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Origin and distribution of biomarkers in the sulphur rich Utrillas coal basin – Teruel mining district – Spain

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Abstract

The Utrillas coal facies are located in the Maestrazgo basin in NE Spain. This mining district of Teruel contains subbituminous deposits from the Middle Albian (Lower Cretaceous 105 Ma) in areas near a delta estuary with abundant sulphur. The high sulphur content is due to an influx of sulphate caused by the geological recycling of Triassic gypsum from the catchment area into the delta estuary. In some outcrops, the weathered coal reveals leonardite deposits. The depositional environment of the basin originated coals, some of which are currently mined. The organic matter of the coals has been the object of scattered reports. Studies have focused on bulk pyrolysis parameters and microscopic observation in Utrillas samples, as well as the inorganic and insoluble organic fraction.

We analysed the organic soluble extract of the Utrillas coals using GC–MS in order to characterize their aliphatic, aromatic and organosulphur compounds. The biomarker distribution allowed us to recognize different inputs, assess their depositional palaeoenvironment and finally determine their degree of maturity. In particular, homologous series of hopanes related to eubacteria were present. Biomarkers characteristic of higher plant inputs were also widely distributed (e.g. phyllocladane or C_{29} steranes). The presence of linear alkylbenzenes allowed us to recognize the palaeodepositional reducing environments where they were deposited. Specifically, thienylhopanes were associated with sulphur-reducing environments. Finally, the abundance of unsaturated biomarkers such as diacholestenes indicated low-maturity coals. Various aromatic ratios such as the methylphenanthrene index also suggested diagenesis in the initial stage.

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1. Introduction

Organic geochemistry plays an important role in the exploration of fossil fuels. It involves identifying organic compounds with hydrocarbon skeletons related to biological molecules present in the tissues of living organisms. These biomarkers allow us to recognize the main input of organic matter, estimate the palaeodepositional environment on which they were deposited and determine the thermal maturity of the sedimentary rocks. Indexes such as palaeosalinity (ten Haven, 1986; Sinninghe Damsté et al., 1989) and oxicity (Didyk et al., 1978) have recently been used to recognize lacustrine lithologies (Cabrera et al., 2002). Elemental analysis and other bulk chemical parameters are major analytical techniques for characterizing fossil fuels (Philp and Ishiwatari, 1993; Yang et al., 2002).

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Bulk geological parameters and microscopic observation of Utrillas coals and their inorganic fraction were firstly studied by Querol et al. (1988, 1991, 1992). Previous geochemical studies of the organic matter, based on the characterization of the insoluble organic fraction by means of pyrolysis coupled to GC–MS, characterized Utrillas coals as sulphur-rich (Sinninghe Damsté et al., 1992). Detailed studies of the sub-bituminous coal have focused on their sulphur content (Gorchs et al., 1995). One molecular study examined the linear, branched and isoprenyl alkylbenzene skeletons and alkenylbenzenes and C_{24}–C_{28} diaromatic compounds in the soluble fraction extracted from a sulphur-rich Utrillas coal (Gorchs et al., 2003). Recently, a leonardite located in the basin was also studied (Olivella et al., in press).

However, little has been reported about the most abundant biomarkers of the soluble organic matter. This paper analyses the organic soluble extract of Utrillas coals and characterizes their aliphatic, aromatic and organosulphur compounds. Using the biomarker distribution and elemental analysis, we identify different inputs of organic matter, determine the palaeoenvironment on which they were deposited and define their degree of maturity.

2. Geological setting

The Teruel mining district is located in the linking zone between the eastern sector of the Iberian Range and the south-eastern most part of the Catalan Coastal Ranges (Fig. 1). The selected coals are located in the Escucha Formation (Middle Albian). The Escucha Formation presents a sedimentary record of six sub-basins: (1) the Utrillas sub-basin, with two coal-mining areas, the Utrillas-Escucha and the Portalrubio areas; (2) the Castellote sub-basin; (3) the Calanda sub-basin; (4) the Oliete sub-basin, with two coal-mining areas, the Ariño Valley and the Estercuel area; (5) the Traiguera sub-basin; and (6) the Santa Barbara sub-basin. The Escucha Formation contains immature sub-bituminous coal deposits (Querol et al., 1991) accumulated during the Middle Albian (Lower Cretaceous 105 Ma) in areas near a delta estuary. In some outcrops, the weathered coal reveals leonardite facies (Olivella et al., 2002a).

Sub-bituminous coals from Ariño (Elvira-13, L-12), Estercuel (Salomé-14), Utrillas and Portalrubio (Cañizara and R-3) were selected for this study.

The high sulphur content in these samples ($S > 4\%$) is probably due to an influx of sulphate caused by the geological recycling of Triassic gypsum from the catchment area into the delta estuary (Querol et al., 1988). The sulphur functionality of Utrillas coals has been examined in previous studies (Gorchs et al., 1995; Olivella et al., 2002a,b and Olivella and de las Heras, 2002c).

3. Experimental

Coal samples were crushed in a disc mill and an aliquot (ca. 20 g) was Soxhlet-extracted with

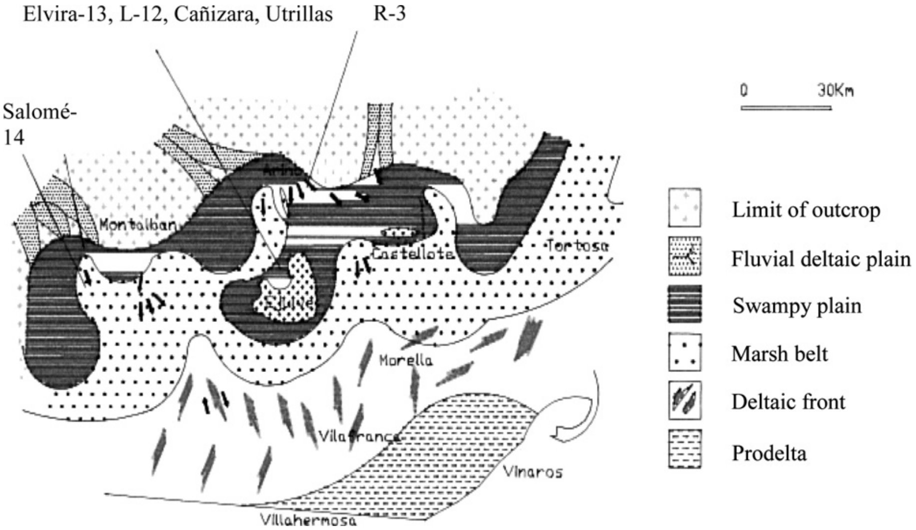

Fig. 1. Geological setting of Escucha Formation (Middle Albian) located in North East of the Iberian Peninsula (modified after Querol, 1990).

150 ml of (2:1) dichloromethane-methanol for 36 h. The extracts were vacuum-evaporated to 2 ml and hydrolysed overnight with 35 ml of 6% KOH/MeOH. The neutral fraction was extracted with *n*-hexane (3 × 30 ml) vacuum-concentrated to about 0.5 ml and fractionated using the following method (Gorchs et al., 2003). A column was filled with 8 g each of 5% water-deactivated alumina (70–230 mesh, Merck) (top) and silica (70–230 mesh, Merck) (bottom). Three fractions were collected: (1) 20 ml of *n*-hexane; (2) 20 ml of *n*-hexane/CH_2Cl_2 (90:10 v/v); and (3) 40 ml of *n*-hexane/CH_2Cl_2 (80:20 v/v).

Gas chromatography–mass spectrometry (GC–MS) was performed using an MD800. A DB-5 ms column of 30 m (0.25 mm i.d.) was used. The chromatographic conditions were 2 min at 60 °C, from 60 °C to 150 °C at 15 °C/min, from 150 °C to 310 °C at 4 °C/min and held at 310 °C for 15 min, with an injector temperature of 275 °C. Helium was used as a carrier gas. Mass spectra were acquired in a scanning range of m/z 50–650 Da at 1.5 s per decade. The MS temperatures were: transfer 200 °C, ion source 200 °C and analyser 225 °C.

Elemental analysis (%C, %H, %N) was performed with a Fisons 1106 and the total sulphur was determined with a Fisons 1108 elemental analyser.

The vitrinite reflectance was calculated using the methylphenanthrene index (MPI) according to Radke (1987) as $Rc = 0.6 * MPI + 0.4$.

4. Results and discussion

Table 1 shows the elemental analysis results (%C, %H, %N, %S). The major inputs from the Utrillas basin indicate that these coal samples are of terrestrial origin with little marine influence. This is consistent with the N/C (Premuzic et al., 1982) and S/C (Sweeney et al., 1987) relationships. The lowest N/C values measured at Salomé-14 and Cañizara could be attributed to the lake drying up (Meyers and Benson, 1988). Fig. 2 shows that, by plotting %N *vs.* %C (Fig. 2A) and %S *vs.* C (Fig. 2B) and the normal marine line (NML), characterized by the slopes 0.125 and 0.33, respectively, all values range from 0.008 to 0.014 ($N/C < 0.125$) and from 0.05 to 0.28 ($S/C < 0.33$), which indicates that the organic matter is dominated by allochthonous input from higher terrestrial plants. $N/C \geqslant 0.125$ and $S/C \geqslant 0.33$ indicate predominant organic matter of autochthonous origin characterized by bacterial input usually present in marine basins. The S/C values close to 0.02 found in Salomé-14, L-12 and Cañizara indicate the predominance of higher plants from humic lakes. These results are consistent with the lipid composition analysis. The carbon preference index (CPI), defined as the ratio of the sum of odd *n*-alkanes to even *n*-alkanes in a hydrocarbon distribution, is a useful parameter for deriving information on the origin of organic matter. All samples except Elvira-13 show a slight predominance of odd carbon numbers over the range C_{14}–C_{33} (Table 1), maximizing at C_{25} and C_{27}. This indicates a predominance of higher plant waxes of terrestrial origin (Tissot et al., 1977). The waxy coatings of terrestrial plants contain *n*-alkanes in the range C_{25}–C_{33} with CPIs ranging from 4 to 10 (Brassell et al., 1978). These coal samples have lower CPIs than purely terrestrial plant waxes, which suggests additional contributions from other sources. The low alkane/hopane ratio, calculated as the sum of *n*-alkanes divided by the sum of hopanes quantified in the TIC (Table 1), denotes a significant contribution of bacterial input in all samples. C_{25} alkanes are more dominant in the L-12 and R-3 samples characteristic of subaquatic plants (Nishimoto, 1974; Simoneit et al., 1984). In contrast, Elvira-13 is dominated by C_{14}, C_{16} and C_{18} alkanes, which

Table 1
Elemental analysis on a dry and ash-free basis and indexes for selected coals

Samples	%C	%H	%N	%O	%S	CPI[a] (C_{14}–C_{33})	Alk/hop[b]	Rc[c]
Salomé-14	70	5.5	0.77	17	6.0	1.8	3.8	0.53
Utrillas	35.1	2.6	0.59	46.8	14.9	1.4	2.2	0.61
R-3	66.5	4.9	0.96	18.3	9.2	1.6	0.4	0.65
L-12	70.6	5.4	0.91	16.3	6.8	2.0	1.9	0.76
Elvira-13	63.7	4.7	0.74	20.6	10.2	0.4	0.2	0.65
Cañizara	73.2	5.8	0.69	15	5.0	n.c.	n.c.	n.c.

n.c. not calculated.

[a] Carbon Preference Index (sum of odd over even *n*-alkanes).

[b] Alk/hop ratio calculated as a sum of alkanes over hopanes.

[c] Calculated from methylphenanthrene index (MPI) as: $Rc = 0.6 * MPI + 0.4$.

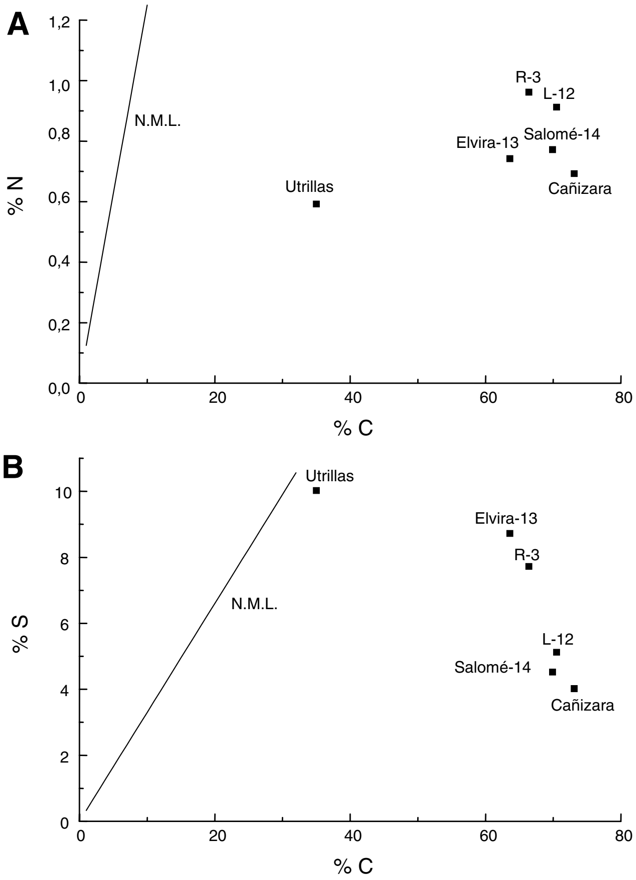

Fig. 2. Relationships N/C (A) and S/C (B) for Utrillas coals.

indicates a significant bacterial input (Grimalt and Albaigés, 1987) consistent with the lowest alkane/hopane relationship (Table 1). Due to the basin's highly sulphate-reducing palaeoenvironment, the ratio of pristane to phytane is not adequate as oxicity index. This character of the palaeoenvironment is also reflected by the significant presence of pyritic sulphur (Querol et al., 1991). This condition, together with high organic-matter content and anoxic conditions, is associated with an abundance of OSC at the bottom of the lake (Sinninghe Damsté et al., 1992). Fig. 3 shows the specific distribution of organosulphur compounds in the leonardite sample. Homologous series of thienylhopanes (*m*/*z* 97), together with 30-(2′-methylenethienyl) and 30-(2′-(5′-methylenethienyl))hopane structures (*m*/*z* 111) related to sulphur incorporation in eubacterial functionalized precursors, are present in the Utrillas coal basin.

A significant amount of diasterenes was found. Fig. 4 shows a typical distribution of diasterenes (*m*/*z* 257). C_{29} isomers of the 24-ethyl-diacholest-13(17)-ene dominate the soluble fraction of Salomé-14 coal, with the maximum peak at 24-ethyl-diacholest-13(17)-ene (20*S*), whereas the maximum peak for Elvira-13 is at 24-ethyl-cholest-13(17)-ene (20*R*). Although the predominance of 24-ethyl-10α-diacholest-13(17)-ene (20*R* and *S*) is associated with siliciclastic acidic environments, other biomarkers in the coal basin, such as diaromatic biomarkers (Gorchs et al., 2003), are more closely related to carbonate-evaporitic environments. We also found small amounts of 4-methyldiacholestenes, which are characteristic of algal dinoflagellates, organisms usually found in marine environments but also detected in freshwater lakes such as Lake Kinneret (Robinson et al., 1986). These unsaturated steroidal distributions indicated that diagenesis was low.

The sterane distribution of the Utrillas coals (not shown) is dominated by the C_{29} ethylcholestane homologue. The predominance of the 5α isomer

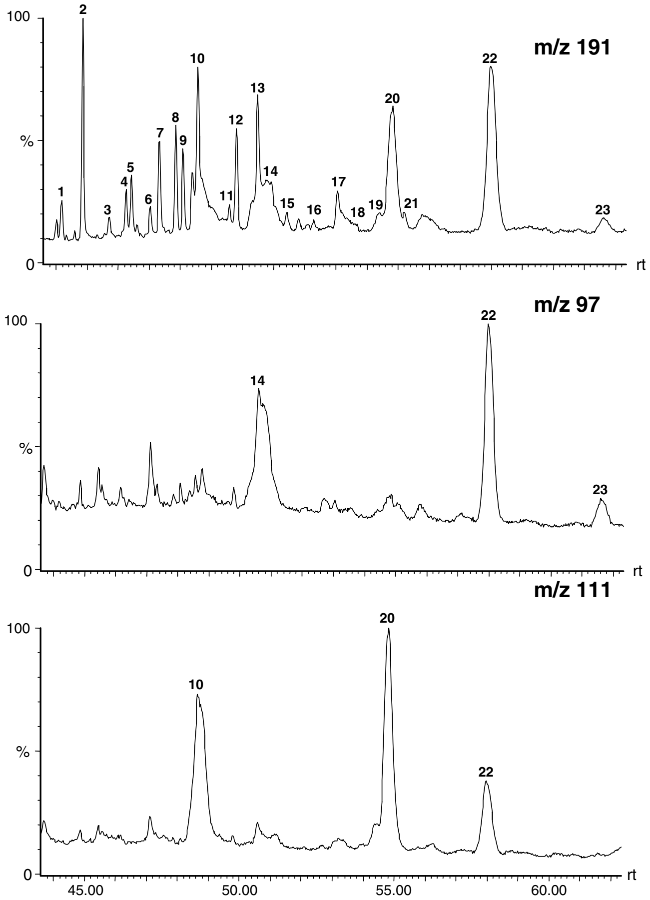

Fig. 3. Mass chromatogram of distribution of hopanoids (*m*/*z* 191), thienylhopanes (*m*/*z* 97) and methylenethienylhopane (*m*/*z* 111) structures. Number assignment corresponds to: (1) 22,29,30-17α(H)-trisnorhopane (C_{27}); (2) 22,29,30-17β(H)-trisnorhopane (C_{27}); (3) 29,30-α,β bisnorhopane (C_{28}); (4) 30-norhop-17(21)-ene (C_{29}); (5) 30-17α,21 β(H) norhopane (C_{29}); (6) hop-17(21)-ene (C_{30}); (7) 30-17β,21 α(H) norhopane (C_{29}); (8) 17α,21β(H) hopane (C_{30}); (9) neohop-13(18)-ene (C_{30}); (10) 17β,21α(H) hopane C_{30} + 30-17β,21β-norhopane (C_{29}); (11) 17α,21β (H)22S-homohopane (C_{31}); (12) 17α,21β(H) 22S-homohopane (C_{31}); (13) 17β,21α-homohopane (C_{31})+17β(H),21β(H) hopane (C_{30}); (14) 30-(2′-methylenethienyl)-17α,21β-hopane (C_{35}); (15) 17α,21β-bishomohopane (C_{32}); (16) 17α,21β-bishomohopane (C_{32}); (17) 30-(2′-(5′-methylenethienyl))-17α,21β-hopane (C_{35}); (18) 17α,21β-trishomohopane (C_{33}); (19) 17β,21α-trishomohopane (C_{33}); (20) 30-(2′-methylenethienyl)-17β,21α-hopane (C_{35}); (21) 17β,21β-bishomohopane (C_{32}); (22) 30-(2′-methylenethienyl)-17β,21β-hopane (C_{35}) + 30-(2′-(5′-methylenethienyl))-17β,21α-hopane (C_{35}); (23) 30-(2′-(5′-methylenethienyl))-17β,21β-hopane (C_{35}).

over 5β in the sterane distribution indicates that the Utrillas coals are in an early stage of diagenesis. The predominance of the C_{29} stereoisomer for steranes and diasterenes suggests a higher plant input (Brassell et al., 1986).

The hopane distribution is similar in all of the coal samples (Fig. 5) except leonardite, in which organosulphur derivatives were also detected (Fig. 3). The maximum of the distribution is at 17α,21β-homohopane. 17α(H)-22,19,30-trisnorhopane and homologues of ββ series were also detected in all samples. The Utrillas coal also contained significant amounts of di- (C,D), tri- (B,C,D) and tetra-aromatic (A,B,C,D) hopanes.

The distribution of sesquiterpanes is dominated by isomers of the bicyclic sesquiterpane 8β(H)-drimane, with lower amounts of *trans*-cadinane and 4β(H)-eudesmane. Sesquiterpanes were most abundant in Elvira-13 and Utrillas. Aromatic sesquiterpanes are characterized by an abundance of cadalene (Fig. 6).

Large amounts of tricyclic diterpenoids were present, in particular retene and simonellite, and lower amounts of dehydroabietane and norsimonellite were present, as shown in Fig. 7. α-Phyllocladane was present in R-3. In this sample, 16α(H)-phyllocladane was clearly predominant, with ratios of (16α/16β > 1; RI ≅ 0), which indicated a vitrinite

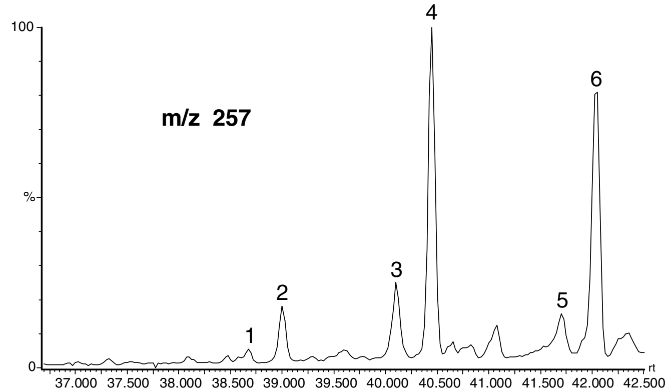

Fig. 4. Mass chromatogram of distribution of diasterenes (*m*/*z* 257). Number assignment corresponds to: (1) 10α(H)-24-methyldiacholest-13(17)-ene (20S); (2) 10β(H)-24-methyldiacholest-13(17)-ene (20S); (3) 10β(H)-24-ethyldiacholest-13(17)-ene (20S) + minor 10α(H)-24-methyldiacholest-13(17)-ene (20R); (4) 10α(H)-24-ethyldiacholest-13(17)-ene (20S) + minor 10β(H)-24-methyldiacholest-13(17)-ene (20R); (5) 10β(H)-24-ethyldiacholest-13(17)-ene (20R); (6) 10α(H)-24-ethyldiacholest-13(17)-ene (20R).

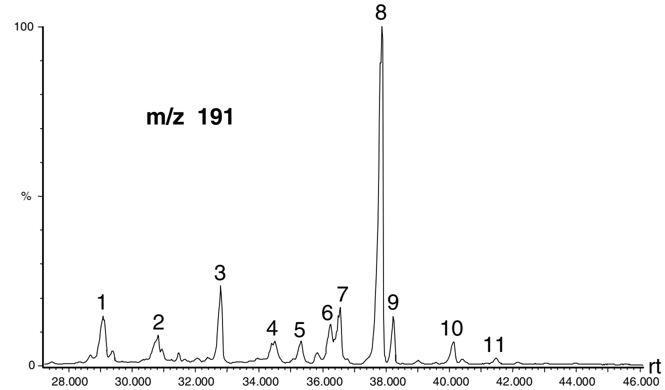

Fig. 5. Mass chromatogram showing the distribution of hopanes (*m*/*z* 191). Number assignment corresponds to: (1) 17α(H)-22,29,30-trisnorhopane; (2) 17β(H)-22,29,30-trisnorhopane; (3) 17α(H),21β(H)-30-norhopane; (4) 17β(H),21α(H)-30-norhopane; (5) 17α(H),21β(H)-hopane; (6) 17β(H),21α(H)-hopane + 17β(H),21β(H)-30-norhopane; (7) 17β(H),21α(H)-hopane; (8) 17α(H),21β(H)-homohopane; (9) 17α(H),21β(H)-homohopane; (10) 17β(H),21β(H)-hopane; (11) 17β(H),21α(H)-homohopane.

reflectance (R_0) of less than 0.6%, according to values given by Querol et al. (1991). Fig. 8 shows isohexylalkylnaphthalenes associated with saturated biomarkers, which are characteristic of higher plants and are formed from natural precursors such as phyllocladane (Ellis et al., 1996).

All of these sesqui- and diterpenoids are associated with an abundance of conifers (Simoneit and Mazurek, 1982), although other origins cannot be ruled out.

As for the depositional palaeoenvironment, a high degree of salinity is estimated for the Utrillas basin by the R_{23} index, defined according to the alkylbenzene homologues as follows: $R_{23} = \frac{2 * C_{23}}{C_{22}+C_{24}}$. R_{23} values were greater than 2 in all samples, which suggests significant salinity. There were also significant amounts of chromanes dominated by the trimethylated homologue, which indicates also significant salinity. This is consistent with the carbonate-evaporitic environment reflected by the even predominance of alkyl and alkenylbenzenes with maximum at C_{18} (Gorchs et al., 2003), ranging from C_{14} to C_{22}. Diaromatic homologous series of phenyl, toluyl, and xylyl alkylbenzenes with linear skeletons from C_{24} to C_{28} related to highly reducing palaeoenvironments were also present.

The thermal maturity of these samples can be estimated from their vitrinite reflectance (Rc) using the aromatic ratio methylphenanthrene index (MPI). The results obtained range from 0.53 to 0.75 (Table 1), which suggests initial diagenesis

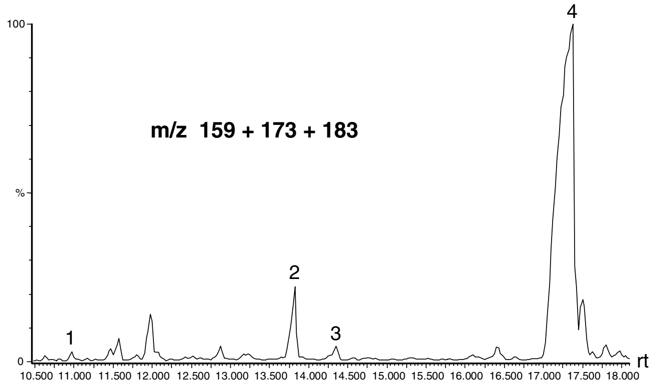

Fig. 6. Mass chromatogram selected for sesquiterpenoids (m/z 159 + 173 + 183). Arabic numbers are: (1) cadinane; (2) calamanene; (3) 5,6,7,8-tetrahydrocadalene; and (4) cadalene.

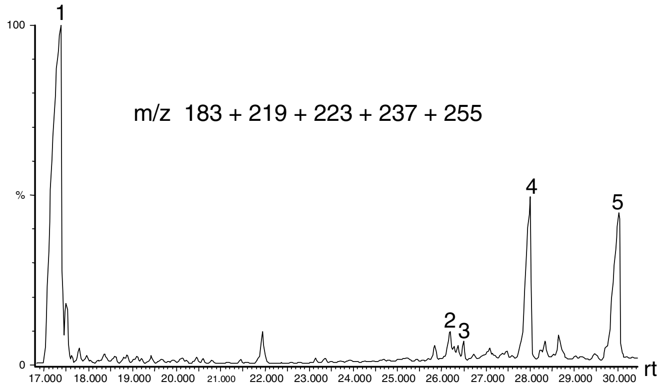

Fig. 7. Mass chromatogram distribution of diterpenoids (m/z 183 + 219 + 223 + 237 + 255). Number assignment corresponds to: (1) cadalene; (2) deshydroabietane; (3) norsimonellite; (4) simonellite; and (5) retene.

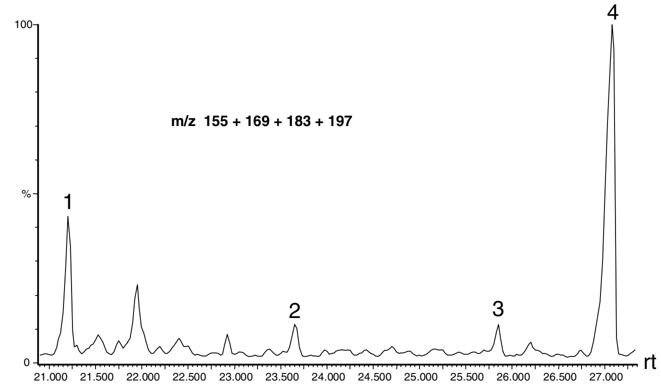

Fig. 8. Mass chromatogram showing a distribution of isohexylalkylnaphthalenes (m/z 155 + 169 + 183 + 197). Arabic numbers are: (1) 1-isohexyl-2-methylnaphthalene; (2) 1-isohexyl-2,6-dimethylnaphthalene; (3) 1-isohexyl-2-methyl-6-ethylnaphthalene; and (4) 1-isohexyl-2-methyl-6-isopropylnaphthalene.

and a similar maturity for these coals, classified as sub-bituminous. Table 2 also shows other values less frequently used to define maturity for the Utrillas representative sample. The ratios obtained are consistent with low-maturity coals, as described above (Querol et al., 1991).

Table 2
Values for different PAH ratios in the Utrillas sample

N/P	0.33
2-MN/1-MN	1.09
$2*(2\text{-MN})/(N+1\text{-MN})$	1.47
$(2\text{-MN})/(1\text{-MN}+2\text{-MN})$	0.52
$4*(2,6\text{-DMN}+2,7\text{-DMN})/(2\text{-MN}+1,2\text{-DMN}+1,3\text{-DMN}+1,4\text{-DMN}+1,5\text{-DMN}+1,6\text{-DMN}+1,7\text{-DMN}+2,3\text{-DMN})$	0.40
$\text{MPI-1}=1.5*(2\text{-MP}+3\text{-MP})/(0.7*P+1\text{-MP}+9\text{-MP})$	0.35
$C/(C+BaA)$	0.35
4-MP/1-MP	1.4
4-MDBT/1-MDBT	2.1
1-MDBT/DBT	0.28
4-MDBT/DBT	0.59
4-MDBT/P	0.12

N (naphthalene); P (phenanthrene); MN (methylnaphthalene); DMN (dimethylnaphthalene); MP (methylphenanthrene); C (chrysene); BaA (benzo[a]anthracene); MDBT (methyldibenzothiophene) and DBT (dibenzothiophene).

5. Conclusions

The organic soluble extract of coals from the Utrillas basin was analysed by GC–MS to characterize their aliphatic, aromatic and organosulphur compounds. The biomarker distribution allowed us to recognize different inputs, assess their depositional palaeoenvironment and determine their degree of maturity.

The abundance of steroids, dominated by C_{29}, indicated the high input of allochthonous higher plants, particularly sesqui- and diterpenoids as well as isohexylalkylnaphthalenes, which are commonly associated with coniferous inputs.

In leonardite, we found homologous series of thienylhopanes related to sulphur incorporation in eubacterial functionalized precursors. Biomarkers characteristic of carbonate-evaporitic palaeodepositional environments were also present in other coals (e.g. chromanes and linear alkylbenzenes).

The abundance of unsaturated biomarkers such as linear alkenylbenzenes and diacholestenes indicates low-maturity coals. Various aromatic ratios such as the methylphenanthrene index suggest diagenesis in the initial stage.

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