MS analyses by removing the normal paraffins (using the urea adduction method detailed in Hall *et al.*, 1985) in order to accentuate the condensed cyclo-paraffins and reduce the effect of co-elution with some n-paraffins.

GC-MS analyses were carried out, in the local laboratory, using a Carlo Erba Mega 5270 GC in on-column mode directly coupled to a Carlo Erba single quadrupole QMD 1000 Mass Spectrometer (equivalent to a VG Trio 1) in full scan mode (1100 ms/cycle). A fused silica WCOT capillary column (45 m x 0.3 mm i.d.) was coated with BPI and the programme conditions were 80-280°C at 1.5°C/minute. The mass spectrometer was operated in EI mode with an electron energy of 70 eV and an ion source temperature of 250°C. The data were captured and processed on a transputer running the LAB-BASE programme.

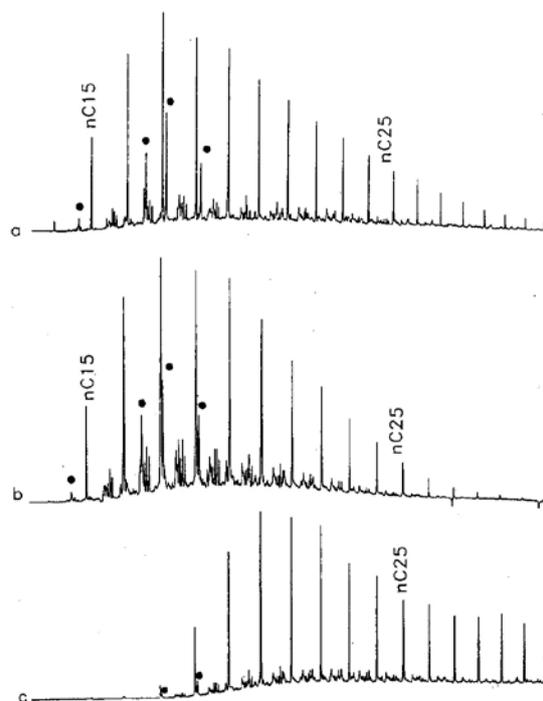


Figure 5: gas chromatographic traces of the total saturated hydrocarbons from (a) E-AJ1 2910 m, (b) Kudu 9A-2 3870 m and (c) Kudu 9A-2 4170 m with normal paraffins (numbered) and isoprenoids (*) indicated

Similar analyses were carried out in an overseas laboratory using a HP 5890A GC in split/splitless mode directly coupled to a Finnegan 4000 single quadrupole MS in MID mode (1200 ms/cycle). The bonded column (30 m x 0.32 mm ID) was coated with BP5 and programmed 20-130°C at 30°C/minute then 130- 300°C at 5°C/minute. The mass spectrometer was also operated

in the EI mode and the data collected using the INCOS data system.

Samples

Gas chromatographic analyses of the saturated and aromatic fractions of the total extracts of each sample were carried out. The results of the analyses of the saturates are shown in Figure 5 whilst the central portion of the aromatics GC's (portraying the three-ring compounds) are shown in Figure 6.

For GC-MS analyses, a total of six samples from early Aptian wet-gas to oil-prone source rocks were used; one from Kudu 9A-2 and five from the Bredasdorp basin. Three of these were analysed by an internationally known contracting laboratory and one of these was then re-analysed (for calibration purposes) with the other three samples by a local laboratory.

GC Results

Evaporation of the low boiling-point fraction during sample capture and subsequent processing resulted in the loss of all saturates lighter than nC14 and in their proportional loss up to nC17. The same effects are also evident in the aromatic fraction where components lighter than phenanthrene have been depleted. The lower Kudu sample, at 4170 m, has a very much smaller content of extractable organic matter (Table 1) probably due to processing losses as above but also, possibly, to the expulsion of light oil because the losses extend up to the methyl phenanthrenes. The lower Kudu sample contains such a small amount of saturated hydrocarbons (only 15% of the upper Kudu sample) that the gas-chromatograph was unable to provide an accurate image of the components which resulted in an uneven n-paraffin envelope.

Saturated Hydrocarbons

The saturated hydrocarbon GC's of the Kudu and E-AJ1 samples (Fig. 5) display similar distributions of

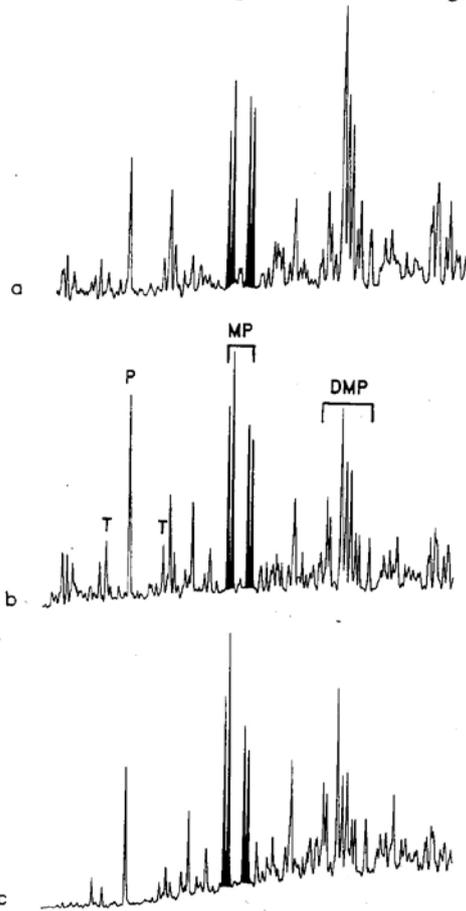


Figure 6: Gas chromatographic traces of the aromatic hydrocarbons from (a) E-AJ1 2910 m, (b) Kudu 9A-2 3870 m and (c) Kudu 9A-2 4170 m with thiophenes (T), phenanthrene (P), methyl phenanthrenes (MP) and dimethyl phenanthrenes (DMP) indicated

SAMPLE	V _{RO}	S1 kg/ tonne	S2 kg/ tonne	S3 kg/ tonne	Tmax °C	Corg %	EOM ppm	Sat %	Arom %	Resin %	Asph %	CPI	MPI3	PI
Bredasdorp well	1,23%	1,14	2,40	0,78	451	2,39	1890	63	18	15	4	0,96	0,90	0,32
Kudu 9A-2 3870m	1,33%	0,31	0,60	1,00	454	1,36	590	47	20	23	7	0,95	1,36	0,34
Kudu 9A-3 4170m	1,78%	0,26	0,38	1,28	?	1,66	285	15	26	32	26	0,95	1,55	0,40

EOM = extracted organic matter

Sat = saturated hydrocarbons

Arom = aromatic hydrocarbons

Asph = asphaltene

CPI maturity index (Bray and Evans, 1961)

$$\frac{2 \times (nC_{23} + nC_{25} + nC_{27} + nC_{29})}{nC_{22} + nC_{30} + 2(nC_{24} + nC_{26} + nC_{28})}$$

MP maturity index after Radke, 1987

$$\frac{2MP + 3MP}{9MP + 1MP + 4MP}$$

PI = production index ie $\frac{S1}{S1+S2}$

normal paraffins and isoprenoids. These homologous series of compounds are known to have been sourced in organic matter (Tissot and Welte, 1984) and are commonly used to demonstrate the source type. Thus source rocks with an extract characterised by small amounts of nC25+ paraffins are interpreted to contain only small amounts of terrestrial organic matter. The n-paraffin envelopes, therefore, suggest that the Kudu samples comprise wet-gas to oil-prone source rocks which supports the earlier conclusions regarding their quality (Davies and Van der Spuy, 1990).

However, the effects of high maturity, indicated by vitrinite reflectances in excess of 1.3% (equivalent to the gas generation zone of Tissot and Welte, 1984) have produced a normal paraffin envelope with the smooth, steep profile typical of high maturity hydrocarbons. It is therefore not possible to determine the original type of organic matter (OM) from the shape of the n-paraffin envelope. The isoprenoids, though, are less affected by high maturity and it is possible to show, because of the relatively low pristane content, that the Kudu shales were not deposited in an oxidising environment (Powell and McKirdy, 1975).

One of the classic ratios used to determine the maturity of oil is that of the carbon preference index (derived from Bray and Evans, 1961) which compares the ratio of even- to odd-numbered normal paraffins against a known maturation parameter such as vitrinite reflectance.

The ratio is evaluated for the hydrocarbons (nC22-nC30) which are usually found in oils and condensates and which are typical of terrestrial organic matter. Thus the plot of carbon preference index (CPI) against vitrinite

reflectance furnishes an accurate measure of the real maturation level of the oil but only as high as $V_{RO} = 1.1\%$ when the ratio reaches its equilibrium value. A plot of the data from the Kudu wells and all available samples of the early Aptian wet-gas to oil-prone source shales in the Bredasdorp Basin (Fig.7) demonstrates that the Kudu samples have CPI values commensurate with a maturity level in excess of $V_{RO} = 1.1\%$ (Table 1).

Aromatic Hydrocarbons

The phenanthrenes (condensed three-ring compounds) have been highlighted in the expanded central portions of the gas-chromatograms (Fig. 6) and several features are evident there from.

The overall similarity between the three aromatic samples is due partly to the effects of the similar type of organic matter and partly to the maturity overprint (as with the saturates).

The latter is fairly well defined by the relative maturation parameter of Radke (1987), which utilises the four methyl phenanthrenes (MPI3). The more usual MPI parameter of Radke (1982) cannot be used because of the loss of phenanthrene from the lower Kudu sample. The ratio, relative to the known vitrinite reflectance of each sample and to the same Bredasdorp Basin-source rocks used in the CPI plot, is given in Figure 8. It is apparent that the Kudu samples have the ratio which could have been predicted from their maturity although the loss of light hydrocarbons has slightly affected the ratio in the deeper shale. The aromatic hydrocarbons are nevertheless considered to be essentially representative of oil generated in the shale.

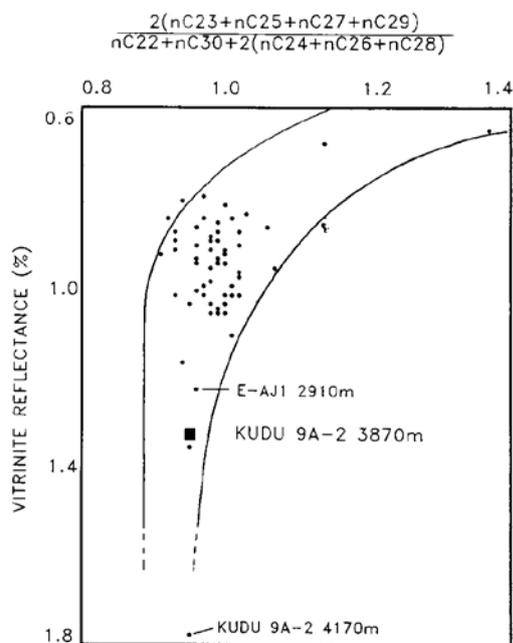


Figure 7: Plot of Carbon Preference Index (CPI) vs. Vitrinite Reflectance

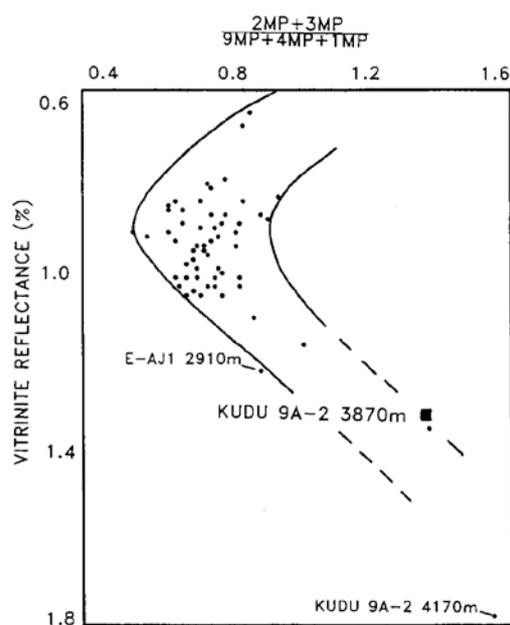


Figure 8: Plot of Methyl Phenanthrene Index (MPI3) vs. Vitrinite Reflectance

GC-MS Results

In order to confirm the original estimation of the source potential and consequently the quantitative estimates of the overall generation and expulsion, "biomarker" GC-MS analyses were carried out on the upper Kudu sample.

This type of analysis investigates the compounds whose carbon skeleton is essentially unaltered from the time of deposition because maturation tends to modify only the functional groups (Mackenzie, 1984).

The saturated hydrocarbon fraction was studied using single ion plots of the characteristic sterane (m/z 217) and terpane (m/z 191) fragments selected from the full scan monitoring carried out during the analysis. The

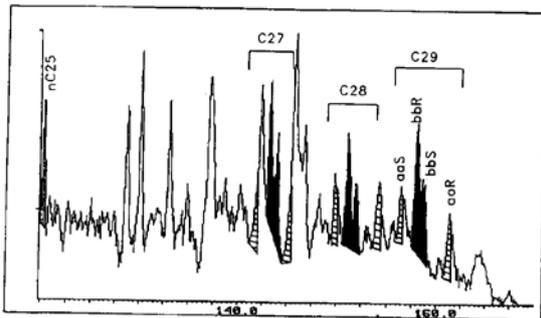


Figure 9: GC-MS trace (m/z 217) of sterane saturated hydrocarbons. Note: 14α 17α (cross hatched) and 14β 17β (filled) cholestanes indicated

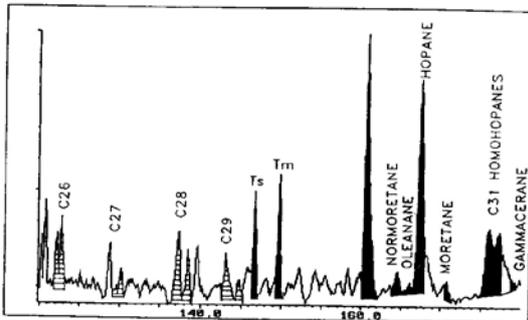


Figure 10: GC-MS trace (m/z 191) of terpane saturated hydrocarbons. Note: tricyclic (cross hatched) and pentacyclic (filled) hopanes and moretanes indicated

relevant portions of each ion plot have been reproduced in Figures 9 and 10 respectively and the peak assignments have been derived from calibrations of analyses carried out at other laboratories.

The relevant ratios from the Kudu sample as well as the ratios for the five Bredasdorp samples are given in Table II.

Source Quality

The triangular plots of the total C27-29 sterane carbon distribution of Difan (1990; Fig. 11) and of the C29 sterane stereoisomers of Moldowan *et al.* (1985; Fig. 12) have been constructed using data from the five Bredasdorp Basin shales as well as from the Kudu sample. Both triangular plots demonstrate that the source for the extracted bitumen is not lacustrine and that it comprises a mixture of marine and terrestrial organic material. Furthermore, the very small gammacerane peak (Fig. 10) indicates normal marine salinity. Organic matter studies carried out previously (Davies and Van der Spuy, 1988 and Benson, 1990) demonstrated that the uppermost source interval in the Kudu wells (between horizons P and P1) was deposited in a marine environment and contained dominantly marine organic matter. Thus these data confirm the conclusion above that the bitumen extracted from the shale was generated *in situ* because the hydrocarbons found are the type that would be expected from the quality and maturity of the known organic matter.

Maturation

Sterane and terpane biomarker ratios have been used successfully elsewhere (Waples and Machihara, 1990) to determine the maturation level of oils and shale extracts. Three of these ratios (C29 steranes, C31 hopanes, C27 hopanes) have been extracted from the GC-MS data presented in Figures 9 and 10 and each of these ratios shows anomalously low maturities for the Kudu sample.

The C29 sterane stereoisomer plot (Fig. 12) shows that the Kudu sample is located within the same range of values as the Bredasdorp Basin samples although, at the known maturation level, it might be expected to plot further away from the $\alpha\alpha R + \beta\beta R$ apex.

SAMPLE	V_{iso}	Cholestanes $\alpha\alpha + \beta\beta$			C29 Cholestanes			C29 Cholestanes S/S+R	C31 Hopanes S/R	C27 Hopanes Ts/Tm	GC-MS Analysts
		C27%	C28%	C29%	$\alpha\alpha S + \beta\beta S$	$\alpha\alpha R + \beta\beta R$	$\beta\beta S + \beta\beta R$				
Bredasdorp 1	0,75%	43	32	25	29%	36%	35%	0,40	1,50	1,54	SU
Bredasdorp 2	0,84%	38	31	31	29%	39%	32%	0,46	1,46	1,25	SU/S-R
Bredasdorp 3	0,98%	42	25	32	31%	33%	36%	0,49	1,41	1,89	SU
Bredasdorp 4	1,02%	45	27	28	28%	32%	40%	0,48	1,47	3,67	S-R
Bredasdorp 5	1,04%	42	27	31	29%	36%	35%	0,46	1,59	1,93	S-R
KUDU 9A-2 3870m	1,33%	38	30	32	27%	35%	38%	0,47	1,12	0,87	SU

Note: Analysts SU = Stellenbosch University, Laboratory for Ecological Chemistry. S-R = Simon-Robertson Laboratories

Table II

Sterane enantiomer ratios have been used by many authors to determine the maturity of oils and shales e.g. Waples and Machihara (op. cit.) and references therein.

The ratios between the two C20 forms of the C29 α 14 α 17 α cholestanes are usually used in preference to those of the C27 and C28 homologous compounds because they are easier to identify and there is minimal co-elution with other compounds. The biologically produced form (20R) declines as the maturity dependant form (20S) is generated and an equilibrium point is eventually reached which comprises 55% 20S and 45% 20R. The ratios can, however, be different for different types of organic material (Strachan *et al.*, 1989) although in this case the optical and chemical data (Davies and Van der Spuy, 1988 and Benson, 1990) demonstrate that the original organic material in the Kudu sample was es-

entially the same as that in the five Bredasdorp samples. Strachan *et al.* (op. cit.) also showed that coals and shales both reach the equilibrium point at a temperature of -110°C which is equivalent to a V_{RO} of 1.0%.

The data have been plotted (Fig. 13) together with the range of correlations given in Waples and Machihara (op. cit.) and, whilst there are not enough data for rigorous statistical controls, it is evident that the Kudu point plots below the range of correlations.

Strachan *et al.* (op. cit.) further stated that where the ratio is lower than predicted from a known maturation parameter (and is less than 0.51) the likely causes are either a predominance of coaly organic matter or a high heating rate (> 5°C/million years). However, neither of these explanations can be supported, firstly because the Kudu organic matter is not coaly (Benson, 1990) and secondly because the overall heating rate (as shown

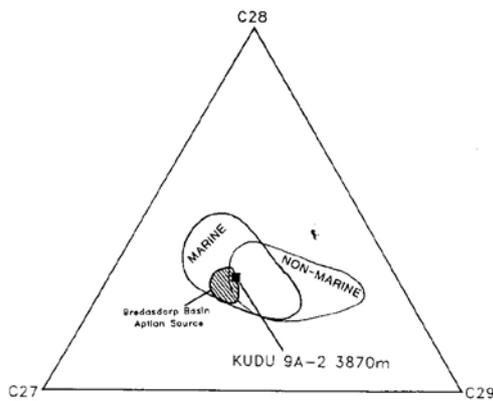


Figure 11: carbon number distribution of the steranes with 14 α 17 α stereochemistry. Note: source specific regions from Moldowan *et al.* (1985)

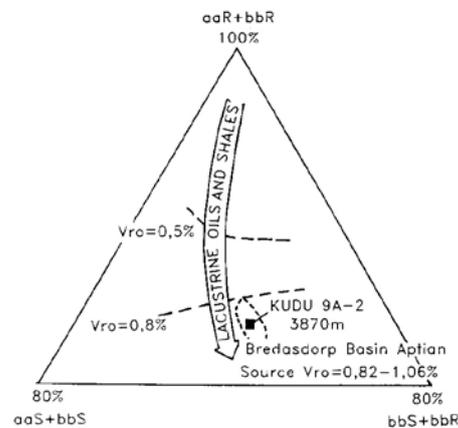


Figure 12: Isomerisation of the C29 steranes including trends from Difan *et al.* (1990)

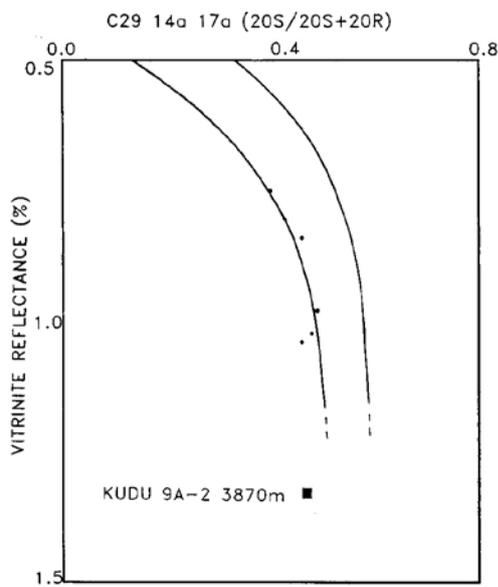


Figure 13: C29 14 α 17 α sterane epimerisation plot including correlation from Waples and Machihara, *et al.* (1990)

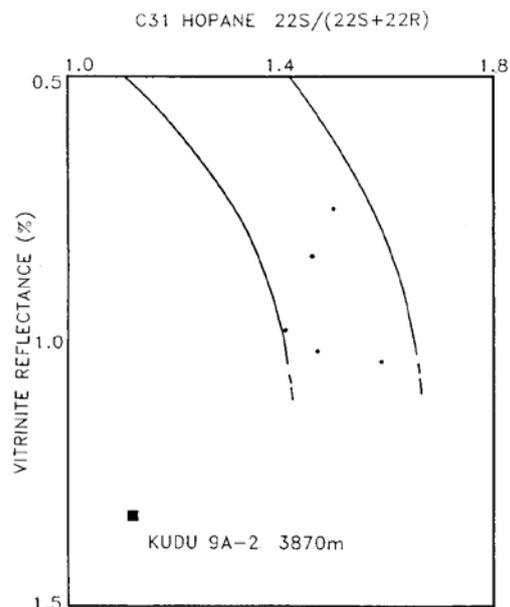


Figure 14: C31 hopane epimer plot including trend region from Palacas *et al.* (1985)

below) is within their normal limits (0.5-5.0°C/million years).

The geohistory reconstruction (Fig. 16) shows overall that 4350 m of sediments were deposited in 148 million years for an overall temperature increase of 165°C at an average rate of 1.1°C/million years. However, the reconstruction also shows that the rates differed and that there were essentially three periods with differing burial rates.

During the first period, Barremian-late Coniacian, a total of 1750 m of sediments were deposited. Excluding the short hiatuses or minor episodes of erosion, this occupied 35 million years (124-89 million years). Assuming that the average palaeogeothermal gradient (3.8°C/100 m) was effective during the period, the burial represents a temperature increase of 66.5°C which confirms a rate of temperature change with time of 1.9°C/million years.

The equivalent temperature increase rate for the second period of burial in the Santonian and Campanian of 9 million years (89-80 million years BP) and 2550 m burial in 10.8°C/million years.

The third episode of sedimentation occupies essentially the Tertiary. The micropalaeontological data (McMillan, pers. comm.) shows that the bulk of this sedimentation took place during two periods of burial in the Oligocene (34-30 million years BP) and Miocene (21-12 million years BP) totalling 750 m. Using the palaeogeothermal gradient, this translates into 2.2°C/million years.

Thus the heating rate exceeded 5°C/million years only during the episode of burial in the Santonian and Campanian. In that interval the sterane epimerisation could be expected (Strachan *et al.*, op. cit) to lag behind the expected values. However, during the further burial

in the Tertiary (at demonstrably lower heating rates) the isomerisation rate could increase to reach its kinetically expected value.

Terpanes

The ratio of the biogenic to thermogenic enantiomers (R and S respectively) of the C31 homohopanes has been used as a measure of maturation by Palacas *et al.* (1985), who showed that the maximum is reached at approximately the same depth as that for the steranes (i.e. $V_{RO} = 1.0\%$) and they provide an envelope which encompasses all their data.

The envelope has been plotted on Figure 14 against Tmax data rather than the more usual vitrinite reflectance, but these can be compared using the calibrations in Espitalie *et al.* (1985). The available data for the Bredasdorp wells have also been plotted on Figure 14 and are clearly located within the envelope yet the Kudu point plots outside the envelope because the ratio is much lower than would be expected from its vitrinite reflectance.

The ratio of rearranged to regular trisnorhopanes ($Ts \pm m$ of Seifert and Moldowan, 1978) is also conventionally used to infer the maturation level.

Samples from the late Jurassic source in the North Sea were used by Comford *et al.* (1983) to demonstrate the almost linear relationship of the ratio ($Ts/Ts+Tm$) with temperatures up to 150°C. The data from Comford have been recalculated to the more usual form of the ratio (Ts/Tm), replotted against the equivalent vitrinite reflectance data of Cooper (1990) and used to modify the envelope of Van Graas (1989) to construct Figure 15. The data given in Van Graas (op. cit) and Comford (op. cit) show that at maturities higher than $V_{RO} = 1.0\%$, the Ts/Tm ratio rises exponentially.

The Bredasdorp data plot within the envelope but the Kudu data plots at far too Iowa value for its known vitrinite reflectance.

Thus the n-paraffin and methyl phenanthrene maturation indices of the Kudu and Bredasdorp samples provide ratios commensurate with the maturation level known from the vitrinite reflectance and pyrolysis measurements. The biomarker data, on the other hand, indicate a much lower maturity level equivalent to $V_{RO} = 0.7-0.9\%$.

Burial History

A compaction corrected geohistory reconstruction (Fig. 16) for the Kudu 9A-2 well site has been constructed using the BASIN MOD package. Depth/porosity relationships are from Sclater and Christie (1980) whilst the age and environment data are from McMillan (1990) and McMillan (1993) (pers. comm.). After the extrusion of the pre-Barremian subaerial lavas, thermal subsidence continued and marine conditions transgressed the area.

Deep marine, base-of-slope sediments were depos-

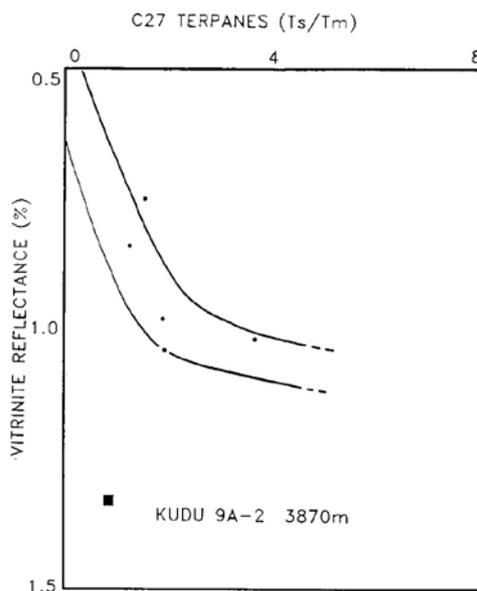


Figure 15: C27 triterpane isomerisation plot showing trend zone from Van Graas (1989)

ited during the late Barremian to early-Aptian whilst, after the mid-Aptian unconformity (horizon P), the water shallowed gradually until the present

Burial rates remained moderate until the Turonian, at which time they became extremely high, and the vast majority of burial was completed by the Santonian. The record of the late Cretaceous and Tertiary burial is unfortunately incomplete due to poor sample control, yet with the help of the seismic record it is possible to produce a reasonably clear sequence of events for this period from the isolated bit samples.

From the start of the Campanian, burial at moderate rates resumed, interrupted by 150 m of erosion in mid-Campanian. This was followed by an hiatus until burial resumed in the Oligocene. The late Tertiary shows an erosive event and further burial in the Miocene. Part of the explanation for the conflicting chemical maturity data is therefore likely to be found in the repeated episodes of burial, uplift and erosion which occurred during the late Cretaceous and Tertiary.

Kinetic (LLNL) maturation zones devised by Burnham *et al.* (1987), and expressed in terms of vitrinite reflectance, have been superimposed over the burial diagram. The limits of these zones are derived from a marine source rock of the same age and depositional environment and with similar organic material (Davies, 1990). Initially, the gradient was assumed to have been high because of the high heat flow (McKenzie, 1981) commonly found during continental rifting and early drifting. The T_{max} and V_{RO} data indicate an average palaeogradient of $3.8^{\circ}\text{C}/100\text{ m}$ across the Cretaceous and Tertiary section, whilst the borehole temperatures indicate a present gradient of $3.5^{\circ}\text{C}/100\text{ m}$. The model was thus constructed using the average palaeotempera-

ture gradient of $3.8^{\circ}\text{C}/100\text{ m}$.

According to the geohistory reconstruction the upper source intersected the oil expulsion zone in the Santonian and, due to uplift, there was no further increase in maturity. This probably caused active expulsion to cease in the middle of the oil window ($V_{RO} = -0.9\%$) in the late Cretaceous. This is supported by simulations using kinetic data derived from similar organic matter (Tissot and Welte, 1984). The lower source followed a very similar pattern of burial with the exception that sufficient maturity may have been gained during this time for some early gas and bitumen generation and some initial gas expulsion.

Both source intervals gained only minimal further maturity during the later Tertiary burial episodes because of the declining temperature gradient, although some further hydrocarbon generation occurred. Thus there were three periods, Santonian/Campanian, Oligocene and later Tertiary, during which bitumen could have been generated from the kerogen.

Some of the bitumen, generated during these three episodes (mostly during the earliest one) should have been able to migrate out of the source into the main reservoir rock. There are, however, no traces of oil in any of the sands. Much of the oil could, however, have been lost during the tilting phase which occurred immediately after the major generation episode in the late Campanian (Fig. 16). Any oil which was not lost at that time could have been displaced later by the copious amounts of gas which now fill the main sands. If any of the oil had remained in the sand, it would have been altered to pyrobitumen either directly or via an intermediate gas deasphalting stage (Tissot and Welte, 1984) by the advanced maturity. Pyrobitumens can often be

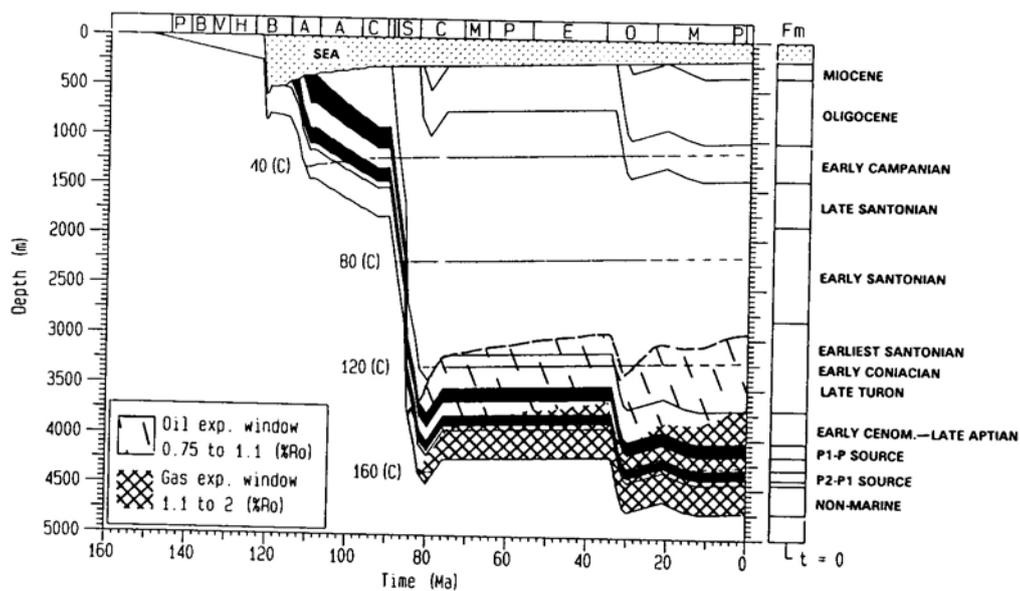


Figure 16: A geohistory reconstruction for the Kudu 9A-2 wellsite, compaction correction according to Sclater and Christie, 1980. Hatched areas indicate zones in which active hydrocarbon generation occurs

found in high maturity sands where they can be seen as discontinuous pseudolaminae or as minute specks of structureless, brittle, carbonaceous material. Marot (1990), in her study of the thin sections of the Kudu sands, made no mention of the presence of such material although Wickens and McLachlan (1990) reported "fine carbonaceous material and occasional wood fragments" in the upper gas sand. They made no comment on the origin of this material which is randomly located (Wickens, pers. comm.) but it may represent remnants of the oil which was trapped in isolated pore spaces by further compaction and subsequently converted to pyrobitumen by later burial.

Discussion

The discrepancy between the chemical maturation parameters derived from the sample of the upper source shale might be explained by one of the following three methods:

1. The sample has been contaminated;
2. the biomarker ratios reverse at high maturities;
3. an unusual maturation effect, such as clay catalysis, has prevailed.

Contamination

No hydrocarbon-bearing substances are known to have been added to the well during the drilling although some of the casing thread protection or drilling rod grease could have contaminated the samples. In the event, it can be shown that there are no unexpected compounds such as high oleananes (which might indicate an impregnation by a late-Cretaceous or younger oil; Ekweozor and Udo, 1987), β -carotene (which might indicate algal organic material; Tissot and Welte, 1984), or gammacerane (indicator for high salinity; Miles, 1989). Moreover, the extractable hydrocarbon contents from other deep boreholes (Price, 1981) confirm that such relatively large amounts of extractable organic matter (EOM) can be found, *in situ*, in high maturity samples. There is therefore no evidence of any contaminant which could have produced the anomalous maturity levels and the EOM content whilst unusually high, is not too great for the maturity of the sample.

The aromatic GC records the presence of small amounts of thiophenes in each of the three samples. It has been suggested that these are indicative of the presence of H_2S in the sediment during burial and its incorporation into the oil during maturation (the H_2S being provided from sulphate reduction by anaerobic bacteria; Demaison and Moore, 1980). The presence of thiophene could, therefore, be a direct indicator of anoxic conditions prevailing on the sea floor. They also state that a severely oxygen-depleted environment is critical for the generation and preservation of oil-prone organic material. The greater amounts of thiophenes in the upper Kudu sample, relative to both the lower Kudu

and the E-AJ1 samples, are therefore an indication that the depletion of oxygen was more severe.

This confirms the belief (Benson, 1990) that the organic matter in the upper source interval is essentially oil-prone whilst in the lower source interval, the organic matter is dominantly of terrestrial origin. It is therefore concluded that the soluble organic matter extracted from the Kudu samples must, in all probability, have been generated by the organic matter in the shale and is representative of that generation.

Reversal of Biomarker Ratios

The biomarker ratios of any oil that was not expelled and which remained in intimate contact with the kerogen would have reached equilibrium during further maturation because of continuous replenishment of the more mature components. Thus any oil which either migrated away from the source rock or remained *in situ* could not be expected to have such anomalously low biomarker ratios.

Marzi and Rullkotter (1990) showed that the sterane stereoisomer ratio may not remain at the equilibrium value indefinitely and that under the right thermal conditions it can decline to as low as 0.40 which would encompass the Kudu data. Their conclusion was, however, based primarily on hydrous pyrolysis experiments, calibrated by only a few natural data points whose maturity had been calculated from an assumed palaeo-geothermal gradient. Strachan *et al.* (1989) showed a similar high maturity reversal (at V_{RO} of 1.62-2.56%) but they also indicated that the kerogen type was probably coaly although its form could not be unequivocally determined.

Moreover, using the same pyrolysis methods, Marzi and Rullkotter (1990) also showed that homohopane enantiomer ratios in siliclastic formations did not reverse at high maturity. This is confirmed by hydrous pyrolysis experiments carried out on samples from the Monterey formation (Peters and Moldowan, 1991). They demonstrated that thermal destruction of certain homohopane epimers, mediated by rock mineralogy, could occur in phosphatic formations but not in siliclastic shales. Furthermore, Van Graas (*op. cit.*) also indicated that the Ts/Tm ratio shows no signs of reversing at high maturity.

Schou *et al.* (1985) also pointed out that biomarker ratios are sensitive to the original starting material. However, as shown above, the Kudu sample has essentially the same type of organic matter as the Bredasdorp samples and its ratios should therefore plot on the same trend.

Marzi and Rullkotter (*op. cit.*) stated that biomarker compound ratios are influenced by only three effects, viz: the initial biomarker assemblage, further generation from kerogen and later thermal destruction. Strachan *et al.* (1989) showed that there was no evidence that thermal destruction of homohopane or trisnorhopane

biomarkers in non-phosphatic rocks had altered their ratios. They also pointed out that the sterane reversal, noted in published examples, may have been due to the high proportion of coaly matter. Raymond and Murchison (1992) provided biomarker ratios from gas-prone organic matter, some of which had been affected by intrusives and the remainder subjected to regional coalification. They stated that "there is an apparent reversal in the trends of many of the ratios with increasing thermal maturity". However the bulk of the data that they reported also came from coaly samples and those had been affected by intrusives and matured beyond $V_{RO} = 1.0\%$. Moreover, the data which they acquired from regionally matured samples showed no signs of reversal although it should be noted that the maturity of those data did not exceed $V_{RO} = 1.0\%$. Thus it appears that isomer ratio reversal is possible only where the original organic matter was coaly.

Clay Catalysis

Some of the oil could have migrated locally into a non-source lithology where clay catalytic reactions could have continued the maturation of certain compound classes such as the normal paraffins (Shimoyama and Johns, 1972) and methyl phenanthrenes (Radke, 1987). In this case, though, unless there were renewed migration from the kerogen-rich intervals, there would be no further change in the biomarker ratios (Thompson, 1992). The Kudu 9A-2 well logs (Davies and Van der Spuy, 1990) show that interbedded silts, which are known to be argillaceous, are present within the upper source interval.

The upper source sample used for these analyses was of ditch cuttings and, as this represented a 10-metre-thick drilled sequence, it is quite possible that there were silty stringers (containing bitumen traces) within the interval - certainly the logs show intervals of low gamma and fast travel time, indicative of silty laminae, within the sampled interval.

There are no clay mineral data from the source intervals in the Kudu 9A-2 or 9A-3 wells but there are data available from the 9A-1 well. These data show that the smectite content is very low at present although the smectite-illite mixed layer minerals comprise 30-40% of the clays. Dunoyer de Segonzac (1970) showed that most smectite is converted to illite and illite-smectite mixed layers by the time maturation had reached $V_{RO} = 0.9\%$. The high contents of such clays in the upper source interval in the Kudu 9A-1 well (and presumably in the Kudu 9A-2 and 9A-3 wells) is a strong indication that the original lithology was smectitic. Smectite, as well as mixed layer (Johns, 1979) catalysis of the normal paraffins and methyl phenanthrenes could then occur. The biomarker ratios would, however, remain unchanged partly because of lack of replenishment and partly because they are unaffected by clay catalysis. It is therefore plausible that the extractable organic mat-

ter, with both high and low maturity indicators, could represent microreservoiring in interbedded silts.

As shown earlier, the maturation level of the low biomarker ratios indicates that the bitumen became isolated at a maturity level of $V_{RO} \%$ which implies that they must be related to the early episode of oil generation during the late Cretaceous. At that time, or shortly thereafter, oil migrated from the kerogen-rich laminae into the silty laminae en route to the edge of the source from where it could finally escape the shale interval. These silts later became sealed, possibly either by clay mineral growth or by compaction, which allowed for continued clay catalytic maturation of some of the saturated and aromatic hydrocarbons but insulated the biomarkers from further kerogen mediated modification.

Conclusions

From the above discussion, it is concluded that the extractable organic matter found in the Kudu 9A-2 shale was generated in that shale. Maturity indices based on saturates and aromatics indicate a present maturity equivalent to that of the shale (demonstrated by optical and pyrolysis analyses) and confirm the mixed nature of the organic material as well as the oxygen-poor environment of deposition.

Sterane and terpane isomerisation ratios which indicate maturities lower than the present level suggest that generation occurred at a relatively early stage and that the hydrocarbons were removed from intimate contact with the shale and possibly trapped in microreservoirs in nearby silty intervals. Original biomarker ratios were thus preserved while some of the other hydrocarbons continued to alter with increasing maturity. It is unlikely that the unusual biomarker signatures are due to reversal of the ratio trends rather than to preservation of an earlier low maturity because, other than a few artificial maturation experiments and studies on coaly material, there are no data to support that contention.

The geohistory model supports these conclusions as it demonstrates an early phase of generation and probable expulsion from the source rocks at a maturation level similar to that suggested by the biomarker data.

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