High-temperature GC evidence for the early formation of C_{40+} *n*-alkanes in coals

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Abstract

High-temperature GC analyses were performed on a coal-sourced waxy oil from the Toka-1 well in the Taranaki Basin and on three bitumens, extracted ultrasonically with boiling toluene, from coals from the Tara-1 well in the Great South Basin, New Zealand. The coals represent an evolutionary trend from immature to post oil expulsion. In all samples the C_{40+} alkanes were characterised by dominant straight-chain members up to about C_{65}, which decreased significantly in abundance in bitumen with increasing maturity. They are present at an early stage of maturity, prior to the main phase of *n*-alkane generation, and may be liberated from cutan/cutin sources within kerogen by thermal decarboxylation of esters or have an earlier origin in the bitumen inherited from diagenesis. An odd-over-even predominance in the C_{40+} *n*-alkanes was most marked in the C_{51}–C_{57} range and decreased with increasing maturity, suggesting that minor amounts of C_{40+} *n*-alkanes with a CPI approaching 1 are also generated during catagenesis. However, the observed C_{40+} *n*-alkane distributions may be affected to a degree by decreasing efficiency of solvent extraction with increasing *n*-alkane molecular weight, and by further long-chain *n*-alkanes generated during catagenesis being partially inaccessible to solvent extraction. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Highly aliphatic biopolymers that resist biodegradation have been detected in extant and fossilised terrestrial plant cuticles (e.g. Nip et al., 1986a, b; Tegelaar et al., 1995). These materials — cutan and suberan — are believed to make significant contributions to kerogen (Hatcher et al., 1983; Tegelaar et al., 1989; Bergren et al., 1995) and may be responsible for the waxy paraffinic oil potential of coals like those from the Taranaki Basin in New Zealand (e.g. Killops et al., 1994). With the development of high-temperature gas chromato-

graphy (HTGC) it has proved possible to examine the distribution of high-molecular-weight (HMW) hydrocarbons in waxy oils up to about C_{120} (Carlson et al., 1993; Philp, 1994). As yet there have been few HTGC studies of source-rock bitumens (Mueller and Philp, 1998), although the technique offers the potential to examine the contribution of biopolymers like cutan and suberan to high-molecular-weight hydrocarbons. Such investigations may shed light on the origins of waxy ozocerites (Carlson et al., 1994b) and other mineral waxes, and enable more accurate assessment of the potential for wax-related production problems in deltaic settings (wax deposition in wells or pipelines, or gelling of oils).

If the structure recently proposed for cutan (Fig. 1; after McKinney et al., 1996) is correct, decarboxylation

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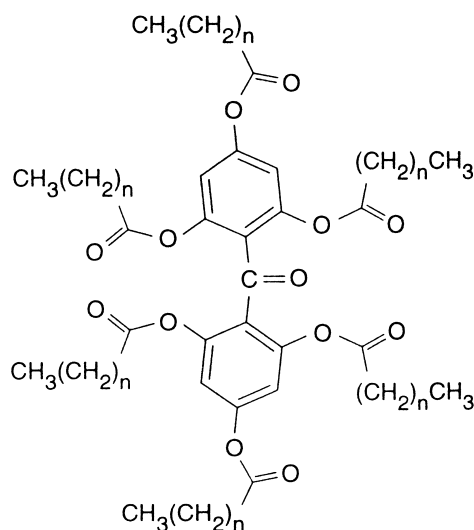*E-mail address:* s.killops@gns.cri.nz (S.D. Killops).

Fig. 1. Proposed structure for cutan (after McKinney et al., 1996).

might be expected to occur relatively early during thermal maturation, leaving HMW *n*-alkanes within the macromolecular network of coal. The relative abundance of these HMW *n*-alkanes would be at its greatest at low-maturity and would decline steadily once oil-expulsion commences. We report here the results of a HTGC study of bitumen from three coals that are consistent with the early generation of HMW *n*-alkanes.

The coal samples were from the Late Cretaceous sequence in Tara-1 well, Great South Basin, New Zealand (2687, 3235, 3674 m). The Tara coals have been the subject of extensive studies (e.g. Killops et al., 1998) and are particularly useful because they extend over a considerable depth (just over 2000 m) and maturity range, encompassing the onset of oil generation and expulsion (vitrinite reflectance ca. 0.45–1.15%, Rank(S) ca. 10.5–14.5). They are reasonably uniform in composition, comprising predominantly vitrinite (ca. 90%), and follow a well-defined trend in hydrogen-index (HI) values which increase to a Rank(S) value of ca. 12 and then decline with increasing thermal maturity (Killops et al., 1998). The selected samples range from immature with respect to oil generation to post oil expulsion; the higher maturity samples broadly follow the evolutionary trend expected for the immature coal.

2. Experimental

An oil sample was taken from a drill-stem test (DST-2) over the depth interval 2396–2364 m below Kelly bushing (bkb) in the Toka-1 well, Taranaki Basin. The oil had a reported API gravity of 30°, and the in-situ reservoir temperature and pressure within the Moki

Formation were 76.7°C and 10.56 MPa, respectively (JFP (NZ) International (1995).

Three coal samples were isolated from the unwashed cuttings from Tara-1 well, Great South Basin (2687, 3235 and 3674 m bkb). The coals were selected from a newly sampled suite by comparison of their Rock-Eval and standard GC data with previously published data for the Tara coals (Killops et al., 1998). Criteria for selection included a lack of contamination by migrated hydrocarbons, a wide maturity range from before the onset of oil generation to after the onset of oil expulsion, and hydrogen indices conforming to the maturity trend anticipated for an individual Tara coal (Killops et al., 1998).

After washing and air drying, a coal fraction of specific gravity $\leqslant 2.0$ was floated from each sample using sodium polytungstate solution. Any minor non-coaly contamination was subsequently picked out and the coal milled to a fine powder. Aliquots of the powdered coals (ca. 5 g) were extracted with boiling toluene (ca. 100 ml) under ultrasonication (30 min). The toluene extracts were rapidly filtered through heated sinters (under IR lamps) and the solvent removed by rotary evaporation.

Whole-extract HTGC analysis was then performed using a WCOT Ultimetal 25 m × 0.25 mm i.d. column with CP-Sil PAH CB stationary phase (0.12 μm film thickness; Chrompack). The column was fitted with a 1.5 m × 0.55 mm i.d., methyl-deactivated, phase-free retention gap (Chrompack) using a low dead-volume stainless steel union with graphite ferrules (SGE). A Hewlett-Packard 5890 Series II gas chromatograph equipped with a model 7673 automated, cool, on-column injection system was used. The carrier gas was high-purity helium, passed through an in-line high capacity gas purifier and OMI-indicating oxygen scrubber (Supelco) at a flow rate of 0.8 ml min^{-1}. Samples were dissolved in HPLC-grade *o*-xylene at a concentration of ca. 5 mg ml^{-1} and injected on-column (1.0 μl). After an initial period of 1 min. at 134°C the oven temperature was programmed at 10°C min^{-1} to 450°C, followed by an isothermal period of 5 min. Data were collected and analysed using a Hewlett-Packard GC ChemStation.

n-Alkanes were quantified by GC analysis of aliquots of the toluene extracts to which an internal standard (squalane) had been added, using a 25 m × 0.2 mm i.d. HP ultra 2 column (5%-phenyl-methylsilicone, 0.33 μm film thickness) with splitless injection in toluene solution (1.0 μl) and a temperature programme of 2 min at 100°C then 100–300°C at 5°/min followed by 25 min at 300°C. The absolute amounts of the two *n*-alkanes eluting immediately adjacent to squalane (*n*-hexacosane and *n*-heptacosane) were calculated from peak areas and used as the basis for quantifying all *n*-alkanes in the high-temperature gas chromatograms.

3. Results

The HTGC chromatogram for the waxy oil from the Toka-1 well in New Plymouth, on the northern shore of the Taranaki Peninsula in New Zealand, is shown in Fig. 2. The oil is believed to originate from coals in the late Eocene Mangahewa Formation, based on bio-marker characteristics that include abundant oleanoid, lupanoid and ursanoid terpanes (Killops et al., 1994, 1995). The pristane/phytane ratio and C_{25}–C_{31} carbon preference index (Pr/Ph and CPI respectively; Table 1) are typical of coal-sourced oils in this part of the Taranaki Basin (Killops et al., 1994). The skewed Gaussian distribution of *n*-alkanes maximises at C_{29} but extends to at least C_{67}. A slight odd-over-even pre-dominance (OEP) is apparent in the C_{25}–C_{33} region (characteristic of leaf epicuticular waxes) and again in the C_{55}–C_{63} region. In the C_{40+} range *n*-alkanes dom-inate; the relative abundance of branched and cyclic alkanes is low compared to the typical marine- and lacustrine-sourced oils previously analysed (Carlson et al., 1993, 1994a, b). The identification of *n*-alkanes was confirmed by co-injection of authentic *n*-tetrapenta-contane with bitumen extracted from one of the coal samples (Fig. 3).

Coals were selected on the basis of a previous study of the Tara-1 well (Killops et al., 1998). They comprised an immature coal that has yet to start generating paraffins (2687 m bkb), a coal within the oil window that is on the verge of expelling oil (3235 m bkb), and a coal nearing the end of primary oil generation and post oil expulsion (3674 m bkb) (Fig. 4). HI values for the three samples in Table 1 follow a maturity trend parallel to that pre-viously described for Tara coals (Fig. 4) but at higher HI. These higher HI samples were selected to provide the greatest potential for waxes. The immature sample was screened for the absence of contamination by migrated oil, which *n*-alkane distributions and biomarker
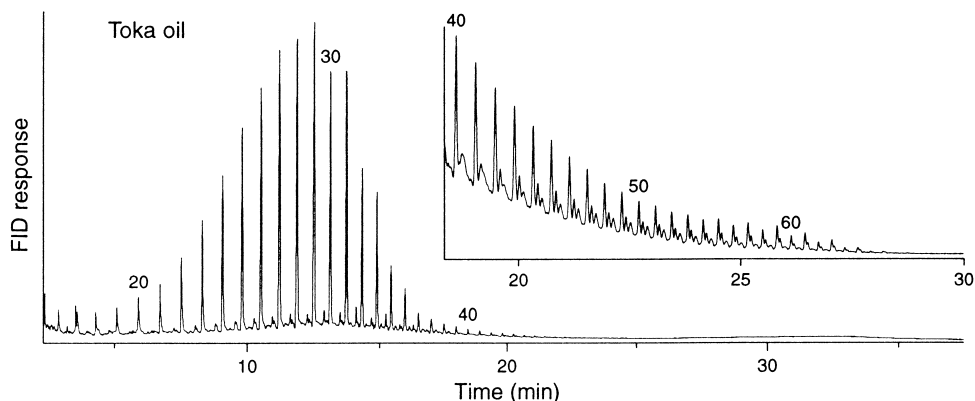

Fig. 2. High temperature gas chromatogram of oil from the Toka-1 well (DST at 2396–2364 m bkb), Taranaki Basin, New Zealand. Main chromatogram covers the C_{15} to ca. C_{90} *n*-alkane range, and inset the C_{40} to ca. C_{70} range, as indicated by peak numbering.

Table 1
Geochemical data for the Toka-1 oil and Tara-1 coal bitumen samples. CPI2 values calculated after Marzi et al. (1993)

	Tara-1 coal 2687 m	Tara-1 coal 3235 m	Tara-1 coal 3674 m	Toka-1 oil
Approx. Rank(S)	11.5	13.0	14.0	na
Approx. R_0 (%)	0.50	0.85	1.00	na
HI (mg HC/g C_{org})	302	282	277	na
Pr/Ph	3.6	7.0	5.2	5.9
nC_{17}/Pr	0.4	0.7	1.5	1.3
CPI2 (nC_{25}–nC_{31})	1.32	1.29	1.14	1.05
CPI2(nC_{51}–nC_{57})	1.79	1.47	1.32	1.09
nC_{15}–nC_{39} (mg/g C_{org})	1.24	1.25	1.46	na
nC_{40}–nC_{65} (µg/g C_{org})	103	25	11	na
nC_{15}–nC_{22} (µg/g C_{org})	422	655	997	na
nC_{23}–nC_{35} (µg/g C_{org})	812	589	452	na
nC_{36}–nC_{44} (µg/g C_{org})	13	10	6	na
nC_{45}–nC_{65} (µg/g C_{org})	96	20	9	na

maturity parameters indicate is present in the topmost coals (above ca. 2500 m) in the Tara-1 well (Killops et al., 1998). To ensure adequate recovery of waxes the bitumen was extracted ultrasonically with gently refluxing toluene (Mueller and Philp, 1998).

HTGC chromatograms for the coal bitumens are shown in Fig. 3 together with insets of the expanded C_{40+} regions. The immature sample (2687 m) exhibits the typical n-alkane abundance maximum with an OEP in the C_{25}–C_{31} range, but there is a second maximum, again with an OEP, in the C_{49}–C_{59} range (CPI values in Table 1 are restricted to the nC_{51}–nC_{57} range because of potential co-elution problems and low signal intensity outside this range in the more mature samples). The
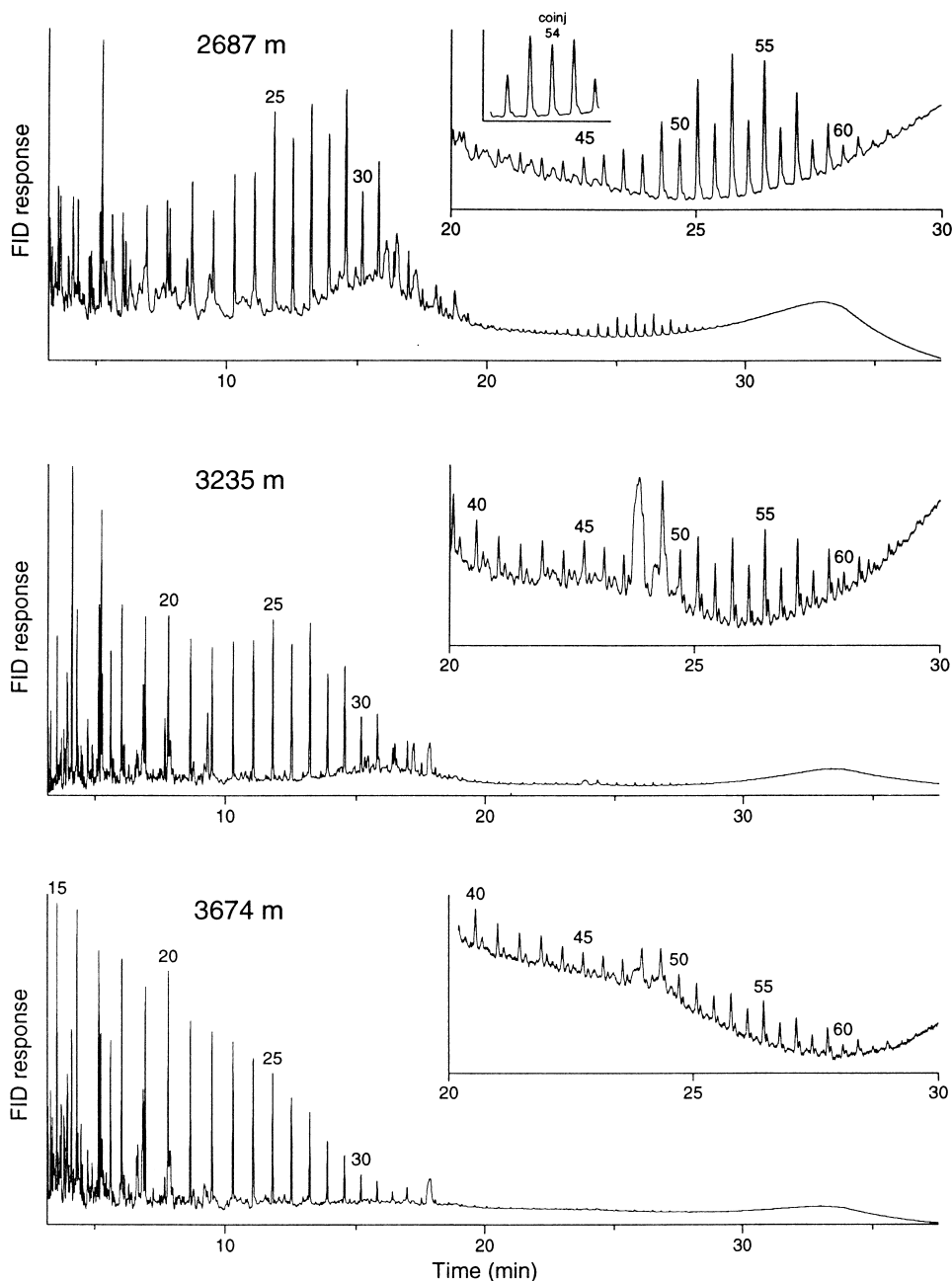

Fig. 3. High-temperature gas chromatograms of bitumens extracted from Late Cretaceous coals in Tara-1 well, Great South Basin, New Zealand from 2687, 3235 and 3674 m. Main chromatograms show the C_{15} to ca. C_{90} n-alkane range, and insets the C_{40} to ca. C_{65} region, as indicated by peak numbering. The top inset in (a) shows the results of co-injection of n-tetrapentacontane (C_{54}).

intermediate maturity sample (3235 m) shows a greater abundance of low-molecular-weight *n*-alkanes but there is still a slight maximum and OEP in the C_{25}–C_{27} range. Compared to the sample from 2687 m the *n*-alkane maximum at C_{49}–C_{59} is less pronounced, although a slight OEP is still present. The most mature sample (3674 m) exhibits steadily decreasing abundance of *n*-alkanes above C_{15}, with no obvious OEP in the C_{25}–C_{31} range. *n*-Alkanes extend to at least C_{65} in all three samples but the abundance of C_{40+} members declines with increasing maturity. As expected, *n*-heptadecane/pristane (nC_{17}/Pr) values increase and CPI values for the nC_{25}–nC_{31} range decrease with increasing maturity (Table 1). CPI values for the nC_{51}–nC_{57} region also decline with increasing maturity (Table 1). The compounds responsible for the broad peaks between nC_{47} and nC_{50} in the samples from 3235 and 3674 m in Fig. 3 have not been identified; they may be derived from resin polymers.

The relative abundance distribution of *n*-alkanes, normalised to total C_{15}–C_{65} *n*-alkanes, for each of the toluene extracts is shown in Fig. 5. Absolute quantities for various C-number ranges are presented in Table 1 and exhibit the expected increase in short-chain members (nC_{15}–nC_{22}) and decline in nC_{23}–nC_{35} members with increasing maturity. There is also a decrease in the abundance of C_{40+} *n*-alkanes with increasing maturity which is most marked in the nC_{45}–nC_{65} range.

4. Discussion

The C_{40+} alkane distributions in the three bitumen samples from the Tara coals are dominated by *n*-alkanes (Fig. 3), as might be expected for an origin from cutan with the structure proposed by McKinney et al. (1996). The distribution for the most mature sample approaches that for the Toka oil (Fig. 2). In addition, the maturity-related trends for the coal bitumens are consistent with early generation of very long *n*-alkanes, the greatest abundance occurring in the least mature sample. Absolute quantities of *n*-alkanes may not give totally reliable indications of the distribution of generated *n*-alkanes because the efficiency of hydrocarbon — and particularly wax — recovery by solvent extraction is routinely poor for coals (e.g. Radke et al., 1990) and because of the loss of components after the onset of oil expulsion. However, changes in relative abundance (e.g. CPI values) can provide indications of generation processes. Variations in the carbon-number distributions of *n*-alkanes for the oil and bitumen samples are shown in Fig. 5 (relative to total C_{15}–C_{65} content).

The relative amounts of *n*-alkanes $< C_{24}$ increase and $> C_{24}$ decrease with rising maturity, resulting from a decrease in the mean *n*-alkyl chain length of precursors within the coal (Fig. 5). Similarly, the CPI value in the C_{25}–C_{31} range decreases and approaches 1 (Table 1), as expected for the production of *n*-alkanes with random carbon numbers together with the expulsion of the components inherited from diagenesis which usually
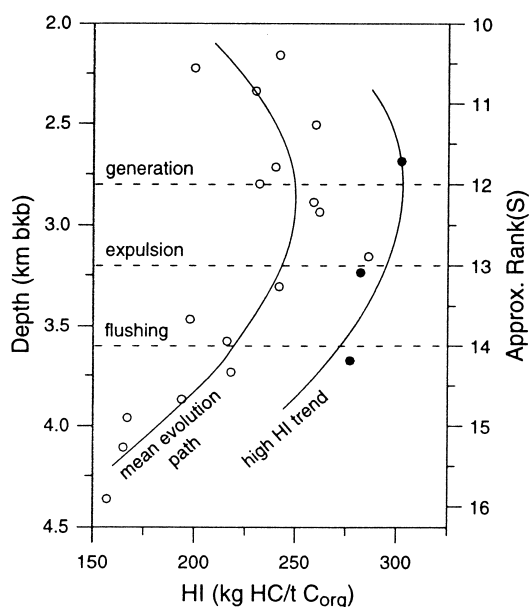
Fig. 4. Maturity-related HI trends for Tara coals, showing the relationship of the three samples used in this study (●) to those in a previous study (○). Likely evolution lines are shown for average and higher HI trends; dashed lines indicate previously proposed thresholds for the onset of oil generation, expulsion and effective flushing of original bitumen (after Killops et al., 1998).
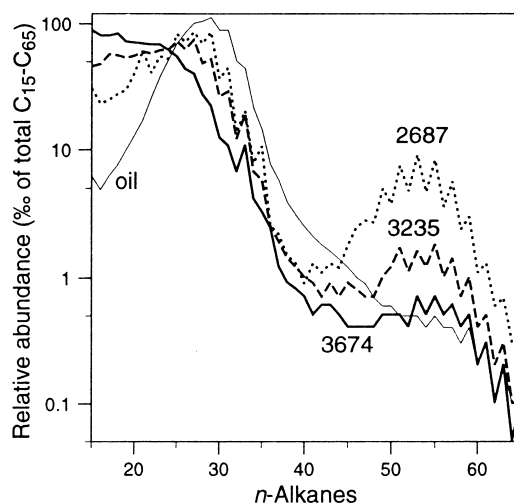
Fig. 5. Distribution of *n*-alkanes in Toka oil and Tara coal bitumens relative to summed C_{15}–C_{65} content (based on peak areas).

exhibit a high CPI (Killops et al., 1998). In contrast to the C_{25}–C_{31} range, there is a much greater decrease in the relative (and absolute) abundance of C_{45+} n-alkanes (ca. an order of magnitude), and the CPI in the C_{51}–C_{57} range decreases but remains significantly > 1 (Table 1). The relative (and absolute) abundance of the intermediate C_{36}–C_{44} n-alkanes is low in all samples but declines slightly with increasing maturity. The abundance of nC_{33} is slightly higher than expected in all three coal samples and is particularly noticeable in the most mature sample (3674 m); a co-eluant may be present in the peak (e.g. a hopane).

The decline in C_{40+} n-alkane abundance with increasing maturity over a range associated with hydrocarbon generation and expulsion suggests that at most only trace amounts of C_{40+} n-alkanes are generated during catagenesis. Although the possibility exists that newly generated HMW alkanes remain effectively trapped within the cutan structure (in "closed" pores) and cannot be solvent extracted, the required change in extractability would appear to have to occur unrealistically sharply at ca. nC_{40}, unless the catagenetic n-alkane distribution is not smooth but exhibits a minimum around nC_{40}. There are no data in support of an uneven distribution; the fact that CPI tends to unity throughout the observed C-number range suggests a random chain-length distribution among catagenetic products.

The HMW n-alkanes up to ca. C_{65} appear to be primarily formed at an early stage of maturity and seem to represent the largest alkyl chains present in coals. The relative timing of C_{40+} n-alkane generation can be investigated by consideration of kinetics. The proposed structure for cutan (McKinney et al., 1996) shares some similarities with that of algaenan (Blokker et al., 1998) in that carboxyl groups link n-alkyl chains to the rest of the biopolymers. The rupture of ester linkages by hydrolysis or decarboxylation is expected to occur relatively early during thermal maturation. In algaenan the proposed ether linkages between the n-alkyl chains would remain intact, but in cutan long-chain n-alkanes could be formed (Fig. 1). Any cutin esters present would likewise be a source of n-alkanes. The kinetic parameters obtained by Alexander et al. (1992) for the first-order decarboxylation reaction of hexadecyl tetradecanoate (E_{act} = 53 kcal mol^{-1}, A = 7.35 × 10^{14} s^{-1}) are believed to be representative of long-chain esters in brown coals. The transformation curve for decarboxylation at a heating rate of 3°C Ma^{-1} (an average heating rate for New Zealand basins) is shown in Fig. 6.

There are limited published kinetic data on n-alkane generation from coals. Data for nC_{24} and nC_{12} generation from type III kerogen (Béhar et al., 1997) are shown in Fig. 6, and suggest that generation of the larger n-alkane occurs at a relatively early stage of maturation. In contrast, nC_{24} generation curves for types I and II kerogens are similar to those for nC_{12}
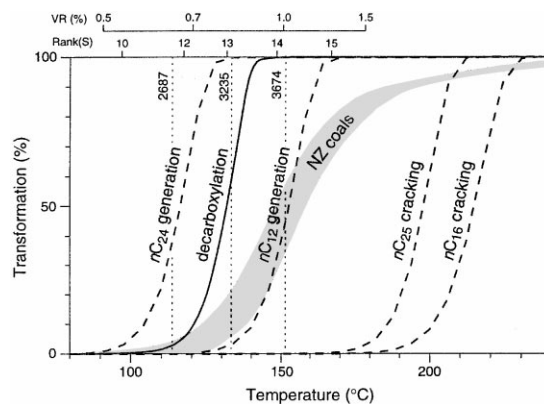

Fig. 6. Transformation vs. temperature plots at a uniform heating rate of 3°C Ma^{-1} for decarboxylation of hexdecyl tetradecanoate (E_{act} = 53 kcal mol^{-1}, A = 7.35 × 10^{14} s^{-1}; after Alexander et al., 1992), n-dodecane (E_{act} = 55.5 kcal mol^{-1}, A = 2.9 × 10^{14} s^{-1}) and n-tetracosane (E_{act} = 46.1 kcal mol^{-1}, A = 6.4 × 10^{11} s^{-1}) production from type III kerogen (after Béhar et al., 1997), n-pentacosane cracking in a terrestrial oil (E_{act} = 67.9 kcal mol^{-1}, A = 3.4 × 10^{17} s^{-1}; after McKinney et al., 1998), n-hexadecane cracking in a paraffinic oil (E_{act} = 63.6 kcal mol^{-1}, A = 4.1 × 10^{14} s^{-1}; after Burnham et al., 1997) and bulk kerogen conversion for typical New Zealand coals nearing the onset of oil generation. The approximate maturities of the three Tara coals are also shown.

generation from type-III kerogen (and also for nC_{12} generation from types I and II kerogen; Béhar et al.; 1997). The apparent ease of nC_{24} generation from the type III kerogen appears to be attributable to lower energy bond dissociation processes rather than a contribution from strongly adsorbed free n-alkanes (Béhar et al., 1997). The nC_{12} generation curve lies within the bulk kerogen transformation range for oil-prone New Zealand coals approaching the oil window (based on best fit of A and E_{act} distribution from KINETICS optimisation of open-system anhydrous pyrolysis), which themselves compare favourably with those obtained from other studies of coals and macerals (Tegelaar and Noble, 1994; Michelson and Khorasani, 1995; as discussed by Killops et al., 1998).

The plots in Fig. 6 suggest that decarboxylation of esters with n-alkyl chain lengths of ca. C_{15} is < 10% complete by the proposed onset of significant paraffinic oil generation in New Zealand coals at Rank(S) ca. 12 (vitrinite reflectance ca. 0.65%; Killops et al., 1998) but is well advanced (50%) by Rank(S) ca.13 (vitrinite reflectance ca. 0.8%). These inferences are consistent with previous reports that few carboxyl groups remain at Rank(S) 13 (Killops et al., 1996) but that paraffinic oil generation is at a relatively early stage (Killops et al., 1998). However, the abundance of C_{40+} n-alkanes is greatest in the coal sample of a maturity corresponding to minimal thermal decarboxylation, and has declined significantly in the intermediate-maturity sample at a

stage corresponding to the maximum decarboxylation rate (Fig. 6). It is likely, therefore, that the bulk of the C_{40+} *n*-alkanes are formed before the onset of thermal decarboxylation involving relatively short chains (ca. C_{15}). Whether the C_{40+} *n*-alkanes are generated from the cutan/cutin component of the kerogen or are present in bitumen inherited from diagenesis is unclear.

The fact that the CPI in the C_{51}–C_{57} range decreases with increasing maturity suggests that there is some additional generation of C_{40+} *n*-alkanes, because simple proportional loss (whether by expulsion or cracking) should not affect CPI2 values (the difference in diffusion rates over this small C-number range would also not affect CPI to any noticeable extent). Because of the loss of ca. 90% of C_{40+} *n*-alkanes between the least and most mature coal samples, the additional catagenetic contribution with an assumed CPI of 1 could be as low as ca. 5% of the initial abundance. In contrast, the CPI change for the C_{25}–C_{31} range would need to be ca. 50% of initial abundance, allowing for diffusive losses of similar amounts to the newly generated alkanes in order to simulate the slight decline in absolute abundance of C_{23}–C_{35} *n*-alkanes. There are clear parallels between the decreasing CPI values observed in the C_{51}–C_{57} and the C_{25}–C_{31} *n*-alkane ranges with increasing maturity, which may reflect a common formation mechanism during the main phase of *n*-alkane generation. Cracking of long-chain *n*-alkanes retained within the coal matrix after generation is unlikely based on reported kinetics for *n*-alkane cracking in reservoirs (e.g. Burnham et al., 1997; McKinney et al., 1998), although whether the physicochemical environment of nC_{40+} alkyl chains within cutan can result in more facile alkyl-chain cracking has yet to be investigated.

The presence of C_{40+} *n*-alkanes in the Toka-1 oil suggests that some of the longest polymethylene chains present in cutan can be expelled. Isomerisation at C-22 and C-14/C-17 in hopanes and at C-20 in steranes has reached equilibrium, but at 50% the 14β(H),17β(H)/(14β(H),17β(H)+14α(H),17α(H)) ratio for 5α(H),24-ethylcholestanes has not quite reached its equilibrium value. These maturity indicators, together with the molecular parameters in Table 1, are consistent with a typical expulsion maturity for New Zealand coals of about Rank(S) 13 (Killops et al., 1998), although contribution to the oil accumulation from an early phase of expulsion cannot be discounted. Factors that may promote expulsion of C_{40+} *n*-alkanes in the New Plymouth area are a high heat-flow (ca. 73 mW m^{-2} at the surface) resulting from Quaternary volcanism (Allis et al., 1995) and a significant flux of mantle-derived carbon dioxide (Giggenbach et al., 1993; Killops et al., 1996). The abrupt recent heating would have caused rapid generation of a large quantity of catagenetic hydrocarbons, possibly aiding flushing of waxy *n*-alkanes. Similarly, supercritical CO_2 percolating through the coals may also have aided wax expulsion (Monin et al., 1988; McKirdy and Chivas, 1992)

The presence of HMW waxes in immature coaly sequences has important implications for petroleum production in deltaic settings, where coaly sediments can be associated with reservoir zones or migration pathways. The presence of HMW waxes in oils significantly increase the risk of wax-related production problems. The potential for such problems are likely to be greatest when waxes are entrained by mature, low-wax oils during migration through or accumulation within immature deltaic sequences containing low-maturity coals.

5. Conclusions

Bitumens and oils generated from New Zealand coals are characterised by dominant straight-chain alkanes from C_{40} to about C_{65}. The longest components (ca. $>C_{50}$) decrease in abundance in bitumen as oil generation progresses; an immature bitumen contained the greatest abundance with a pronounced OEP in the C_{51}–C_{57} range. The decrease in C_{50+} abundance with increasing maturity is significantly greater than that of the C_{25}–C_{33} members. These observations suggest that the C_{40+} *n*-alkanes represent the longest *n*-alkanes that can be liberated from cutan or other higher-plant material and that they are mostly formed relatively early during thermal maturation, although a decline in CPI in the C_{51}–C_{57} range suggests that a small amount of C_{40+} *n*-alkanes with a CPI of 1 is generated during catagenesis. The observed variations in C_{40+} *n*-alkane distributions may be influenced to a degree by the decreasing efficiency of solvent extraction with increasing chain length, and reduced solvent extraction efficiency for alkanes in closed pores.

A potential source for long-chain *n*-alkanes is the thermal decarboxylation of cutan and cutin derivatives, which is likely to occur at an early stage of maturation on the basis of changes in the carboxyl-group content of coals and decarboxylation kinetic data. For average geothermal histories decarboxylation should be well advanced before significant *n*-alkane generation commences. However, the highest levels of C_{40+} *n*-alkanes apparently occur prior to the onset of significant thermal decarboxylation involving short alkyl chains, so it is unclear whether the bulk of C_{40+} *n*-alkanes are formed from kerogen at an earlier maturity stage or may even be inherited from lipids not incorporated into kerogen.

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