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Chemical–structural characterization of solvent and thermal extractable material from perhydrous vitrinites

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Abstract

In this work, the characterization of the non-covalently bonded compounds present in a set of perhydrous coals of different age and geographical location (Cretaceous coals: UCV and TCV and Jurassic coals: AJV, PGJV, WJVh and WJVl) was carried out by means of a combination of the analyses of the material soluble in chloroform and the thermal extract. The extract in chloroform was studied through GC/MS and NMR and the thermovaporized fraction was obtained by means of flash pyrolysis at the Curie temperature of 350 °C and quantified by on-line GC-MS. The results obtained for the Cretaceous coals confirm that the substances responsible for the hydrogenation are those covalently bonded to the vitrinite network as a result of the modifications undergone by the botanical precursors. Despite the striking similarity in the global characteristics of these two coals (TCV and UCV) significant differences between the material non-covalently bonded to their coal matrices were found. These differences are attributed to the type of resins present in the coals and/or to their different degree of evolution. With respect to the Jurassic coals, the present study allows the process by which the hydrogenated substances were assimilated into their structure to be established. The characterization of the assimilated substances in the WJVl coal reveals an unexpectedly high incorporation of alkanes given the humic origin of this sample. From these results the assimilation of hydrogen-rich substances from the decomposition of the organic remains in the sedimentary environment in which WJVl precursor were deposited, is proposed. The incorporation of products derived from the primary decomposition of organic material is not evident for the WJVh and AJV coals. The substances assimilated into the coal matrices show a higher aromaticity, the aromatic structures of WJVh being more condensed than those found in AJV. The compositional differences between them probably arise from the different source of the hydrogen-rich material. In the case of AJV coal the source was the adsorption of hydrocarbons generated and migrated from the Pliensbachian source-rocks whereas in WJVh, assimilated compounds come from the material generated by the thermal transformation (coalification) of the adjacent organic rocks of similar age. Finally, PGJV shows two types of non-covalently bonded compounds. Solvent extractable material is mainly composed of the first type of compounds, which is predominantly aliphatic in nature with a preponderance of alkanes. The second type of compounds is more aromatic and they are probably located in the close porosity of this coal. They are not accessible to chloroform but they are the most abundant in the thermal extract.

Author Keywords: Perhydrous coal; Vitrinite; Soluble material; Thermal extract; Trapped compounds; NMR; Py–GC/MS (Curie temperature: 350 °C)

1. Introduction

Perhydrous coals are those anomalous enriched in hydrogen due to natural causes [1 and 2]. Thus, the perhydrous coals are characterized by huge anomalies and discrepancies in all their petrological and chemical parameters in relation to both composition and rank. Consequently, these coals show unexpected physico-chemical and technological properties, which differ from those of normal (non-perhydrous) coals. In perhydrous coals, vitrinite reflectance is suppressed, the characterization parameters lose their predictive potential and the rank indicators become less useful. The unexpected and anomalous behavior of this type of coals may therefore be, thus, explained and rationalized in terms of the chemical–structural modifications of their vitrinite (the main component of the whole coal) due to the process of hydrogen-enrichment.

A high liptinite content may cause the perhydrous character in coals, but also, perhydrous vitrinite has been related with the red-ox conditions and degree of bacterial activity in the sediments, adsorption of bitumen, and the nature of the botanical precursors [1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11]. However, there is little information in the literature about the chemical structures present in such perhydrous materials.

The vitrinite-rich perhydrous coals used in this work have been subjected to several studies in recent years [12, 13, 14, 15, 16, 17, 18, 19, 20, 21 and 22]. The main objective of such studies was to establish the relationships between hydrogen content and the molecular structure in order to understand the properties and behavior of perhydrous coals better, as well as obtain a deeper knowledge of the development of the coalification process and the mechanism of vitrinite reflectance suppression. Such investigations allowed the source of natural hydrogen-enrichment in these coals to be established. At the same time, it has been shown that different sources of hydrogen affect the chemical structure of the vitrinites differently, and striking variations in the aliphatic moieties present in the samples have been suggested. Nevertheless, a set of general features found for all of the studied samples indicate that vitrinite reflectance suppression in these perhydrous coals is related with modifications at the level of the chemical molecular structure of the huminite/vitrinite induced by the hydrogenated compounds present in their matrices. The irreversible structural modifications undergone by perhydrous vitrinites imply that they develop their own unique evolution pathway that differs from the one followed by normal (non-perhydrous) vitrinites. The presence of highly hydrogenated structures affects the vitrinite in two main ways: (i) retarding the structural reorganization of the aromatic lignin framework with respect to the oxygenated functionalities of the lignin and (ii) preventing the condensation of phenols into dibenzofuran-like substances and aromatic polycyclic hydrocarbons. It is, therefore, necessary to know the chemical structural composition of the hydrogenated substances present in perhydrous vitrinites. Such knowledge could be attained through the analysis of the trapped compounds. The GC/MS analyses of the volatile fraction of the soluble fraction of the perhydrous vitrinites and their comparison with data from the molecular characterization by means of Py-GC/MS [17] show that the extractable material of these coals could at least in part be, representative of the nature of the such hydrogenated compounds present in their matrices.

There is great controversy concerning the extent of the relationship between the nature of the trapped compounds and the macromolecular structure of the coal. Nevertheless, the study of fractions derived from the coals with minimal alteration is widely used to obtain information about the chemical structures present in a material of very difficult analytical accessibility. It is generally accepted that the trapped compounds are products and residuals of the original

coalification process so that they may be used to draw conclusions about the origin and thermal history of coals. Furthermore, it has been clearly established that the mobile phase in coals, which can be extracted with organic solvents, plays an important role in their coking ability [19]. The development of a mobile phase during the bituminous coal rank is the factor mainly responsible for the thermoplastic behavior of coals and for the development of the secondary fluorescence in vitrinites [23]. At the same time, the mobile phase also plays an important role during the process of hydrogen transfer which takes place during the thermal treatment and probably also during the coalification process [24, 25, 26, 27 and 28].

In this work, the chemical–structural characterization of the non-covalently material present in six selected vitrinite-rich perhydrous coals is described. This characterization was achieved by means of the combined analyses of the fraction soluble in chloroform and the thermal extractable material. A study of the nature of the substances which are not-covalently bonded to the coal network cannot be restricted to the extractable material. This is because some of the compounds trapped in the matrices of such coals may not be accessible to the solvent and/or the dissolving power of the solvent used (chloroform) may not be strong enough to overcome the interactions between assimilated substances and the coal matrix. Thermal extraction could solve these problems because heat treatment may open up the porous structure and so allow compounds strongly retained in the closed porosity of the matrix to be characterized. Curie-point heating systems at 350 °C permits the study of thermally extractable material in coals. Thermovaporized compounds are quantified by on-line GC/MS so that the information obtained only concerns the volatile fraction of the trapped compounds. The study of the chloroform extract allows not only the analysis of the volatile fraction through GC/MS but also a structural characterization of the whole material through the application of spectroscopic methods.

The aim of the combined study of the thermal extract (Py–GC/MS using a Curie temperature of 350 °C) and the structural NMR analysis of the whole soluble fraction in chloroform shown here is to provide information concerning the source, nature and structure of hydrogenated compounds present into the vitrinite of the perhydrous coals. This will supply new insights concerning the modifications of the coal network as result of a natural enrichment in hydrogen. At the same time, the chemical–structural differences found in the trapped compounds allow differences in the structural parameters, the properties and behavior of the raw materials to be rationalized.

2. Samples and analytical procedures

2.1. General characteristics of selected perhydrous coals

The sample code, location and age of the selected coals are shown in Table 1. On the basis of the different age, sedimentary environment and botanical precursors [29, 30, 31, 32, 33 and 34] two groups of perhydrous coals can be distinguished: Cretaceous coals, UCV and TCV (Turonian and Albian age, respectively) and Jurassic coals, AJV, PGJV and WJVh, WJVl (Kimmeridgian and Toarcian, respectively). The complete petrographic and geochemical characterization of these coals has been previously reported [12, 13, 15 and 17] and two different hypotheses for explaining their perhydrous character have been proposed:*Cretaceous coals (UCV and TCV)*

Table 1. Sample code, location and age of the selected perhydrous vitrinite-rich coals

Sample code	Provenance	Age
UCV	Wayne County Basin, Utah, USA	Turonian (Cretaceous) [29]
TCV	Teruel Basin, Spain	Albian (Cretaceous) [30]
AJV	Asturias Basin, Spain	Kimmeridgian (Upper Jurassic) [31,32]
PGJV	Peniche Area, Portugal	Kimmeridgian (Upper Jurassic) [33]
WJVh	Whitby, England, UK	Toarcian (Lower Jurassic) [34]
WJVl	Whitby, England, UK	Toarcian (Lower Jurassic) [34]

The abnormal hydrogen enrichment for these coals is of a pre-sedimentary type (before peatification) as a result of the extremely lipid-rich nature of their botanical precursors. This lipid-rich nature was caused by the saturation of the botanical tissues, generally composed of lignin and cellulose, by terpene-type resin.*Jurassic coals (AJV, PGJV, WJVh, WJVl)*

The perhydrous character of these materials is of a post-sedimentary type (i.e. during peatification and/or coalification processes) and is attributed to the assimilation into their coal matrices of highly hydrogenated secondary substances (bituminous and/or oil-like material) from the adjacent organic-rich sedimentary rocks and at different stages of transformation.

The true coal rank of these coals was estimated [12, 13, 14, 15 and 17] as subbituminous and subbituminous/high volatile bituminous coal rank for the Cretaceous and Jurassic samples, respectively. A brief summary of the most relevant characteristics of these coals is given below.

The coals are mainly composed of huminite/vitrinite (100–96.6 vol.%) with a very low mineral matter content. Resinite was found in the two Cretaceous coals (UCV and TCV, 1.4 and 3.4 vol.%, respectively) while exsudatinite was only detected in the voids and disseminated in the huminite of the TCV coal. The huminite/vitrinite reflectance is strongly suppressed in all cases. It is reduced by about 0.2–0.3% in Cretaceous coals and by 0.3–0.4% for Jurassic coals.

Given the humic origin and petrographic composition, the location of the coals on the van Krevelen diagram [35] reflects their perhydrous character (Fig. 1). The coals have a very high volatile matter and carbon contents (52.1–72.1% and 77.3–84.8, respectively). They have also developed a low and abnormal aromaticity ("*fa*", Table 2) with a low degree of condensation/substitution. They contain aromatic structures with 1–2 rings with a very small contribution of aromatic rings of large size and an unusually high amount of aliphatic structures over condensed aromatic structures. Their molecular characterization [17] has shown that the major structural units are simple phenols with a preponderance of *para*-substituted phenols.

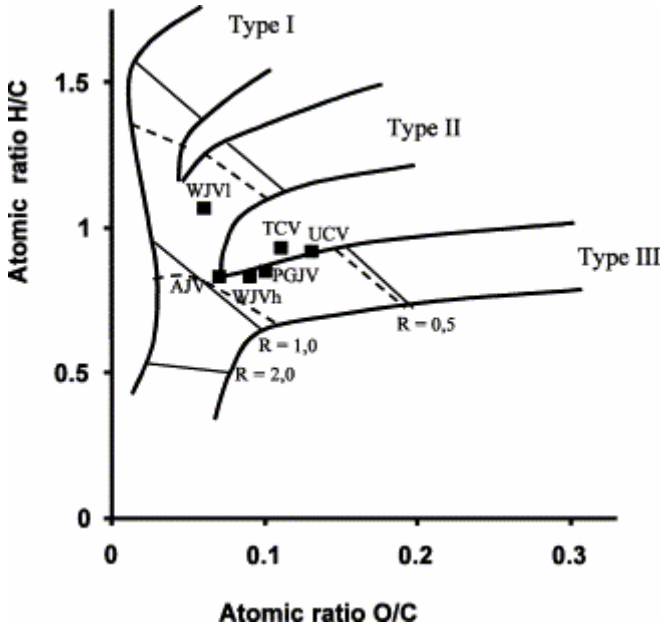

Fig. 1. Location of the perhydrous coals in the van Krevelen diagram [35].

The hydrogen enrichment also strongly affects the Rock–Eval indices as well as the textural and technological properties of these coals. They present a low thermostability and anomalously high oil potential (Tmax and S2 values, Table 2). For PGJV and WJVl coals, a high amount of free hydrocarbon should be also mentioned (S1 values, Table 2). All of them are characterized by a low density (Table 2). Cretaceous coals show normal values of porosity in accordance with the assigned rank (Table 2). The lower value of TCV with respect to UCV is explained by the generation of exsudatinite in TCV, which is mainly found in pores and cavities. The porosity of Jurassic coals is exceptionally low [15 and 35] which is especially relevant in AJV and PGJV (Table 2). Jurassic coals develop a high fluidity during carbonization and present abnormal swelling as shown by the swelling index (FSI) values [19 and 22].

Table 2. Main physico-chemical parameters used in this study for the perhydrous coals selected

Samples	Aromaticity factor "*fa*"	S1 (mg HC per g coal)	S2 (mg HC per g coal)	Tmax (°C)	Real density (g cm^{-3})	Porosity (%)
UCV	0,50	2,6	305	408	1,39	17,73
TCV	0,45	0,9	291	397	1,34	15,94
AIV	0,51	2,9	363	417	1,24	5,04
PGIV	0,52	10,2	303	415	1,22	2,46
WIVh	0,56	3,5	250	424	1,25	10,48
WIV1	0,33	57,9	473	425	1,19	8,09

"*fa*"=[(100−%VM $_{daf}$)×1200]/(1240×%C$_{daf}$).

2.2. Analytical procedures

A soluble fraction from each raw coal was obtained using chloroform as solvent in an ultrasound bath at room temperature. Approximately 10 g of sample crushed to <1 mm, was inserted in an ultrasonic bath (Selecta Ultrasounds) and kept at 25 °C for 2 h. The solution was then filtered (pore size of 5 μm) and the residues washed until the filtrate became clear, and then dried to constant weight.

The ^{1}H (400.13 MHz) and ^{13}C (100.61 MHz) NMR spectra were measured on a Bruker AMX400 spectrometer equipped with a 5 mm broad band (^{31}P–^{104}Ag) reverse probe. Samples were prepared by dissolving the extracts in $CDCl_3$. The ^{13}C spectra were obtained in the inverse gate decoupling mode on samples doped with 5 mg of $Cr(acac)_3$. Exponential multiplication of LB=2 was applied prior to the Fourier transformation.

Pyrolysis–gas chromatography for thermal extraction was performed at 350 °C using a Varian Satum 2000 GC-MS apparatus, with a 30 m×0.25 mm DB-5 column (film thickness 0.25 μm), coupled to a Curie-point pyrolyzer (Horizon Instruments Ltd.). 100 μg of finely ground sample was used for the analysis. The samples were deposited on ferromagnetic wires, inserted in a glass liner and placed in the pyrolyzer. The pyrolysis time was 4 s and the chromatographic conditions were the same as those previously reported for the Py–GC/MS at the Curie temperature of 610 °C [17].

3. Results and discussion

3.1. Structural analysis of the soluble fraction by means of NMR

Fig. 2 shows the ^{1}H-NMR spectra of the soluble fraction derived from perhydrous coals. The data obtained in the quantitative analysis of the spectra are given in Table 3.

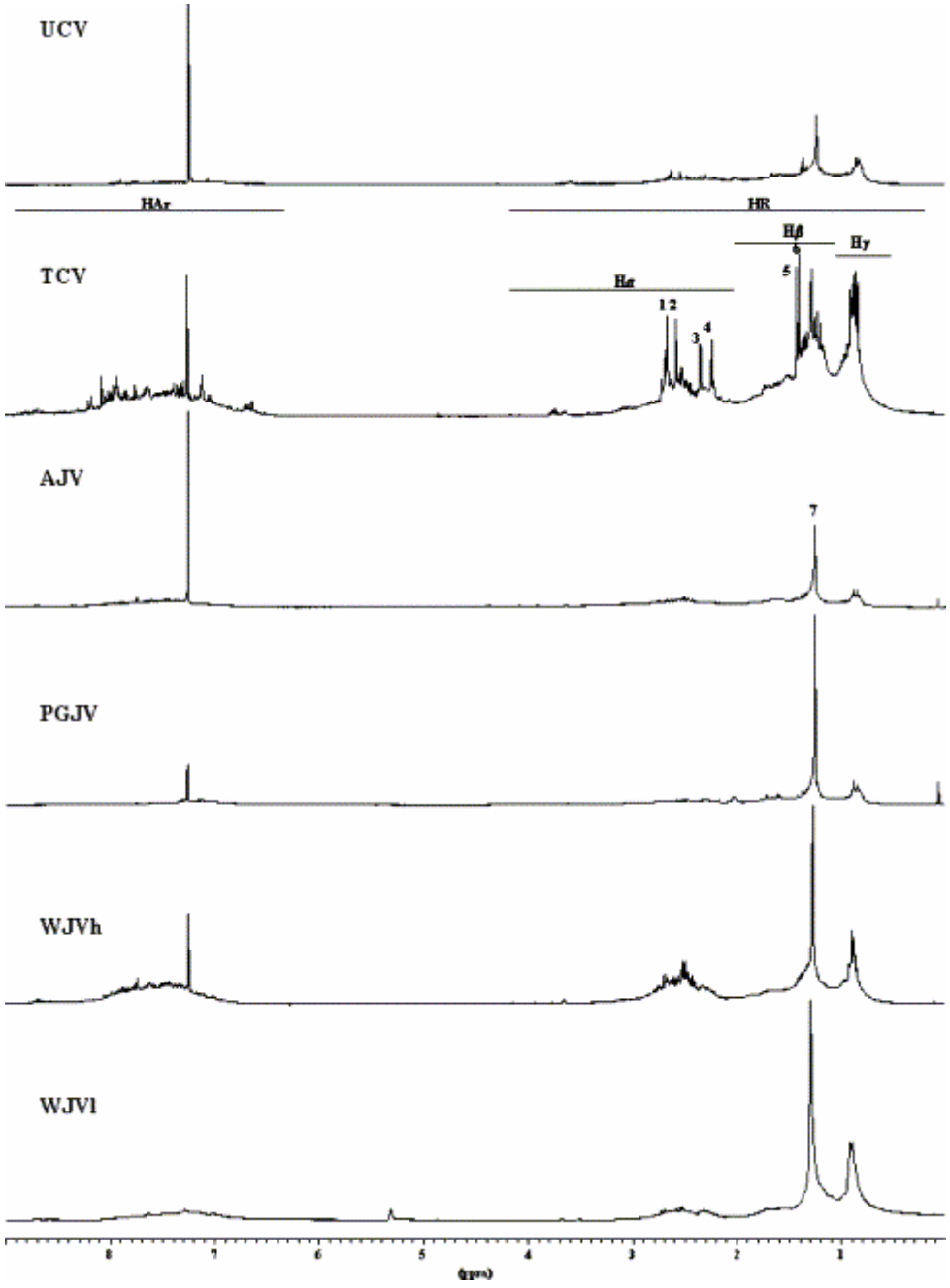

Fig. 2. [1] H-RMN spectra of the soluble fraction from the Cretaceous and Jurassic coals. (Chemical shifts for peaks 1–7; δ 2.7, 2.6, 2.3, 2.2, 1.42, 1.40 and 1.26 ppm, respectively).

Table 3. [1]H-NMR proton distribution (%) in the soluble fractions

Sample	HAr	HR	H_γ	H_β	H_α
UCV	17	83	20	50	30
TCV	23	77	24	45	32
AJV	28	72	18	50	32
PGJV	16	84	22	58	20
WJVh	28	72	20	43	37
WJVl	14	86	23	56	21

HAr calculated as: (integrated area in the 6.5–9.0 ppm range)/(integrated area in the 6.5–9.0 ppm range+integrated area in the 0.5–4.3 ppm range). HR calculated as: (integrated area in the 0.5–4.3 ppm range)/(integrated area in the 6.5–9.0 ppm range+integrated area in the 0.5–4.3 ppm range). H_γ calculated as: (integrated area in the 0.5–1.1 ppm range)/(integrated area in the 0.5–4.3 ppm range). H_β calculated as: (integrated area in the 1.1–2.1 ppm range)/(integrated area in the 0.5–4.3 ppm range). H_α calculated as: (integrated area in the 2.1–4.3 ppm range)/(integrated area in the 0.5–4.3 ppm range).

The integration of the spectral regions corresponding to the aromatic and aliphatic protons (6.5–9.0 and 0.5–4.3 ppm, respectively) shows that aliphatic hydrogen preponderates over the aromatic hydrogen in all extracts (see HAr and HR, Table 3). The WJVl, PGJV and UCV extracts are characterized by the strongest aliphatic character with very low values of hydrogen aromaticity (HAr from 14 to 17%, Table 3). In contrast the AJV and WJVh extracts show the highest values of HAr (28%) and a relatively high value for this parameter was also obtained for the TCV extract (23%). Most of the signals in the aromatic region of the spectra (6.5–9.0 ppm) fall between 7.2 and 8.5 ppm. This implies that the aromatic hydrogen in these extracts belongs mainly to di-aromatic structures [36 and 37].

The high aliphatic content of the WJVl extract was also found in the chromatographic study previously reported [17] in which n-alkanes were the dominant class of identified compounds. The present analysis of the volatile fraction from the soluble material derived from the coals studied revealed the presence in the PGJV extract of a series of n-alkanes of relatively high molecular weight (Fig. 3). n-Akanes were, however, not detected in the chromatographic study of the UCV extract. This implies that the aliphatic material of the UCV extract is probably present mainly in the non-volatile fraction. In the volatile fraction from the WJVh extract, alkanes were also identified which was not the case for the AJV extract (Fig. 3). This suggests, in principle, a higher contribution of the aliphatic material in the former sample, WJVh. However, the ^{1}H-NMR study shows a similar aromatic proton content for both extracts (HAr, Table 3). This apparent contradiction may be explained as derived from the size of the aromatic entities present in both extracts. Thus, the WJVh extract should contain the most condensed aromatic structures, and these may not be detected by GC/MS.

The degree of substitution of the aromatic structures in the extracts was measured by the Hα/HAr ratio [38] and plotted in Fig. 4 versus the degree of substitution of the whole coals. The latter was estimated from the FTIR through the intensity (measured as absorbance) of the aromatic mode at 750 cm^{-1} (four adjacent aromatic C---H bonds) relative to the total intensity (absorbance) of the aromatic C---H out-of-plane bending modes, $\%750=Abs_{750}/(Abs_{870}+Abs_{815}+Abs_{750})$. In general, the degree of substitution of the aromatic structures in both extracts and whole coals, follows a similar trend. However, the differences found in the degree of substitution of the aromatic extracts between TCV and UCV and WJVh and WJVl are very significant because the whole coal shows a very close distribution of the aromatic hydrogen [17].

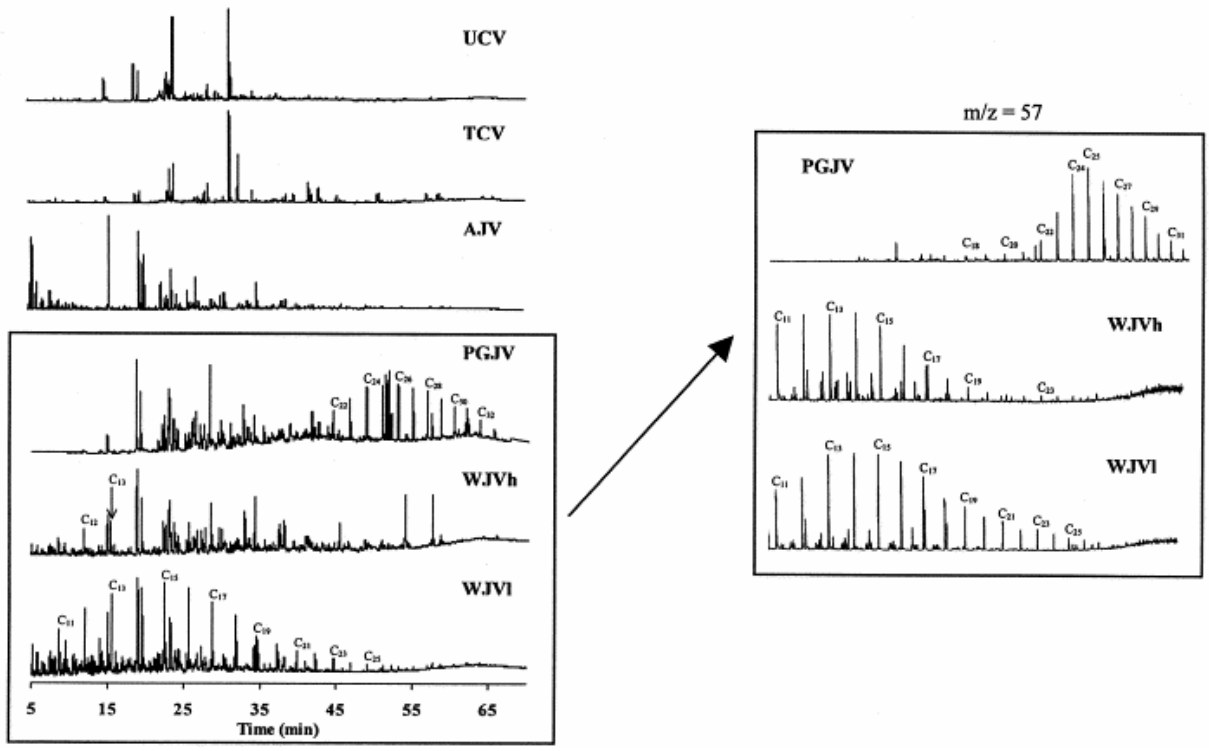

Fig. 3. Gas chromatograms of the soluble organic fraction from perhydrous coals (for peak identification see reference [17]). Mass fragmentogram, *m/z* 57, showing the alkane distribution for the PGJV, WJVh and WJVl coal extracts.

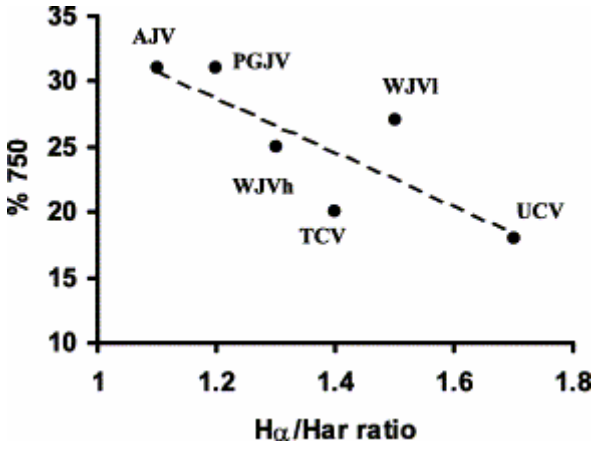

Fig. 4. Relationship between the relative intensity of the infrared mode at 750 cm^{-1}, $\%750=Abs_{750}/(Abs_{870}+Abs_{815}+Abs_{750})$, in the whole coals and Hα/Har ratio of the chloroform extracts.

The aliphatic region (0.5–4.3 ppm) of the ^{1}H-NMR spectrum of the TCV extract strongly differs from the other extracts (Fig. 2). This region is divided into three sub- regions, H_α, H_β and H_γ, depicted at the top of the TCV spectrum (Fig. 2). The 2.1–4.5 ppm region (H_α) is assigned to aliphatic protons in α position to the aromatic ring [35 and 39]. For all samples, most of these protons fall in the 2.1–3.5 ppm range, the contribution of the signals between 3.5 and 4.3 ppm to the total amount of aliphatic hydrogen being very small (<3% of the total amount of aliphatic hydrogen). The signals in this region (3.5–4.3 ppm) arise from ring joining methylenes and/or from protons of methine or methylene groups α to ethereal oxygen [35]. Structures of this type are, therefore, very scarce in the studied extracts. Between 2.1 and

3.5 ppm the spectrum of the TCV extract shows four clear differentiated singlets at δ 2.7, 2.6, 2.3 and 2.2 ppm (peaks 1–4, Fig. 2). This indicates the presence in this extract of methyl groups attached to the aromatic ring in a different environment. The chemical shifts of peaks 1 and 2 denoted the presence of methyl groups directly attached to the aromatic ring in polynuclear structures, whereas peaks 3 and 4 are assigned to the α CH_3 in monoaromatic structures [39]. The spectra of the other extracts show overlapping multiplets in this region without any clear sharp signals. This suggests that the signals mainly arise from the CH_2 and CH groups directly attached to aromatic rings, the contribution of the methyl substituents on the aromatic rings not being of great significance [40]. The quantitative data (Table 3) show the highest contribution of aliphatic hydrogen in α position to the aromatic ring in the total amount of aliphatic hydrogen, Hα, for the WJVh extract (37%). In contrast, the extracts of WJVl and PGJV are characterized by the lowest contribution (20–21%). The other coal extracts (TCV, UCV and AJV) show similar intermediate values for Hα (30–32%).

The Hγ region (0.5–1.1 ppm) contains the contribution of γ-CH_3 to the aromatic-ring and straight-chain or alkane branch methyl protons [35 and 36]. The contribution of the protons in this region to the total amount of aliphatic hydrogen (Hγ, Table 3) varies from 18% (AJV extract) to 24% (TCV extract). Signals due to the CH_3, CH_2 and CH groups β to the aromatic ring, β-CH_2 and β-CH in the hydroaromatic structures, straight-chain alkane methylene protons, protons in the CH_2 groups of cycloparaffins as well as protons in the CH groups of saturated overlap in the spectral region between 1.1 and 2.1 ppm (H_β, Fig. 2). Except for the TCV extract this region is narrow, showing an intense singlet at δ=1.26 ppm (peak 7, Fig. 2). This indicates that the major contributors to this region are straight-chain alkanes and/or n-alkyl groups of long chain alkyl aromatics [40, 41, 42 and 43]. According to the chromatographic results (Fig. 3) in the AJV and UCV extracts the singlet mentioned is only due to long chain alkyl aromatics. Such compounds must also be the main contributor to WJVh extract because of the low amount of alkanes found in the chromatographic study of this extract. On the other hand, for WJVl and PGJV without discarding the presence of long chain alkyl aromatics, n-alkanes are important contributors to the signal at 1.26 ppm. In the spectra of the TCV extract, overlapping multiplets are superimposed over this signal. This implies that the aliphatic structures present in this extract are much more complex than in the others with a lower proportion of long chain alkyl aromatics. A higher degree of branching of the aliphatic structures for the TCV extract than in the others can be also inferred. Furthermore, besides the singlet at 1.26 ppm this sample also shows another two sharp signals in this region (peaks 5 and 6, Fig. 2) at 1.42 and 1.40 ppm. These signals can also be observed in the spectrum of the UCV extract, although their relative importance is much smaller than in TCV. The signals appear in the characteristic spectral region of the protons present in cyclohexane rings. The different distribution of the aliphatic hydrogen in the TCV extract and the significant presence of cycloparaffinic counterparts could extend to the whole coal, thus explaining the unexpected low intensity of the aliphatic infrared modes [14 and 17]. The reduction of the intensity of the infrared absorption bands due to the stretching vibration of aliphatic C---H bonds which result from the increase in the degree of tension in the closed polyethylene chain has also been reported for other special and perhydrous coals [44].

The greater complexity of the aliphatic structures present in TCV is also reflected through the analysis of the aliphatic region of the ^{13}C-NMR spectrum. Unfortunately, the low amount of extract obtained did not allow a good ratio signal/noise to be achieved for all the extracts. Thus, as an example, Fig. 5 shows the corresponding aliphatic region of the ^{13}C-NMR for the TCV and WJVl extracts which represent, respectively, the highest and lowest degree of complexity among the studied samples. This region, in the WJVl extract is dominated by the

signals at δ 14, 23, 29, 29.5 and 32 ppm (peaks a–e, respectively, in Fig. 5). These signals are associated with carbon chains which have a number of carbon atoms greater than nine [36, 45, 46 and 47]. Peak d (δ=29.5 ppm) corresponds to the internal CH_2 groups responsible for the singlet at δ=1.26 ppm the most intense signal in the ^{1}H-NMR spectrum of this extract (WJVl, Fig. 2). Although signals assigned to straight aliphatic chains may be discernible in the ^{13}C-NMR spectrum of the TCV extract, they are not the dominant ones (Fig. 5). Several intense signals in the 18–24 ppm range indicate the presence of methyl groups in different types of aliphatic structures. Carbon signals between 18 and 20.5 ppm can be mainly ascribed to aliphatic branching methyl groups [45]. Furthermore, signals around 19 ppm are much more intense than the one at 14 ppm corresponding to terminal CH_3 groups in straight chains. These results confirm the high degree of branching of the aliphatic structures for TCV. This is also evident from several intense signals in the 35–40 ppm range which have been assigned to the resonances of internal carbons that are at, or immediately adjacent to a branching point [47]. At the same time, the signals between 20 and 23 ppm agree with the presence of methyl groups directly bonded to the aromatic ring [48] inferred from the sharp signals in the H_α region of the ^{1}H-NMR spectrum of this extract (TCV, Fig. 2). The presence of shorter aliphatic chains in the TCV extract is also evident in the ^{13}C-NMR which shows a clear signal around 15 ppm typical of CH_3 in ethyl groups. The ^{1}H-NMR spectrum of TCV suggests a higher proportion of naphthenic and hydroaromatic structures for this extract than for the others. Thus, the signals between 22.5 and 31 ppm probably contain a large contribution of resonances due to α- and β-carbons in unsubstituted six-membered hydroaromatic rings [48].

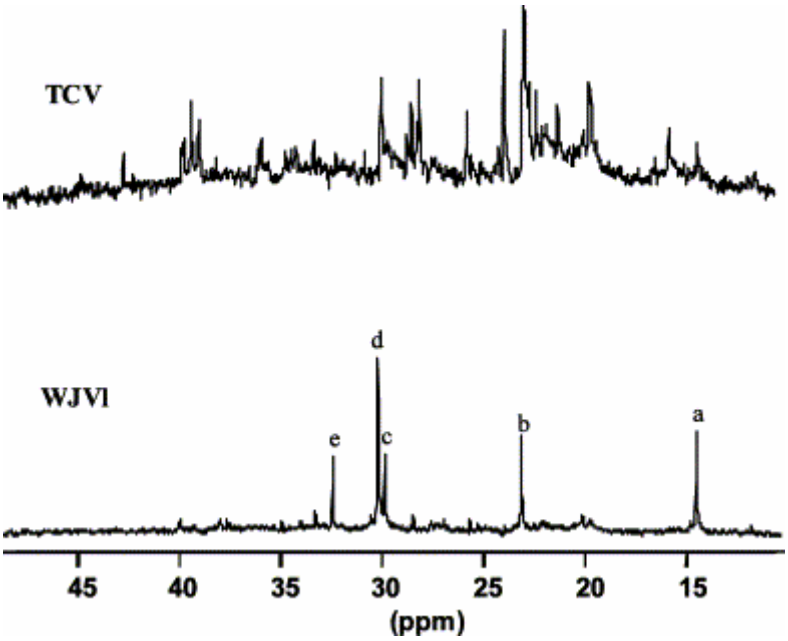

Fig. 5. Examples of ^{13}C-RMN spectra of the soluble fraction from the TCV (Cretaceous) and WJVl (Jurassic) coals. (Chemical shifts for peaks a–e; δ 14, 23, 29, 29.5 and 32 ppm, respectively).

3.2. Characterization of the thermal extracts by means of Py–GC/MS

Fig. 6 shows the chromatograms obtained through the Py–GC/MS analysis of the perhydrous coals at the Curie temperature of 350 °C. The identification of the most significant peaks is given in Table 4.

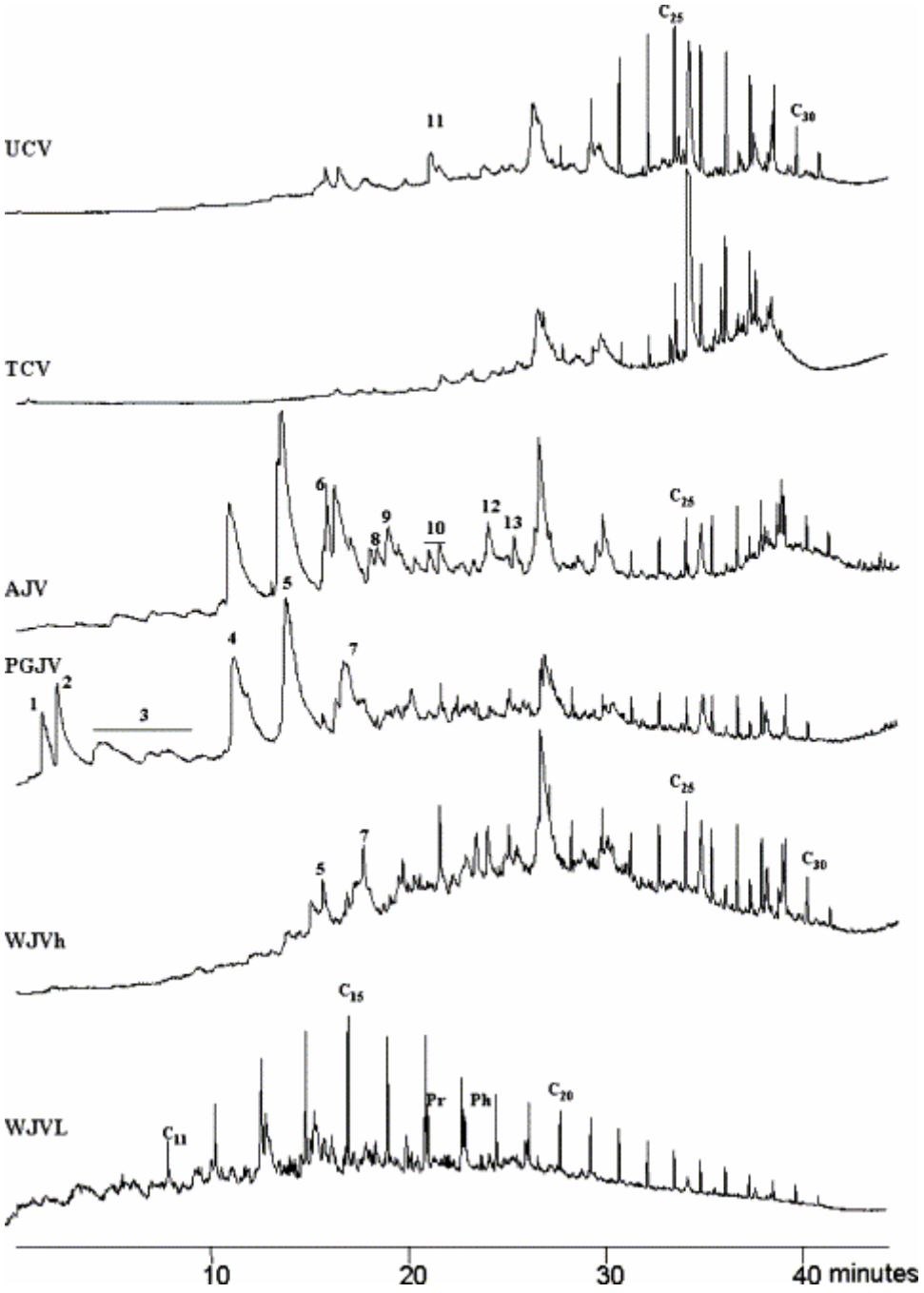

Fig. 6. Chromatograms of the thermovaporized fraction from the Cretaceous and Jurassic coals obtained through flash-pyrolysis. Peak identification is given in Table 4.

Table 4. Py–GC/MS, Curie temperature 350 °C: main compounds identified in the thermal extracts of the perhydrous coals (for peak code see Fig. 6)

Peak code	Compound	Peak code	Compound
C_n	Alkanes	6	Biphenyl
Pr	Pristane	7	C2-Naphthalenes
Ph	Phytane	8	C1-Biphenyls
1	Benzene	9	C3-Naphthalene
2	Toluene	10	C1-Dibenzofurans
3	Alkylbenzenes (C_2–C_4)	11	Cadalene
4	Naphthalene	12	Phenanthrene/anthracene
5	C1-Naphthalenes	13	C1-Phenanthrene/anthracene

At the Curie temperature of 350 °C, the coal matrices are not totally degraded [49 and 50]. Thus, the compounds obtained from this type of analysis are those non-covalently bonded to the coal matrix. In agreement with this, phenolic compounds which were the major constituents of the flash pyrolysates performed at a Curie temperature of 610 °C [17] are totally absent in the chromatograms obtained when the pyrolysis was performed at the Curie temperature of 350 °C. Likewise, compounds containing sulfur or nitrogen were not detected in accordance with the low amount of these elements (<2.3 and <1.2%, respectively) found in the chemical analyses [17]. However, some thermal reactions involving alkyl chains have been found to occur at temperatures lower than 350 °C [51]. The occurrence of such reactions, therefore, cannot be discarded during the thermovaporization experiments. Thus, the origin of the n-alkanes released by flash pyrolysis at 350 °C from some of the samples studied could be pyrolytic. They may be formed through the breaking up of alkyl groups next to aromatic rings and/or by thermal cracking of branched alkyl structures leaving straight chain alkanes.

In the chromatographic study of the soluble fraction from TCV, UCV and AJV coals n-alkanes were not detected even by means of the mass spectrometric study and the analysis of the *m*/*z* 57 fragmentograms (Fig. 3). However, alkanes of relatively high molecular weight (C_{24}–C_{30}) are clearly present in the thermovaporized fraction of these three coals. Moreover, they are the major contributors to the thermal extract of TCV and UCV (Fig. 6). The similar distribution of the alkanes identified in the AJV and UCV extracts (Fig. 7) suggests that they are originated by thermal alteration of similar aliphatic structures. The most probable source of these alkanes are long chain aromatics that cleave preferentially at the α position leading to an alkyl radical one carbon atom shorter than the initial chain. Other favored sites for the breakdown of the alkyl chains are the C---C bonds around a branching carbon. This probably occurs in the TCV coal for which a higher degree of branching is expected showing a different distribution of alkanes with respect to the other samples (Fig. 7). The alkyl radicals formed could evolve in different ways. In the samples studied, a high contribution of compounds that play an important role in the processes of hydrogen donation and transfer [16] is expected. Therefore, the stabilization of the alkyl radicals produced by thermal alteration of the alkyl side chains through hydrogenation and probably recombination reactions may be favored over unsaturation reactions [25], leading to alkanes. Series of alkenes were not detected.

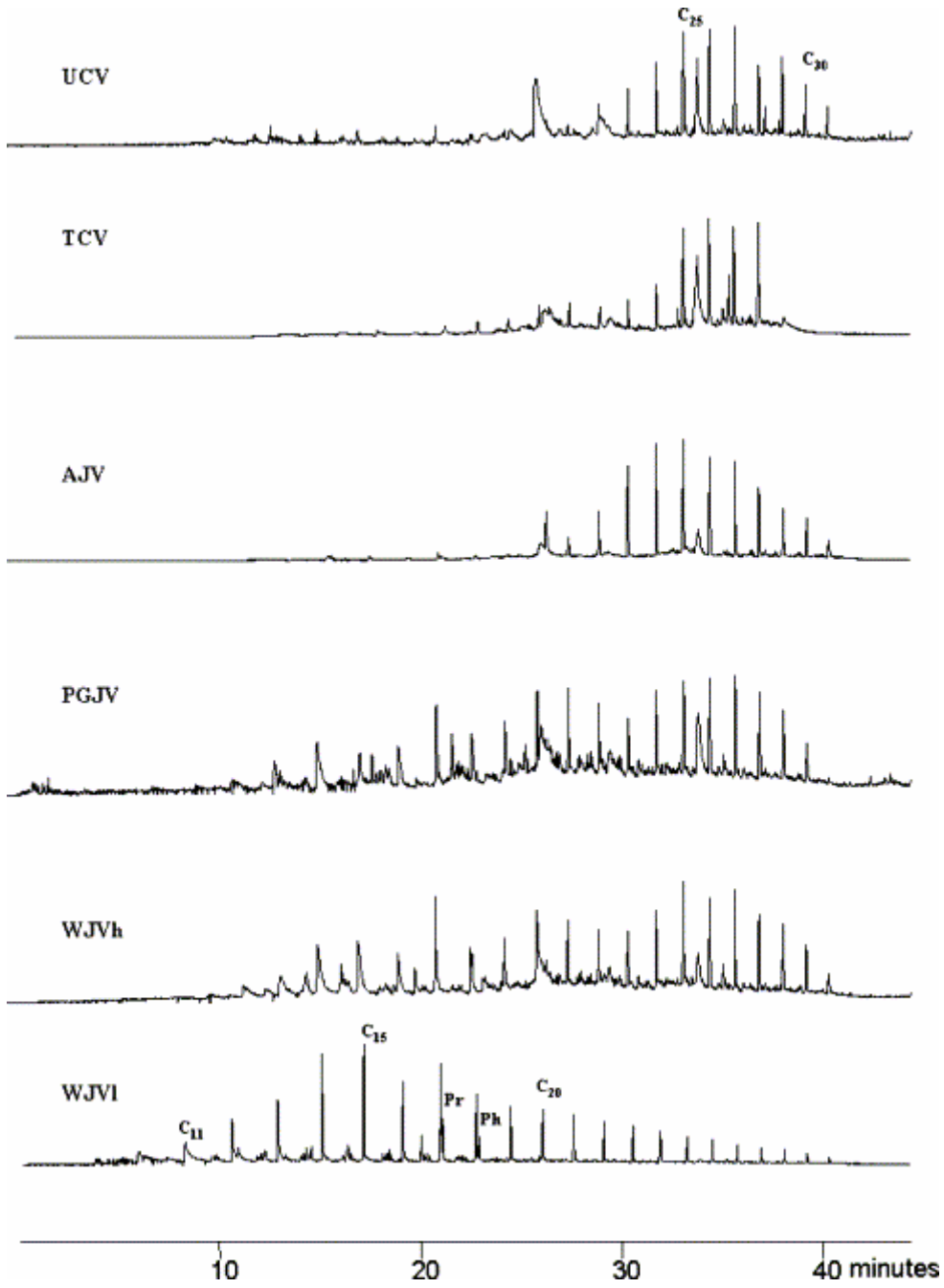

Fig. 7. n-Alkanes series detected in the thermovaporized fraction from the coals (*m*/*z* 57 fragmentogram). Pr: pristane, Ph: phytane.

Most of the n-alkanes identified in the thermovaporized fraction of WJVh coal also arise from thermal alteration of some of the compounds trapped inside the matrix. Thus, the relative contribution of these compounds is higher in the thermal extract than in the solvent extractable material and their distribution also differs in both fractions (Fig. 3, Fig. 6 and Fig. 7). The thermal extract is enriched in alkanes of higher molecular weight than those found in the chloroform extract. For PGJV and WJVl coals a similar series of alkanes were identified in the thermal and soluble extractable fractions (Fig. 3 and Fig. 7). This result suggests that the high aliphatic content of the chloroform extract derived from these two coals is mainly due to the presence of alkanes. Nevertheless, the existence of long chain alkyl aromatics among the non-covalently bonded compounds in PGJV and WJVl cannot be discarded,

although they may be structurally different to those present in the other coals studied. Evidence for the aforementioned structural differences may be its high thermal stability. It should be noted that the facility with which they rupture depends on the chain length and the degree of branching in the aliphatic side groups. This is because, as is well known, both these factors affect the bond dissociation energies considerably.

The thermovaporizable material from Cretaceous coals (TCV and UCV) is made up mainly of alkanes of pyrolytic origin as was discussed above. On the other hand, compounds associated with terpene resinite, such as cadalene, which are the major components of the volatile fraction of the chloroform extracts [17], are only minor components of their thermal extracts (see the relative intensity of peak 11, Fig. 6). From these results a predominantly non-volatile nature for the non-covalently bonded material present in the TCV and UCV coals can be inferred.

The chromatograms obtained for the thermovaporized fraction derived from Jurassic coals (Fig. 6) are qualitatively similar to the chromatograms corresponding to the volatile fraction of the chloroformic extract (Fig. 3). The most striking difference relates to the detection, in the thermal extract, of n-alkane series of pyrolytic origin and the relative proportion between alkanes and aromatic hydrocarbon derivatives. The closest similarity between thermal and soluble material was found for WJVl. All the analyses performed show a highly aliphatic character for the substances non-covalently bonded to the coal matrix. This aliphatic material is dominated by n-alkanes with a clear preponderance of those of relatively low molecular weight and smooth carbon distribution. The relatively short chain of the alkanes identified and their distribution agrees with the data concerning the thermal maturity of the black shales from Whitby and the high contribution of a material of algal type to the sediments [52]. The unexpectedly high incorporation of aliphatic material in WJVl, given the humic origin of this coal, explains its strong perhydrous character which is responsible for the location of this coal inside the type II kerogen band on the van Krevelen diagram (Fig. 1). At the same time, the results obtained also help to understand the differences that this perhydrous character entails for structural parameters between this sample and the others. The composition of the compounds trapped in the WJVh coal from the same basin is substantially different. The contribution of alkanes to the non-covalently material present in WJVh coal is low. The aliphatic structures mainly belong to long chain alkyl aromatics but, in relation to the other coals, the non-covalently bonded material in this coal displays a higher aromatic nature and also a higher degree of condensation.

The material soluble in chloroform (NMR analysis) from the PGJV coal is similar to that from WJVl. It has a predominantly aliphatic nature with a high contribution of alkanes. However, compared with WJVl, the identified n-alkanes are of a higher molecular weight, suggesting a larger input of products derived from terrestrial organic material in PGJV than in WJVl. A higher contribution of alkanes to the non-covalently bonded substances in WJVl and PGJV is responsible for the values of the S1 peak from the Rock–Eval pyrolysis (Table 2). Such values are higher than those found for the other Jurassic coals and for coals of a similar degree of evolution and normal hydrogen content. However, in the thermal extract from PGJV coal, a large incorporation of aliphatic material is not evident. On the contrary, aromatic hydrocarbons, mainly naphthalene derivatives, preponderate over the alkanes (Fig. 6 and Table 4). The composition of the PGJV thermovaporized fraction is, thus, close to that found for AJV despite the differences in the aromaticity of their respective chloroformic extracts (HAr, Table 3). The compositional differences between the solvent and thermal extractable material found in PGJV can be rationalized through the presence in this coal of two types of

non-covalently bonded compounds. One is predominantly aliphatic explaining the highly aliphatic character of the soluble fraction which is mainly composed of this type of compounds. The second is more aromatic in nature and these compounds are probably located in the close porosity of this coal. They are, therefore, not accessible to chloroform. Thermal treatment at 350 °C may open up the close porosity, thereby expelling these aromatic compounds. This would, thus, explain their preponderance in the thermovaporized fraction.

For AJV coal the chromatograms corresponding to the soluble and thermovaporizable fractions are similar. The major difference is the presence of alkanes in the thermal extract, which are originated by the thermal alteration of the long chain alkyl aromatics. These compounds are of a non-volatile nature so that they could not be detected in the chromatographic analysis of the chloroform soluble fraction (Fig. 3). However, they were clearly identifiable in the ^{1}H-NMR study through the intense singlet at δ 1.26 ppm (Fig. 2). The aliphatic material contained in the trapped substances mainly arises from such type of structures as those found for WJVh. In both coals, AJV and WJVh, the trapped compounds show a similar aromaticity, although the degree of condensation of such compounds can be expected to be lower for AJV than for WJVh coal.

4. Conclusions

The most significant conclusions from this research are the following:

The substances non-covalently bonded to the coal matrix in Cretaceous coals, UCV and TCV, are mainly of a non-volatile nature. UCV coal mainly contains long chain alkyl aromatics in normal amounts, in accordance with its low rank. Such compounds seem to derive from the resinite component. The compounds identified in TCV coal agree with the presence of resinite but mainly with the early generation of coalification products as exudates.
The differences found in the composition of the non-covalently bonded material present in UCV and TCV coals are attributed to the type of resin present into the coal matrices and/or to the differences in the degree of evolution of both coals.
The results obtained for TCV indicate that the aliphatic structures in this coal must be very different to those expected for the other coals. For this coal more branched aliphatic structures and a higher presence of cycloparaffinic counterparts should be expected. This explains the low intensity of the infrared modes due to aliphatic C---H bonds in the whole coal.
A comparison of the results obtained for the two coals from the same basin, WJVl and WJVh, besides the difference in vitrinite reflectance between them (0.22 and 0.40% for WJVl and WJVh, respectively) indicates that the assimilation of substances into their coal matrices must have taken place at different stages of their diagenetic evolution.
The hydrogen-rich substances assimilated by WJVl might be derived from the primary decomposition of the organic remains from the surrounding sedimentary environment in which the WJVl precursors were deposited. These substances could have been mobilized and transported into the environment and thus incorporated mechanically or via soluble phase into the different coal structures. Microscopic examination has revealed, in the mineral matter associated with this coal, well preserved algal remains and a diffuse organic material with a strong fluorescence in the short wavelengths. This confirms the presence of a relatively immature organic matter and amorphous organic products, which were mobilized during early peatification.
Evidence of incorporation of hydrogen-rich compounds from the primary decomposition of organic material in the sedimentary environment for WJVh and AJV coals was not found. The compositional differences found in the non-covalently bonded material present in these two

coals probably arise from the different sources of hydrogen-rich material. In AJV the absorption of hydrocarbons generated and migrated from the Pliensbachian source-rocks was the process responsible for its hydrogen enrichment. In the case of WJVh the most probable source of assimilated compounds was the substances produced during the coalification of the adjacent organic rocks of similar age.
Finally, PGJV shows two types of non-covalently bonded compounds. One is predominantly aliphatic with a preponderance of alkanes. The other type of compound is more aromatic in nature. They are probably located in the close porosity and are mainly responsible for the special properties detected in this perhydrous coal.

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