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Effect of Process Variables in Catalytic Hydropyrolysis on the Release of Covalently Bound Aliphatic Hydrocarbons from Sedimentary Organic Matter

Gordon D. Love, Alan McAulay, and Colin E. Snape*

Fuel Chemistry Research Group, Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

Andrew N. Bishop

Fossil Fuels and Environmental Geochemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.

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Hydropyrolysis has considerable promise for application as an analytical tool for release of biomarker hydrocarbons in high yields with minimal structural rearrangements. In this study, the effect of key reactor variables on the product yield and distribution of alkanes obtained from temperature-programmed fixed-bed hydropyrolysis of a Tertiary oil shale (Göynük, NW Turkey, classified as a type I kerogen) and a Tertiary lignite (Hambach, Lower Rhine Basin, Germany) has been investigated. A combination of slow heating rate (5 °C/min), high hydrogen pressure (15 MPa), and use of a dispersed sulfided molybdenum catalyst represents the best regime for achieving high conversions to dichloromethane-soluble oil while minimizing the structural rearrangement of biomarker species. Staged hydropyrolysis has confirmed that hopanes released at higher temperatures through cleaving relatively strong bonds are quantitatively more significant than those released at lower temperatures. These findings have reinforced the unique ability of hydropyrolysis to maximize the yields of covalently bound alkanes while maintaining the biologically inherited 17β(H),21β(H) stereochemistries of the hopanes, largely intact, even for the lignite investigated.

Introduction

Considerable advances have been made in understanding the source and fate of organic material over geological time in relation to the formation of carbon-rich sedimentary deposits such as coal, oil shale, and petroleum. The development of commercially available gas chromatography−mass spectrometry (GC−MS) systems, since the late 1970s, has been mainly responsible for the rapid growth of this discipline. This facilitated the detection and identification of important classes of trace compounds present in sedimentary organic matter, known as *biological markers* (see, for example, Fu Jiamo et al.,[1] Chaffee et al.,[2] and Mackenzie[3] and references therein). Biological markers (or biomarkers) are organic compounds detected in the geosphere whose basic carbon skeleton suggests an unambiguous link with a known, contemporary natural product. Their carbon skeletons survive, in a recognizable form, from the effects of microbial action and thermal maturation associated with the burial of the host sedimentary rock. Biomarkers can yield valuable information about the thermal maturity of sediments and petroleum, the paleoenvironmental conditions which prevailed at the time of deposition (e.g., oxicity and salinity), and the types of organisms (e.g., algal, bacterial, or higher plant sources) contributing to bulk sedimentary organic matter. Their distribution is often exploited in exploration applications for identifying the source rock of a particular oil and for correlating crude oils derived from the same source.

The most commonly studied alkane biomarkers to indicate the thermal stress experienced by fossil organic matter are the cyclic alkanes, the hopanes and the steranes,[1−3] which are derived from hopanoid and steroid natural products, respectively, and are ubiquitous components of fossil organic matter. The biologically synthesized configurations of their precursors are not the most thermally stable and epimerization is observed at certain chiral centers as maturation proceeds. Polyhydroxybacteriohopanes, in particular bacteriohopanetetrol[4] (**I**, see Chart 1 for compound structures), are thought to be the major precursors of hopanes, although two C_{30} hopanoids, diploptene (**II**) and diplopterol (**III**), are present in all hopanoid-producing bacteria and some higher plants and cryptogams.[5] A series of C_{27}−C_{35} hopanes is the most commonly observed distribution in ancient sediments, but

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

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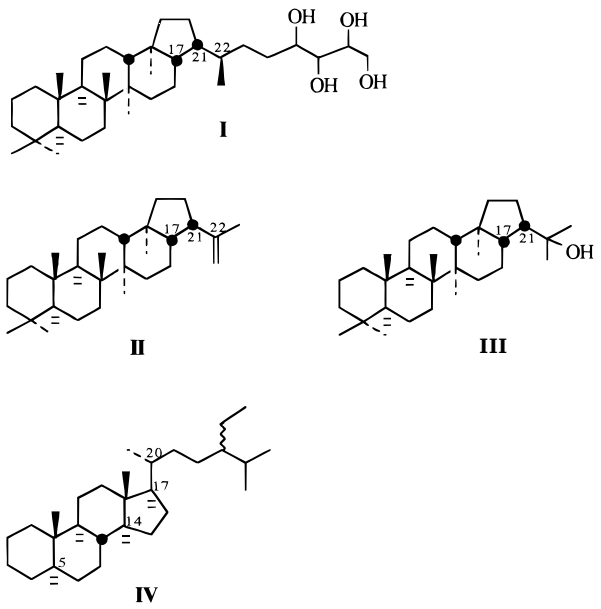
Chart 1



usually the C_{28} member is missing.[1−4] The biological 17β(H),21β(H) configuration inherited by the alkanes of immature sediments is lost rapidly with increasing maturity, forming a mixture of 17α(H),21β(H) and 17β-(H),21α(H) stereochemistries. Eventually the 17β(H), 21α(H)-hopanes also convert to the 17α(H),21β(H) form and/or are selectively depleted relative to the 17α(H), 21β(H) stereoisomer. For $C_{31}-C_{35}$ hopanes, there is an additional chiral center at C-22 which is biosynthesized exclusively with the *R* configuration. As time and temperature increases, they undergo isomerization to form an equilibrium mixture containing approximately equal amounts of 20*R* and 20*S* isomers. The sterol precursors of the tetracyclic steranes are widely distributed in nature and the most commonly encountered steranes (**IV**) are those of carbon number C_{27}, C_{28}, and C_{29} although variable amounts of C_{21} and C_{22} isomers with shorter alkyl side chains are also often present. Sterols have a 5,6 double bond and occur naturally as the 20*R* epimer with a 14α(H),17α(H) configuration. During diagenesis, the double bond is hydrogenated and a new epimeric center with a mixture of 5α(H) and 5β-(H) is formed, although the 5α(H) epimer predominates due to its greater thermal stability. As maturity increases, 14β(H),17β(H) isomers are formed as a mixture of the 20*R* and 20*S* epimers. At the later stages of diagenesis, the main steroidal components are usually alkanes and ring C monoaromatics.

Conventional procedures for biomarker assessments make extensive use of free (molecular) hydrocarbons which are obtained by low-temperature solvent extraction of sediments using chloroform, dichloromethane (DCM), or methanol (or their mixtures). Since this type of treatment removes only a small proportion of the total organic matter (usually <5% w/w), it does not follow that the distributions of biomarkers are necessarily representative of those covalently bound to the macromolecular structure (kerogen). Indeed, previous studies have shown that hopanes and steranes which are bound to kerogen are protected from the effects of thermal alteration occurring during diagenesis and maturation, such that configurational isomerization is often inhibited.[6,7] Additionally, it is known that coals contain a significant amount of physically trapped, low molecular mass moieties which are inaccessible to treatment with the solvents mentioned above.[8−10] However, these components can partly be removed when more powerful solvents such as pyridine or binary solvent mixtures[11] that destroy the stronger noncovalent interactions within the macromolecular matrix are used.[12] Bearing this in mind, an elaborate sequential extraction/degradation scheme was devised by two of the authors, to differentiate between molecular alkanes (both easily extractable and clathrated) and covalently bound alkyl moieties in sedimentary organic matter.[13−15] After an initial DCM Soxhlet extraction, refluxing in pyridine allowed the removal of more occluded material. Mild batchwise hydrogenation using a dispersed sulfided molybdenum (Mo) catalyst was then performed to cleave weak ester, sulfide, and (some) ether linkages. The key and final stage in this procedure to release strongly bound kerogen constituents was fixed-bed pyrolysis at high hydrogen pressures (up to 15 MPa), which is known as *hydropyrolysis*.

Thermolysis in a high hydrogen pressure limits the extent of char-forming chemistry encountered in conventional analytical pyrolysis (performed in inert atmospheres). Indeed, fixed-bed hydropyrolysis of petroleum source rocks (type I and II kerogens) and high volatile coals (type III kerogens) at a pressure of (15 MPa) in the presence of a dispersed sulfided molybdenum catalyst gives rise to extremely high oil (DCM-soluble) yields (>60%) with overall conversions of the organic matter being greater than 85%.[13,14,16] Furthermore, vastly greater quantities of hopanes and steranes are released by hydropyrolysis than by solvent extraction, conventional pyrolysis, and hydrogenation and, remarkably, their sterochemistries are generally much closer to the original biological configurations, despite the apparent severity of the hydropyrolysis process. Thus, hydropyrolysis is viewed as having considerable promise for application as an analytical tool for release of biomarker hydrocarbons in high yields with minimal structural rearrangements.

The purpose of this study has been to investigate the effect of systematically altering key reactor variables on the product yield and distribution obtained from

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Table 1. Analytical Data for Samples Investigated

	Göynük	Hambach
% moisture (ad)	8.0	44.0
% ash (dry basis)	17.4	4.1
% total organic carbon (TOC)	58.4	64.7
% dmmf C	69.6	67.5
% dmmf H	9.4	4.4
% dmmf N	1.4	1.8
% total S (dry basis)	4.2	trace
H/C atomic ratio	1.63	0.78
carbon aromaticity[a]	0.25	0.62
R_o (av), %	~0.20	~0.30

[a] Fraction of total sp^2 carbon, from Bloch-decay solid-state ^{13}C NMR spectroscopy.

temperature-programmed fixed-bed hydropyrolysis of selected kerogens. In all related work reported previously,[13−15] a combination of slow heating (5 °C/min), high hydrogen pressure (15 MPa), and the use of a dispersed molybdenum catalyst was employed intuitively, based on our experience of hydroliquefaction of coals and kerogens.[16−18] However, further investigation has been required to ascertain the optimum conditions of heating rate and hydrogen pressure which should be employed for routine catalytic hydropyrolysis tests. As well as monitoring the total yields of soluble products, the distribution of the principal aliphatic products (*n*-alkanes) from GC gives a measure of the relative extent of thermal cracking of the products under the different experimental conditions. Furthermore, a comparison of the hopane and sterane biomarker profiles represents a relatively sensitive indicator of the extent of product rearrangement prevailing, since these species undergo configurational isomerization when subjected to thermal stress that is easily monitored by GC−MS.

Experimental Section

Samples. The two samples used in this study consisted of a Tertiary oil shale (Göynük, NW Turkey) classified as a type I kerogen and a Tertiary lignite (Hambach, Lower Rhine Basin, Germany, sample obtained from the CRE sample bank). Both samples are organic-rich and are also expected to yield appreciable amounts of immature biomarker species, in particular the 17β(H),21β(H)-hopanes, when subjected to hydropyrolysis. Note, however, that the Göynük oil shale (GOS) sample differed in petrographic composition and bulk isotopic composition from the sample used in previous work,[13,15] despite both being located in close proximity. The sample used in this study was composed, predominantly, of lamalginite and contained much lower contributions from huminite and higher plant liptinite compared with the previous sample. The Hambach lignite (HL) was composed mainly of vitrinite but contained appreciable amounts of liptinite (ca. 17 vol %, mainly alginite). Proximate and ultimate analyses and bulk geochemical data for the two samples are summarized in Table 1.

Solvent Extractions. Each sample was ground to <220 μm, dried in a vacuum oven at 50 °C for 24 h, and then Soxhlet extracted with DCM for 72 h. The samples were then washed with 5 M HCl for 1 h at 60 °C to remove carbonates. The filtered residue was then exhaustively washed with distilled water to remove all traces of HCl and then dried in vacuo overnight. The solid residue (2−5 g) was then refluxed rapidly with 200 cm^3 boiling pyridine (2 × 45 min) in an inert (N_2) atmosphere. The soaking time in pyridine was relatively short, to limit the structure rearranging to a more tightly bound conformation due to the formation of more noncovalent interactions.[19] After each pyridine reflux step, the solids were refluxed in a DCM/methanol solvent mixture (3:1 v/v) and then dried in vacuo to remove as much entrained pyridine as possible.

Table 2. Heating Rates and Hydrogen Pressures Used in Hydropyrolysis Experiments

sample	run no.	heating rate, °C/min	H_2 pressure, MPa
Göynük	1	5	15
	2	20	15
	3	300	15
	4	5	5
	5a	5 (to 350 °C)	15
	5b	5 (to 520 °C)	15
Hambach	1	5	15
	2	300	15

Catalytic Fixed-Bed Hydropyrolysis. Catalyst impregnation of solvent-extracted samples was performed as described previously[16−18] with aqueous/methanol solutions of the precursor, ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$], to give a nominal a Mo loading of 1 wt % sample. This precursor reductively decomposes upon heating, below 250 °C, to yield catalytically active oxysulfide Mo species with a phase corresponding fairly close to MoS_2 being obtained at ca. 400 °C. Fixed-bed hydropyrolysis tests were conducted on catalyst-loaded samples using the apparatus and procedure that have been described in detail elsewhere.[17,18] Briefly, vacuum-dried samples (typically 1−2 g) were mixed with sand (1:5 w/w) in an Incoloy reactor tube, which was heated resistively from ambient temperature to 520 °C under various conditions of heating rate and pressure. The heating rates and pressures used for each run are listed in Table 2. A hydrogen sweep gas flow rate of 10 dm^3 min^{-1}, measured at ambient temperature and pressure, ensured that products were quickly removed from the reactor in each of the experiments. The oils were collected in a dry ice-cooled trap and recovered in DCM for subsequent fractionation.

For GOS (run 5, Table 2), a sequential hydropyrolysis experiment was performed to investigate the effect of final pyrolysis temperature on product yields and distributions. In this instance, the first stage of the experiment was terminated after the temperature reached 350 °C. The oil was recovered from the trap, and the solid residue was refluxed in DCM for 60 min to ensure complete removal of DCM-soluble products. In the second stage, hydropyrolysis was conducted on the solid residue up to a temperature of 520 °C, as in the normal tests above.

Product Workup and Analysis. The DCM-soluble products from each stage of the extraction procedure were dried to constant weight in a stream of dry nitrogen. These were then separated by open-column silica gel adsorption chromatograhy into alkanes, aromatics, and polars by eluting successively with *n*-hexane, *n*-hexane−toluene (1:1 v/v), and DCM/methanol (1:1 v/v). The yields were determined by transferring relatively concentrated solutions of the fractions into preweighed vials and evaporating the residual solvent under a stream of nitrogen. The aliphatics were subjected to urea adduction to separate the cyclic and branched alkanes from straight chain aliphatic components.

Gas chromatographic analyses of the urea-adducted (straight chain) aliphatic fractions were carried out on a Carlo Erba 4130 GC equipped with an FID detector. Separation was achieved with a SGE 25 m fused silica capillary column (0.22 mm i.d.) coated with BP-1 (0.25 μm thickness). Helium was employed as the carrier gas and a temperature program of 50 °C (2 min) to 300 °C (15 min) at 5 °C/min was used. The injection and detection temperatures were both set at 300 °C.

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Table 3. Product Yields Obtained from Sequential Extraction/Hydropyrolysis of Göynük Oil Shale and Hambach Lignite[a]

		yield, mg of extract (g TOC sequential residue)$^{-1}$			
	stage	aliphatics	aromatics	∑DCM solubles	% HyPy conversion[b]
Göynük	DCM	1.0	6.2	42	
	PYR	1.2	4.0	119	
	HyPy 1	273	52	1232 (83%)	100
	2	253	59	1147 (77%)	95
	3	275	46	1172 (79%)	100
	4	150	42	1149 (77%)	96
	5a	20	14	379	43
	5b	211	32	782 (78%)[c]	100[c]
Hanbach	DCM	2.6	5.0	52	
	PYR	1.9	1.5	38	
	HyPy 1	17	183	973 (81%)	100
	2	16	93	875 (74%)	94

[a] DCM = dichloromethane extraction. PYR = pyridine reflux. HyPy = catalytic hydropyrolysis. Estimated error for fraction yields is ±5% of listed values. The yield of polar material (NSO fraction), including asphaltenes, is the difference between that of the total recovered DCM-soluble extract and those of the alkanes and aromatics. [b] Total % w/w conversion of organic matter to DCM solubles plus gas and water. [c] Combined sequential yields for low-temperature (350 °C) plus higher temperature (520 °C), two-step hydropyrolysis (see the Experimental Section).

GC−MS analyses were performed on branched/cyclic aliphatic fractions using a Hewlett-Packard 5890 GC split/splitless injector (280 °C) linked to a Hewlett-Packard 5972 MSD (ionizing energy, 70 eV; filament current, 220 μA; ion-source temperature, 160 °C; multiplier voltage, 1600 V; interface temperature, 300 °C). The acquisition was controlled by an HP Vectra Chemstation in selected ion monitoring mode (30 ions, 0.7 cps, 35 ms dwell). The sample (1 μL) in DCM was injected by an HP 7673 autosampler and the split opened after 1 min. Separation was performed on a fused silica capillary column (30 m × 0.25 mm) coated with HP-1 phase (0.25 μm thick). The GC was temperature programmed from 40 to 175 °C at 10 °C/min, 175 to 225 °C at 6 °C/min, and 225 to 300 °C at 4 °C/min. The final temperature (300 °C) was held isothermal for 20 min. The selected ions monitored of most interest were *m/z* 191 (for triterpanes), 217 (for steranes), and 231 (for methylsteranes).

Results and Discussion

Product Yields. Table 3 lists the yields of total products and individual fractions obtained from sequential solvent extraction of both samples, with DCM followed by pyridine, and from temperature-programmed catalytic hydropyrolysis of the resultant kerogens under the experimental conditions used (see Table 2). The results confirm that, while the yields of solvent extractables are relatively low in each case, hydropyrolysis gives rise to high overall conversions of solid organic matter to, principally, a DCM-soluble oil. In the case of GOS, conversions approaching 100% are achieved, regardless of the heating rates and the hydrogen pressures used. Previous work has shown, however, that when hydrogen pressures are reduced below 5 MPa the conversions and yields of liquid products are significantly reduced, even for labile type I kerogens.[16] For HL, slow heating was found to slightly enhance (the already high) conversions and oil yields for the high hydrogen pressure regimes considered (15 MPa). This, again, is consistent with previous hydropyrolysis work performed with low-rank coals.[16]

The absolute yields of the different fractions (aliphatics, aromatics, and polars) obtained from the GOS hydropyrolysis experiments are more clearly represented in Figure 1. It is obvious that, with high hydrogen pressure (15 MPa), the product distributions are extremely similar, regardless of the heating rate

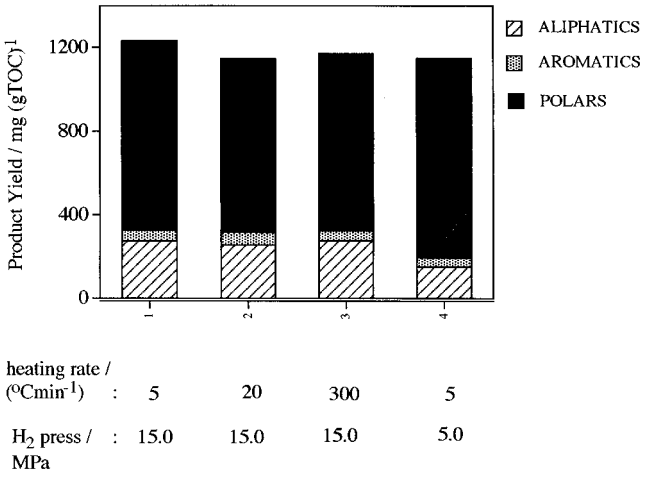

Figure 1. Effect of hydrogen pressure on product yields from temperature-programmed catalytic hydropyrolysis of Göynük oil shale.

employed. However, the amount of aliphatic and aromatic fractions (these components being readily GC-amenable) which form at this high pressure is significantly greater in comparison to that produced using a lower hydrogen pressure environment (5 MPa). This is an important consideration for the geochemist who aims to maximize the proportion of routinely analyzable products. In this respect, again, slow heating appears favorable for HL, where a significant increase in the yield of aromatic hydrocarbons compared with fast heating was achieved, although no discernible increase in the aliphatic hydrocarbon yield accompanies this (Table 3).

Analysis of Urea-Adducted Aliphatic Fractions from Hydropyrolysis Experiments. The aliphatic hydrocarbons from high-pressure hydropyrolysis (15 MPa which results in the highest yields of GC-amenable material) of GOS were analyzed by GC in order to help assess the optimum conditions of heating rate required for minimizing thermal cracking of products. The principal constituents are the series of *n*-alk-1-ene/*n*-alkane doublets (the *n*-alkanes being dominant), with the *n*-alk-1-enes paralleling the distribution of their saturated analogues. The relative abundances of *n*-alkane products (after urea adduction was performed) plotted as a function of carbon number are displayed in

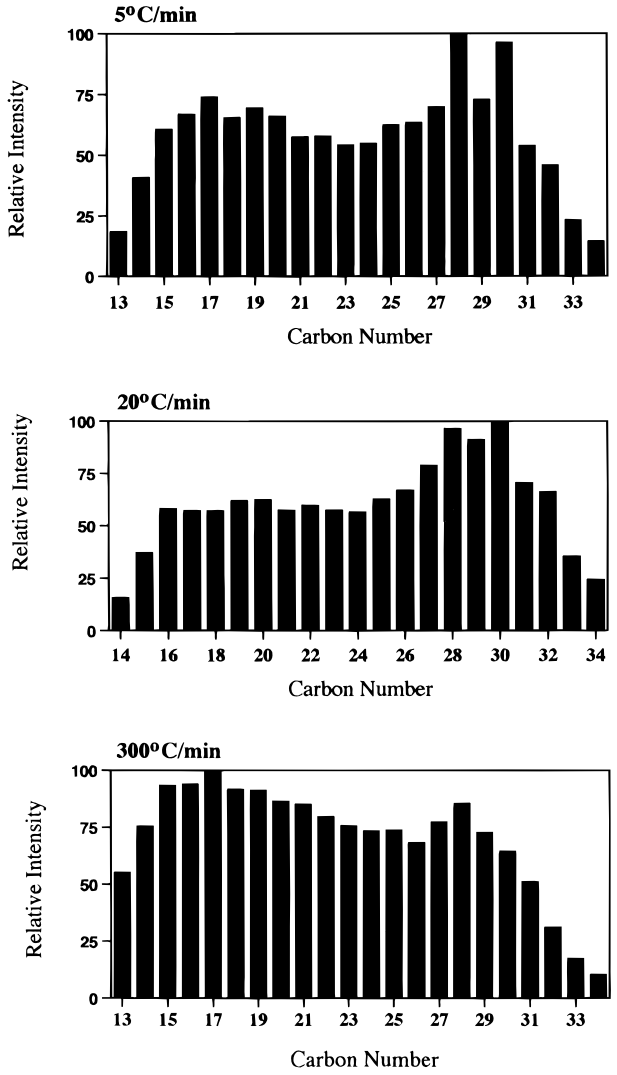

Figure 2. Effect of heating rate on the distribution of *n*-alkane products (relative abundance) from high-pressure (15 MPa) hydropyrolysis of Göynük oil shale.

Figure 2. In each case, a bimodal distribution of *n*-alkanes is observed, maximizing at ca. C_{17} and C_{28}. However, it is apparent that the lower the heating rate used, the greater the proportion of heavier alkanes ($>C_{25}$) produced, relative to the lighter ones. Furthermore, an even-over-odd predominance (EOP) of the *n*-alkanes is more evident at lower heating rates. An EOP results from reductive cleavage of even carbon numbered *n*-alkyl moieties bound through heteroatomic linkages (most probably, ether bonds, in this case).[7,20] Cracking of alkane products serves to reduce the magnitude of the EOP. Thus, analysis of straight chain aliphatic products suggests that slow heating rates reduce the extent of cracking and favor the preservation of structural integrity of released products. This may be attributed to volatiles being released from the reactor at lower temperatures in the case of slow heating, in comparison to fast heating, when operating at high hydrogen pressures.

Biomarker Profiles. As discussed in the Introduction, monitoring of the distribution of biomarkers species, such as the hopanes (*m*/*z* 191) and steranes (*m*/*z* 217), which are particularly susceptible to undergo

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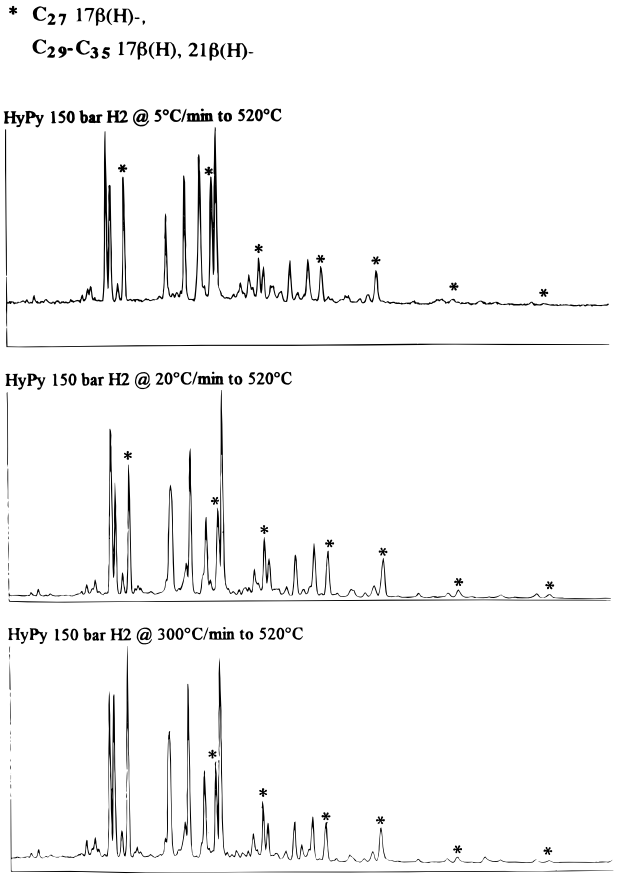

Figure 3. Effect of heating rate on the distribution of hopane products (*m*/*z* 191) from hydropyrolysis of Göynük oil shale (NB. only stereoisomers eluting up to C_{34} 17β(H),21β(H) are shown here).

configurational isomerization when subjected to mild thermal stress, allows a measure of the extent of product isomerization prevailing under different hydropyrolysis regimes. Figure 3 shows the effect of heating rate on the hopane profiles produced from temperature-programmed hydropyrolysis of GOS at high hydrogen pressures (15 MPa). Major components, in each case, are stereoisomers with the biologically inherited, but thermodynamically unstable, 17β(H),21β(H) configuration of carbon number up to C_{35}. This is equivalent to the carbon number of the probable precursor of the extended hopanes (C_{31}−C_{35}), if derived from bacteriohopanetetrol.[4] In fact, slow heating results in a slightly greater abundance of hopanes with the 17β(H),21β(H) stereochemistry, relative to other configurations (Figure 3). Although no biomarker standards were added to allow direct quantification by GC−MS, the fact that total aliphatic yields are equivalent (within experimental error, Table 3) and the proportions of branched/cyclic alkanes are similar (ca. 15% w/w of total aliphatics, containing hopanes, steranes, and methyl steranes as major constituents), suggests that the absolute amounts of hopanes and steranes that are released at different heating rates does not vary significantly (only the relative distributions of isomers). Thus, the results for GOS suggest that slow heating would appear to represent the best option for minimizing structural rearrangement of products.

The hopane profile produced from hydropyrolysis of HL (Figure 4) shows that the higher molecular weight extended 17β(H),21β(H)-hopanes (C_{33}−C_{35}), which are

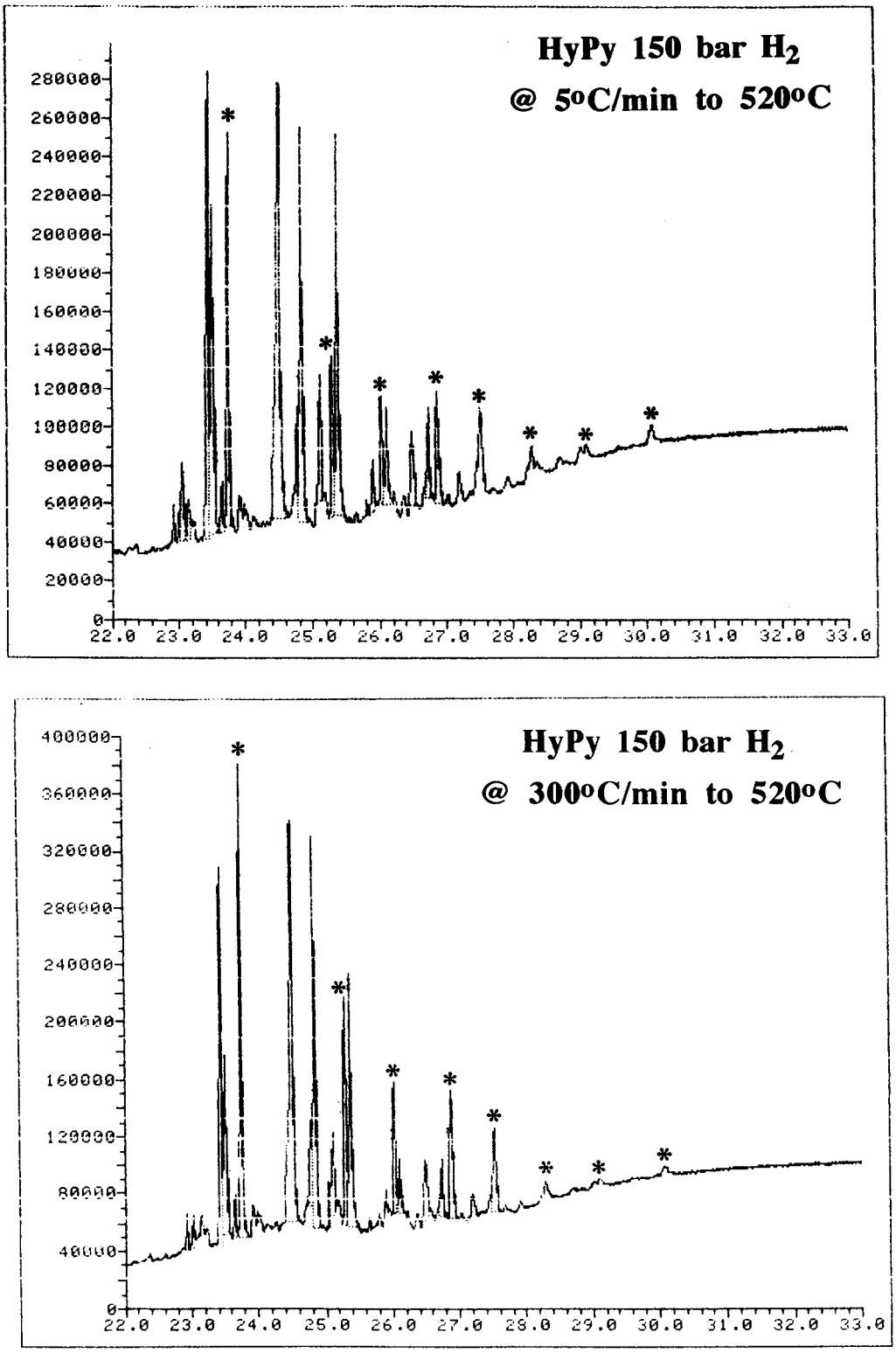

Figure 4. Effect of heating rate on the distribution of hopane products (*m*/*z* 191) from hydropyrolysis of Hambach lignite.

most susceptible to isomerization and/or cracking of the alkyl side chain, are more prominent from the run performed at 5 °C/min than that at 300 °C/min. This further supports the case for slow heating to be employed routinely in hydropyrolysis to yield liquid products that are structurally representative of the kerogen constituents, which was also noted in a previous study. Interestingly, a major aliphatic constituent of the DCM-extractable bitumen phase of HL was the C_{31} 17α(H), 21β(H)-(22*R*)-hopane stereoisomer which was by far the most dominant free hopane compound present. Indeed, a very strong predominance of C_{31} hopanes is often found in the solvent extracts of peats and lignites.[6] This has been attributed to decarboxylation and configurational isomerization, during early diagenesis, of C_{32} hopanoic acids and/or alcohols, which result from degradation of bacteriohopane polyols in acidic, nutrient-deficient depositional environments. Thus, the covalently bound hopanes with preserved 17β(H),21β(H) configurations (up to C_{35}) must have been incorporated into the kerogen network at the earliest stages of diagenesis.

Figure 5 compares the distributions of hopanes pro-

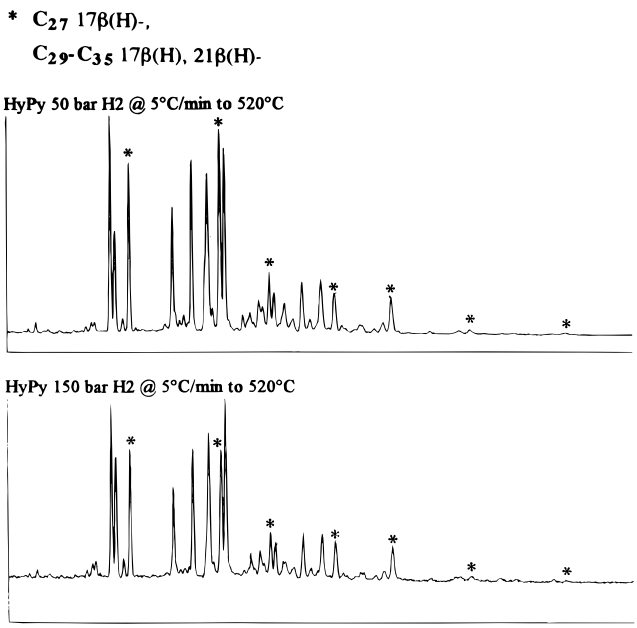

Figure 5. Effect of hydrogen pressure on the distribution of hopane products (*m*/*z* 191) from hydropyrolysis of Göynük oil shale (NB. only stereoisomers eluting up to C_{34} 17β(H),21β(H) are shown here).

duced under different hydrogen pressures regimes (5 and 15 MPa), both experiments being performed at slow heating rates (5 °C/min). Although the lower pressure run yields slightly higher concentrations of 17β(H),21β-(H)-hopanes relative to other isomers, it should be remembered (Table 3) that the total yield of aliphatic products was significantly reduced when operating at lower hydrogen pressure. Again, although no biomarker standards were added to compare absolute yields of trace compounds, the proportion of branched/cyclic alkanes in aliphatic fractions is similar in the lower pressure run to that obtained in the high-pressure runs (ca. 15% w/w). Thus, a reduced yield of biomarker species is likely to accompany the drop in aliphatic yield occurring in a lower hydrogen pressure environment. This illustrates the need for high hydrogen pressure conditions to be employed to release compounds of geochemical interest in maximum quantities.

In terms of sterane products, much less variation in profiles from hydropyrolysis was observed, regardless of the experimental conditions employed (see Figure 6 for GOS). Only sterane structures usually associated with immature geological settings are observed in the hydropyrolysis products. In particular, only isomers with the 14α(H),17α(H) and 20*R* configurations are found in significant quantities. Thus, isomerization of sterane products does not occur to an appreciable degree in the well-swept hydropyrolysis reactor.

Sequential Hydropyrolysis. Figure 7 compares the total yields and product composition of the DCM solubles released up to, and above, 350 °C from two-step sequential hydropyrolysis experiment on GOS (see the Experimental Section). It is obvious that the bulk of the products released below 350 °C consist of polar material/asphaltenes, which are, largely, too polar and/or nonvolatile to be readily analyzable by routine chromatographic methods. Moreover, the conversion achieved below 350 °C represents a high proportion of the total organic matter present (43% conversion). Clearly, it would be beneficial, in the future, to try and reduce the heteroatom (N,S,O) content of this product, thereby increasing the amounts of hydrocarbons released at low temperatures. Vapor phase hydrotreating of the primary volatiles released from hydropyrolysis over a suitable catalyst[16,21] offers the possibility of achieving this goal.

Figure 8 illustrates the contrast in the distribution of *n*-alkane products formed up to 350 °C with those produced between 350 and 520 °C. The *n*-alkanes released at the lower temperature regime exhibit a more noticeable EOP, while the smooth bimodal distribution of the additional *n*-alkanes suggests that cracking occurred during thermal breakdown of the bulk of the kerogen network. From the lower temperature hydropyrolysis step, it appears that even-carbon-numbered C_{28}−C_{34} linear alkyl chains moieties are, most probably, major structural constituents of GOS. In geochemical samples, the production of such long-chain, even-carbon-numbered alkanes by reductive degradation usually implies an input from cuticular waxes of the continental higher plants.[22] However, the sample of GOS used in this study contains only, relatively, minor higher plant input and is instead composed, predominantly, of lamalginite which was shown to correspond to accumulations of *ultralaminae*, derived from selective preservation of thin algaenan-composed cell walls of green freshwater microalgae.[15] Due to their high resistance, the algaenans which compose these outer walls were not degraded during deposition and diagenesis while all the other cell constituents were heavily mineralized. Interestingly, recent work has shown that the algaenans isolated from two marine microalgae of the class, Eustigmatophycaea, are also, predominantly, composed of even-carbon-numbered C_{28}−C_{34} linear alkyl chains, linked by ether bridges.[23]

Figures 9 and 10 display the profiles of the hopanes and steranes, repectively, released from the low-temperature and subsequent high-temperature stages in sequential hydropyrolysis of GOS. For the hopanes (Figure 9), the profiles obtained for the low-temperature stage exhibit a less mature profile than those released at higher temperatures. In particular, the concentrations of 17β(H),21β(H)-hopanes relative to their 17α-(H),21β(H) and 17β(H),21α(H) isomers are noticeably higher in the initial (low-temperature) product. For the steranes (Figure 10), the profiles obtained for the low- and high-temperature stages are very similar. In terms of regular (4-desmethyl) steranes, the 5α(H),14α(H), 17α(H)-(20*R*) diastereoisomers are dominant, while only low abundances of 5α(H),14β(H),17β(H)-steranes exists. This represents an immature molecular profile and suggests that little structural rearrangement of steranes occurs during hydropyrolysis, even at high temperatures. However, configurational isomerization of free (extractable) steranes is known to occur more slowly than for free hopanes[1−3] and, so, steranes are expected to be less sensitive indicators of product rearrangement in hydropyrolysis than hopanes.

The hopane distributions described above suggest that the more severe temperature regime is inducing some

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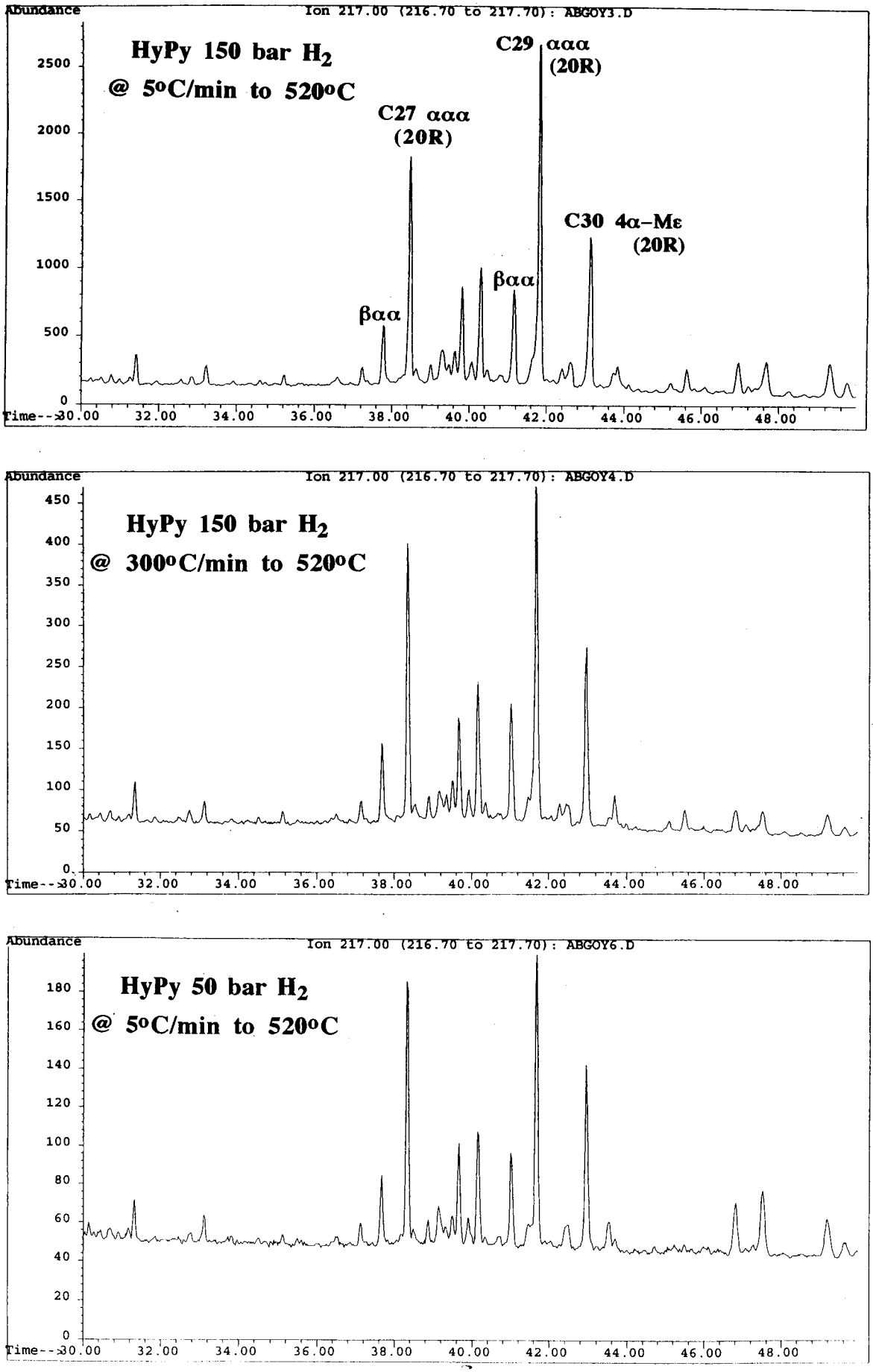

Figure 6. Comparison of sterane distributions (*m*/*z* 217) from hydropyrolysis of Göynük oil shale.

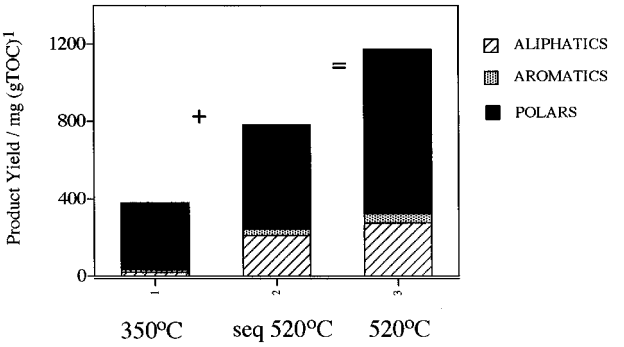

Figure 7. Composition of DCM solubles recovered from sequential (temperature-resolved), high-pressure (15 MPa) hydropyrolysis of Göynük oil shale.

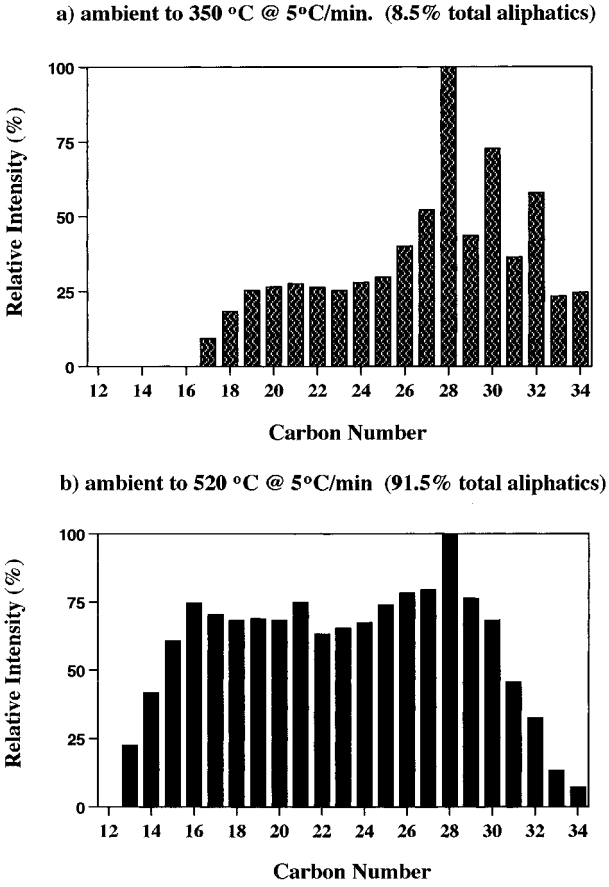

Figure 8. Comparison of the distribution of *n*-alkane products (relative abundance) from sequential (temperature-resolved), high-pressure (15 MPa) hydropyrolysis of Göynük oil shale.

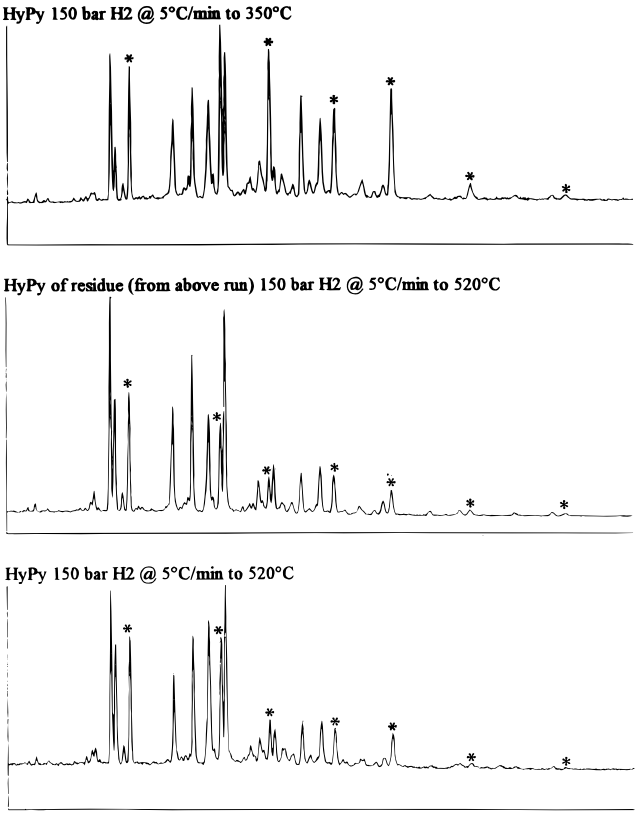

Figure 9. Comparison of hopane profiles (*m/z* 191) from sequential (temperature-resolved) hydropyrolysis of Göynük oil shale (NB. only stereoisomers eluting up to C_{34} 17β(H),21β-(H) are shown here).

structural rearrangement of biomarker products. However, one cannot rule out the possibility that the more tightly bound biomarkers have undergone a greater degree of diagenetic alteration prior to incorporation in the kerogen network and, as such, are not bound through the heteroatoms present in the original biolipids. Another possibility exists, in that the hopanes released during the low- and high-temperature stages are derived from different precursors (e.g., diplopterol, C_{30}, and bacteriohopanetetrol, C_{35}) since hopanes with 30 carbon atoms and less are more dominant in the higher temperature profile. Calibration of the hydropyrolysis apparatus using suitable biomarker-containing solid probes, for example, sterane moieties either immobilized on silica[24] or incorporated into a phenol formaldehyde matrix,[25] are required to help assess the extent of isomerization caused by different temperature regimes.

Interestingly, from Figures 6, 9, and 10, it is apparent that the high-temperature hopane and sterane profiles are similar to those obtained from normal single-stage hydropyrolysis. This means that biomarkers released at higher temperatures are quantitatively more significant than those released at lower temperature through cleavage of relatively weak bonds. These findings reinforce those reported from a different sample of GOS[13,15] and for certain vitrinite concentrates.[14] The quantitatively important pool of relatively strongly bound biomarkers is otherwise difficult to access or isolate in sufficient quantities using chemical reagents or other conventional analytical pyrolysis methods. Thus, hydropyrolysis represents an attractive route to provide a better insight into the preservation, structural modification, and degradation mechanisms prevailing in covalently bound biomarkers and should prove useful for aiding oil/source correlations.

Conclusions

A combination of slow heating rate (5 °C/min), high hydrogen pressure (15 MPa), and use of a dispersed

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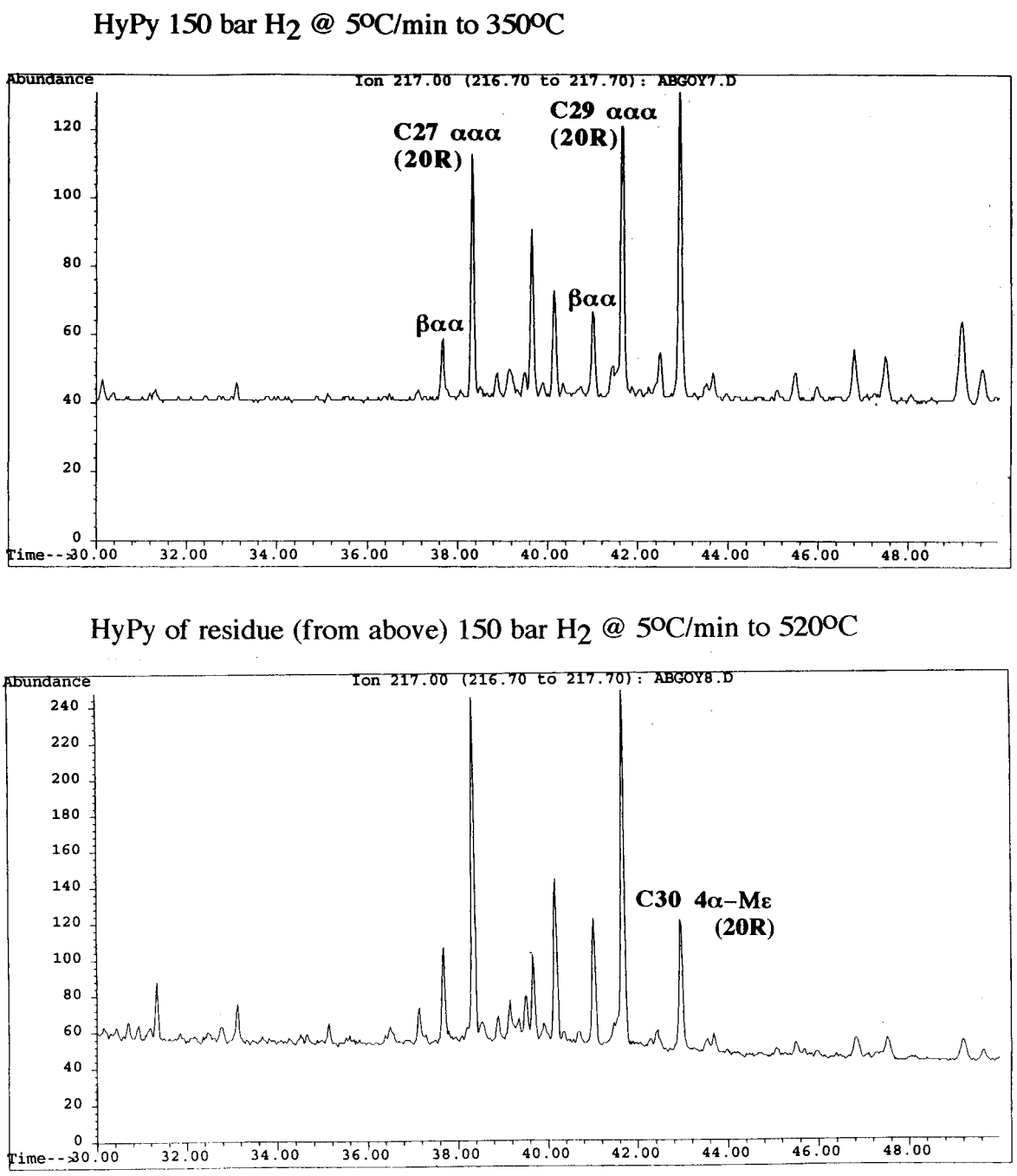

Figure 10. Comparison of sterane profiles (*m/z* 217) from sequential (temperature-resolved) hydropyrolysis of Göynük oil shale.

sulfided molybdenum catalyst for hydropyrolysis represents the best regime for achieving high conversions of kerogens to, principally, DCM-soluble oils. Using these conditions, the fraction of readily analyzable products is maximized while structural rearrangement of biomarker species is minimal. Indeed, it is reported elsewhere that bulk compositional changes in carbon aromaticity and long alkyl chain content are relatively minor compared to traditional pyrolysis techniques.[26] Staged hydropyrolysis has confirmed that hopanes released at higher temperatures through cleaving relatively strong bonds are quantitatively more significant than those released at lower temperatures. Although the use of a slow heating rate means that hydropyrolysis becomes much more time-consuming than conventional analytical pyrolysis methods, such as flash pyrolysis, valuable biogeochemical information on kerogens is obtained that is unlikely to be retrieved via other degradation methods.

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