



## Note

## Cyclic diaryl ethers in a Late Permian sediment

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**Abstract**

Abundant cyclic diaryl ethers, such as dibenzofuran and its alkyl derivatives are found in solvent extracts and kerogen pyrolysates of a Late Permian organic-rich marl from northern Italy. These organic compounds are distinguishable from biphenyl and its alkyl derivatives by high resolution GC–MS. Bulk geochemical (Rock-Eval) and transmitted/reflected light microscopic analyses indicate that the dominant source of organic matter in the sediment is from partially decomposed land plant debris which has been transported into the marine depositional setting. A likely origin for the cyclic diaryl ether moieties is dehydrated and condensed polysaccharides. Possible sources for the polysaccharides are the organic constituents of land plants, microbes and fungi. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Permian; dibenzofuran; high resolution mass spectrometry; kerogen; pyrolysis; polysaccharides

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**1. Introduction**

Cyclic diaryl ethers, such as dibenzofuran and its alkyl derivatives, have been found in a range of geological samples including crude oils (Williams et al., 1986), aromatic fractions of petroleum (Yew and Mair, 1966), solvent extracts of vitrinite (Halleux and de Greef, 1963; Kessler et al., 1969), coal tar (Borwitzky and Schomburg, 1979) and coal (Hayatsu et al., 1975; Hayatsu et al., 1977; White and Lee, 1980). Other studies have detected dibenzofuran as an abundant or-

ganic component in sediments affected by migrating oxidising brines (Püttmann et al., 1988).

Dibenzofuran moieties have also been detected within the high molecular weight structures of geomacromolecules. Aqueous sodium dichromate oxidation released these units from coals (Hayatsu et al., 1975) and flash pyrolysis has revealed dibenzofuran entities in fossil charcoal from samples representing the Cretaceous-Tertiary boundary (Kruge et al., 1994). Oxidation experiments have established that these units are particularly dominant in bituminous coals where they represent the most abundant heterocyclic compounds (Hayatsu et al., 1977). It is unsurprising therefore that the dibenzofuran unit is an important constituent in structural models for bituminous coal (Heredy and Wender, 1980).

During our investigations of the latest Permian sediments in the Dolomites of northern Italy, an organic-

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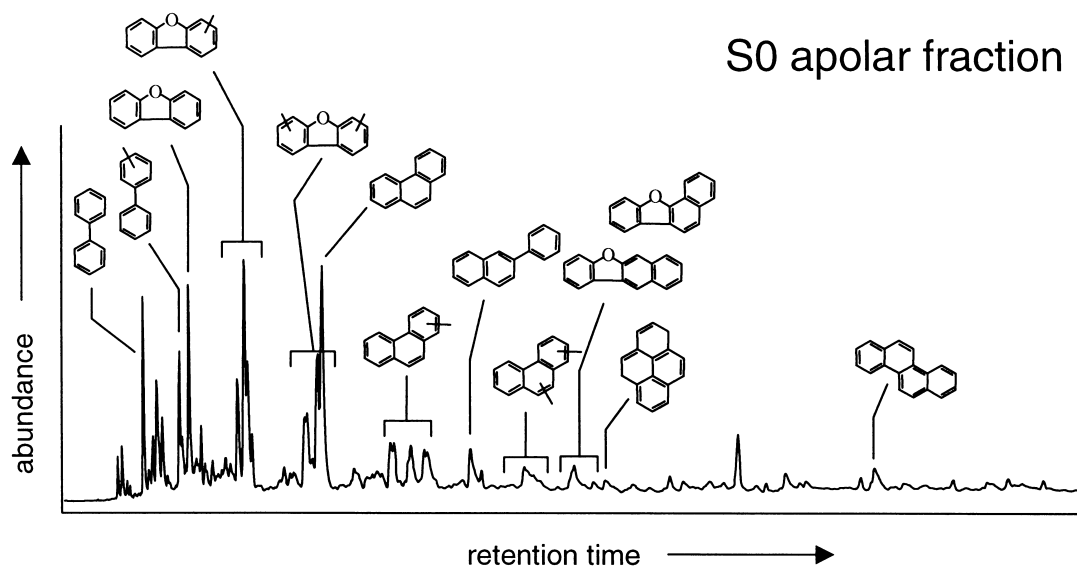


Fig. 1. Gas chromatogram of the apolar fraction of a solvent extract of the Val Badia organic-rich marl (S0).

rich marl was found to contain cyclic diaryl ethers as dominant components of the aromatic compounds present. The discovery of these compounds, in an unusually high abundance, provides us with the opportunity to investigate the origin and geochemical significance of these moieties.

## 2. Experimental

The latest Permian sediments at Val Badia, northern Italy (full location details in Cirilli et al., 1998), consist of the dark fossiliferous limestones and occasional marl layers of the Bellerophon Formation. These sediments were deposited on a shallow shelf in the western Tethys Ocean (Bosellini and Hardie, 1973) and contain the debris of land plants (Visscher and Brugman, 1986). The sample used for this study was the youngest Bellerophon marl (S0) which lies 30 cm below the palynologically-defined Permian-Triassic boundary (Cirilli et al., 1998).

The S0 marl (145.2 g) was Soxhlet extracted (250 ml dichloromethane/methanol, 97:3) and separated into maltene and asphaltene fractions by precipitation ( $\times 7$ ) in a 40-fold excess of heptane. The maltenes were used to obtain apolar and aromatic (A3) organic fractions as in Kohnen et al. (1990).

Compound detection and identification was performed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) using Carlo Erba 8130 and Hewlett Packard 5890 gas chromatographs respectively. GC and GC–MS conditions were

as in Koopmans et al. (1995) except that all temperature programs began at 70°C. The S0 aromatic fraction was analysed further by high resolution GC–MS at 70 eV with a mass range  $m/z$  50–250 and a cycle time of 0.7 s (resolution 6500).

To isolate the kerogen from its mineral matrix, the S0 marl (61.2 g) was subjected to cyclic treatments with hydrofluoric (HF) and hydrochloric (HCl) acids. In preparation for pyrolysis, the HF/HCl residue was exhaustively extracted with methanol, dichloromethane/hexane (1:1) and hexane. The kerogen and asphaltene fractions were analysed by flash pyrolysis (Py–GC and Py–GC–MS) as in Koopmans et al. (1995). Rock-Eval pyrolysis was used to ascertain the temperature of maximum hydrocarbon generation ( $T_{max}$ ) to indicate the degree of thermal maturity of the kerogen and to determine the hydrogen (HI) and oxygen (OI) indices to chemically characterise the organic matter. Reflected and transmitted light microscopy were used to obtain vitrinite reflectance measurements to establish the thermal maturity of the S0 kerogen and to identify the organic components present.

## 3. Results and discussion

Gas chromatography of the apolar organic matter, obtained from a Soxhlet extract of the S0 marl, reveals a distribution dominated by peaks reflecting cyclic diaryl ethers and polycyclic aromatic hydrocarbons (PAHs) (Fig. 1). To further isolate these components

Table 1

Bulk properties and sample characteristics of the Val Badia organic-rich marl (S0)

TOC <sup>a</sup> (wt%)	% R <sub>o</sub> <sup>b</sup>	T <sub>max</sub> <sup>c</sup>	HI <sup>d</sup>	OI <sup>e</sup>	EOM <sup>f</sup> (wt%)	Maltenes <sup>g</sup> (wt%)	Asphaltenes <sup>h</sup> (wt%)	Apolar <sup>i</sup> (wt%)	Polar <sup>j</sup> (wt%)	A3 <sup>k</sup> (wt%)
2.56	0.62	439	145	139	0.45	49	51	17	32	8.5

<sup>a</sup> TOC = total organic matter.<sup>b</sup> % R<sub>o</sub> = vitrinite reflectance in oil (%).<sup>c</sup> T<sub>max</sub> = temperature of maximum hydrocarbon evolution.<sup>d</sup> HI = hydrogen index.<sup>e</sup> OI = oxygen index.<sup>f</sup> EOM = extractable organic matter as a percentage of the whole rock.<sup>g</sup> Maltene fraction as weight percentage of EOM.<sup>h</sup> Asphaltene fraction as weight percentage of EOM.<sup>i</sup> Apolar fraction as weight percentage of EOM.<sup>j</sup> Polar fraction as weight percentage of EOM.<sup>k</sup> Aromatic (A3) fraction as weight percentage of EOM.

an aromatic fraction was separated from the apolar organic matter by thin layer chromatography. This aromatic fraction makes up ca. 8% of the total extract (Table 1) indicating that the cyclic diaryl ethers and

PAHs are major components of the extractable organic matter in this sample.

To confirm the identity of the cyclic diaryl ethers, the aromatic fraction was subjected to high resolution

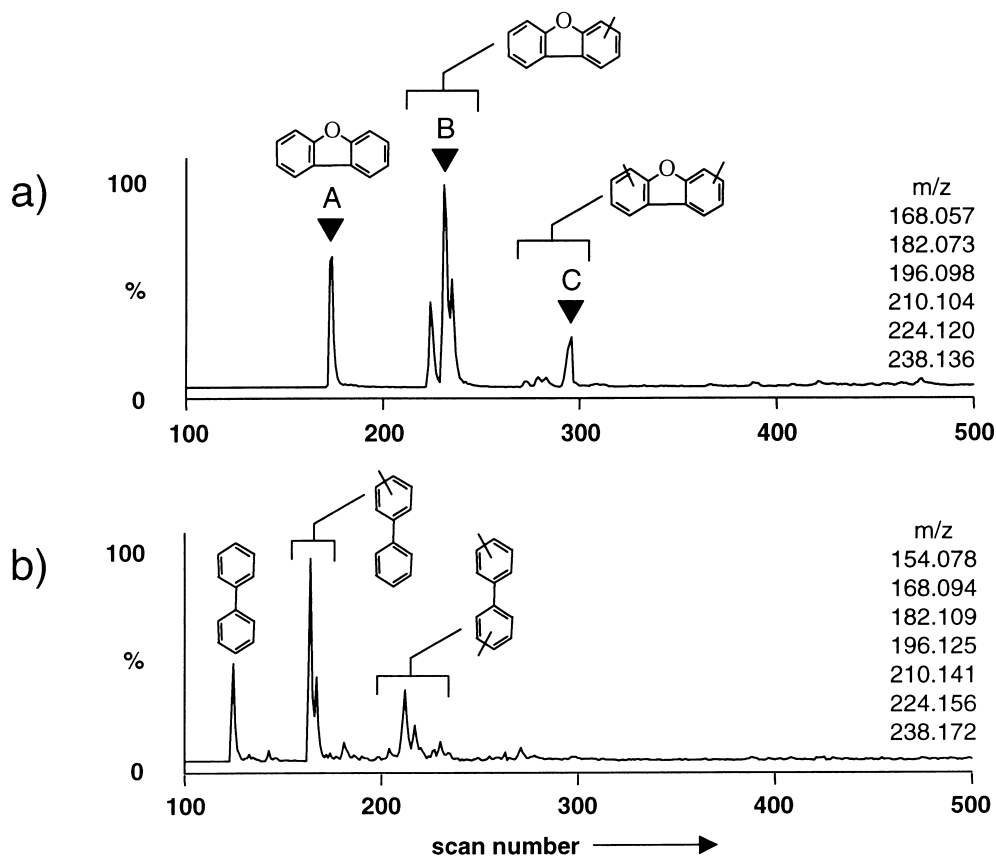


Fig. 2. Summed mass chromatograms representing (a) dibenzofuran and its alkyl derivatives and (b) biphenyl and its alkyl derivatives in the aromatic (A3) fraction of the Val Badia organic-rich marl (S0).

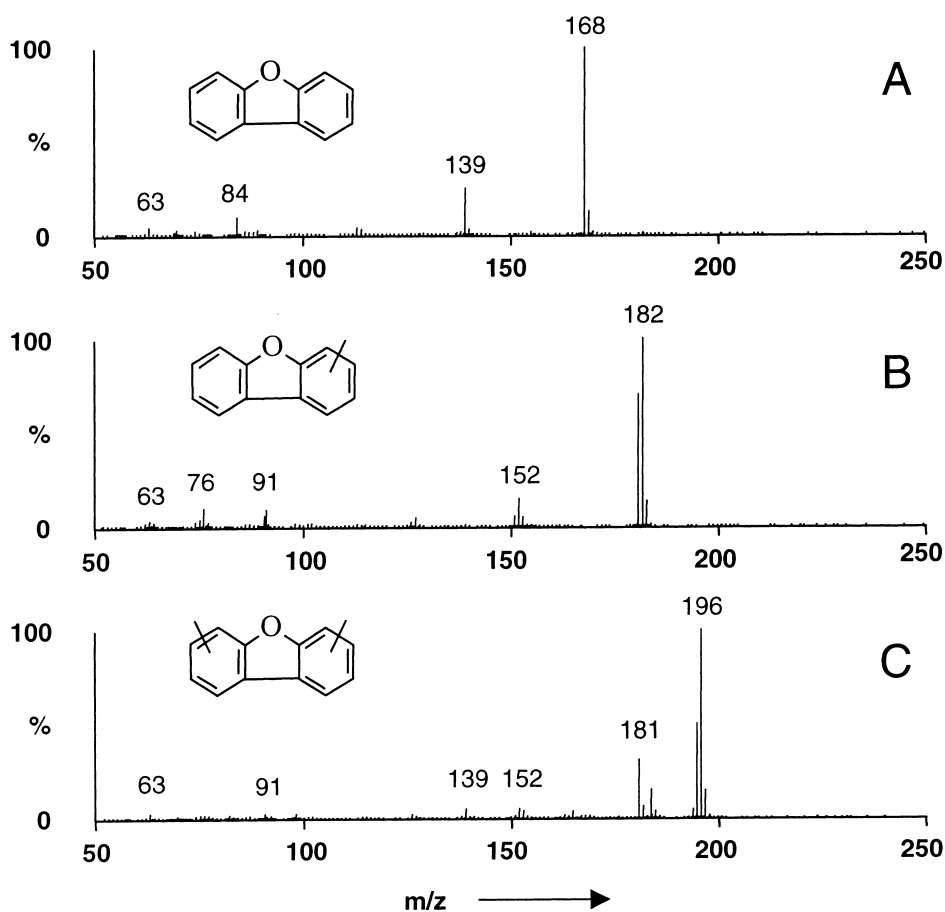


Fig. 3. Mass spectra corresponding to the retention times of compounds A to C in Fig. 2(a). The exact positions of the methyl substituents are unknown.

GC–MS. The mass chromatogram in Fig. 2(a) reveals the internal distribution pattern of dibenzofuran and its  $C_1$  to  $C_2$  derivatives. Masses corresponding to the molecular ions of the  $C_3$  to  $C_5$  derivatives are also included but these compounds do not appear to be present in significant amounts. The mass chromatogram in Fig. 2(b) reveals the internal distribution pattern of biphenyl and its methyl derivatives. These results confirm the identity of the cyclic diaryl ethers and illustrate the ability of the high resolution GC–MS method to distinguish between cyclic diaryl ethers and biphenyls based on their different masses.

Fig. 3 shows the mass spectra of the GC–MS scans which correspond to the retention times of the representative peaks in the mass chromatogram of dibenzofuran and its  $C_1$  to  $C_2$  derivatives. Spectrum A is that of dibenzofuran and shows an intense molecular ion at  $m/z$  168 and a fragment ion at  $m/z$  139. This fragment ion can be rationalised as the result of cleavage of the carbon–oxygen bond followed by the loss of  $HCO^+$

( $m/z$  29). Mass spectra B and C represent the  $C_1$  and  $C_2$  derivatives, respectively.

To investigate the presence of cyclic diaryl ethers in the higher molecular weight organic fractions in the S0 marl, the kerogen and asphaltene were subjected to Py–GC and Py–GC–MS. Fig. 4(a) indicates that the S0 kerogen is a potential source of cyclic diaryl ethers in the sediment. The S0 asphaltene fraction (Fig. 4b) also contains cyclic diaryl ether moieties. Vitrinite reflectance measurements and the  $T_{max}$  value (Table 1) for the organic matter in the S0 marl reveal that it has a maturity which places it within the main zone of hydrocarbon generation or ‘oil window’ (Espitalié et al., 1986). Hence, these results indicate that the kerogen is thermally decomposing to release cyclic diaryl ether moieties into the intermediate molecular weight asphaltene and the lower molecular weight free organic matter.

The maturity of the sample may also have a bearing on the abundance of cyclic diaryl ethers in the sedi-

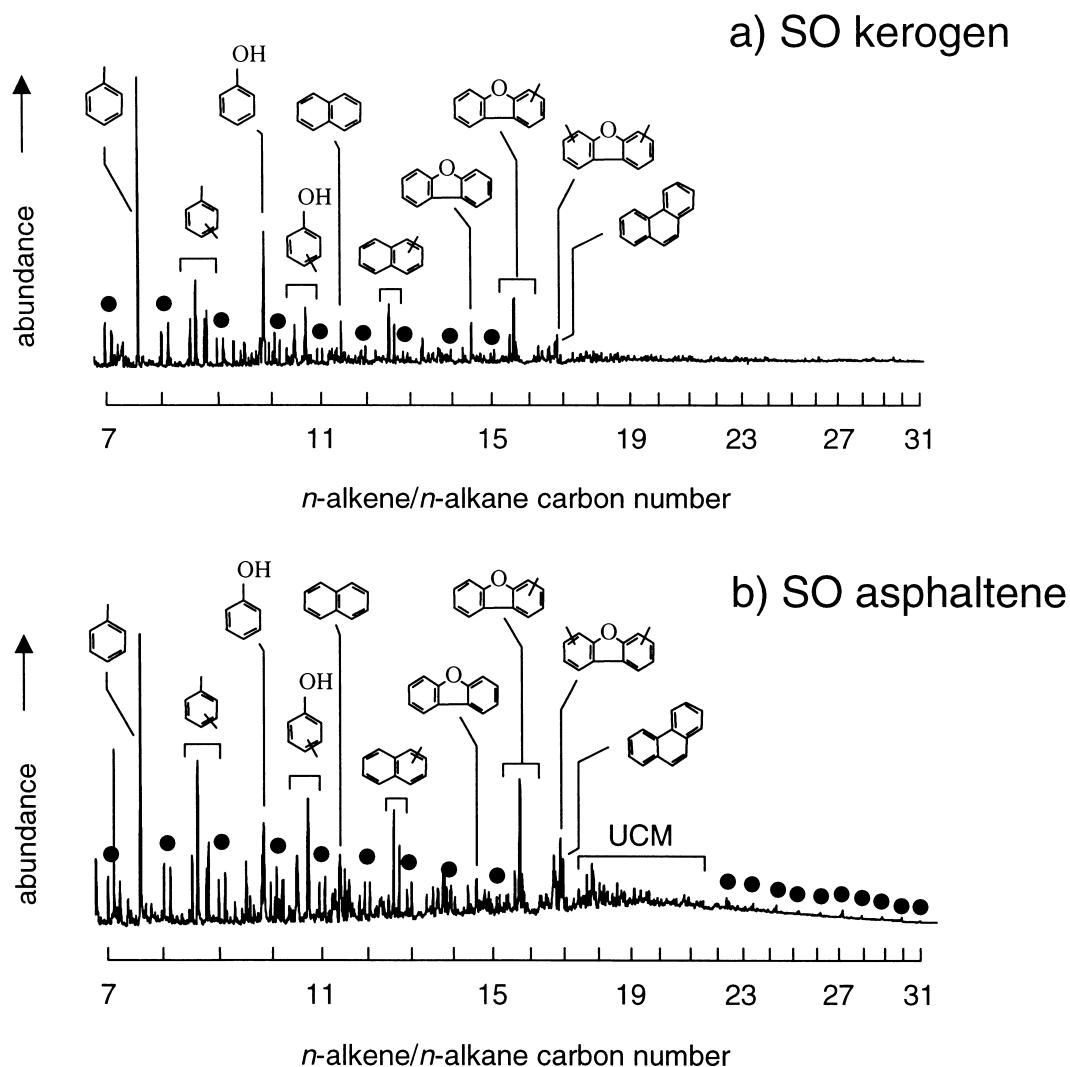


Fig. 4. Gas chromatograms of flash pyrolysates (Cu-temp 610°C) of (a) asphaltene and (b) kerogen from the Val Badia organic-rich marl (S0). *N*-alkene/*n*-alkane doublets are indicated by filled circles and carbon number retention times.

ment. These compounds are stable to thermal and hydrous stress to 250°C (Siskin and Kitritzky, 1991). Furthermore, they become more abundant in bituminous coals when compared to less mature lignites or more mature anthracites (Hayatsu et al., 1977). It is interesting to note, therefore, that the organic matter in the S0 marl is at a similar stage of maturity to that in bituminous coals. It is conceivable that the concentrations of cyclic diaryl ethers in the S0 marl and in bituminous coals are a result of the selective enhancement of these moieties during maturation due to their resistance to thermal and aqueous stress. In organic matter of lower maturities, less stable compounds are more abundant and dilute the cyclic diaryl ethers. In

more mature organic material of this type, the ether bonds are broken to produce macromolecules dominated by aromatic hydrocarbons. Hence, a level of maturity which corresponds to that seen in bituminous coals may be necessary to produce an abundance of cyclic diaryl ether moieties.

To determine the origin of the cyclic diaryl ethers, the S0 kerogen was analysed by transmitted and reflected light microscopy. These investigations revealed that the kerogen consists of an amorphous humic cement with occasional woody fibres and particles of vitrinite and inertinite. These observations suggest a major input from land plants debris and are in agreement with the results from the bulk geochem-

ical analyses in Table 1 which assign the organic matter as type-III kerogen (Espitalié et al., 1977). Furthermore, these results are consistent with previous work which indicates that the debris of land plants becomes the major source of organic material at the top of the Bellerophon Formation in the southern Alps (Visscher and Brugman, 1986). The amorphous nature of much of the organic matter suggest that the land plant debris has decomposed on land prior to its transport into the marine depositional environment (e.g. Durand and Espitalié, 1976). The particular degradational and depositional history of the S0 organic matter may be partly responsible for the unusual dominance of cyclic diaryl ethers in this sample.

The furan ring of the cyclic diaryl ethers in the S0 organic matter may originate from polysaccharides. Py–GC–MS has revealed that furan derivatives in decomposing vegetation from Irish peat deposits originate from the dehydration of glucose subunits (van der Heijden, 1994). Similar transformations may have been significant in Late Permian accumulations of decomposing terrestrial vegetation. Following the dehydration of polysaccharides, the furan rings contain side chains with reactive carbonyl and hydroxyl groups. These functional groups are available for thermally-driven aldol or retro aldol type reactions followed by decarbonylation steps. Diels–Alder type reactions may also occur. These reactions can lead to the condensation of furans into cyclic diaryl ethers (Pastorova et al., 1994). Such condensation reactions may have occurred during the maturation of the partially decomposed land plant debris following its redeposition and burial in the Tethys Ocean.

The exact origin of polysaccharides, prior to their diagenetic transformation to cyclic diaryl ethers and other moieties, is difficult to identify, as polysaccharides are widely distributed in organisms where they have both structural and energy storage roles. Nonetheless, as the sediments at Val Badia are dominated by land plant debris, it is likely that much of the original polysaccharide-containing material came from terrestrial vegetation. However, during the decomposition of the organic matter, microbial or fungal action may have also contributed significant amounts of new polysaccharides.

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#### References

- Borwitzky, H., Schomburg, G., 1979. Separation and identification of polynuclear aromatic compounds in coal tar by using glass capillary chromatography including combined gas chromatography–mass spectrometry. *Journal of Chromatography* 170, 99–124.
- Bosellini, A., Hardie, A.L., 1973. Depositional theme of a marginal evaporite. *Sedimentology* 20, 5–27.
- Cirilli, S., Pirini Radrizzani, C., Ponton, M., Radrizzani, S., 1998. Stratigraphical and palaeoenvironmental analysis of the Permian-Triassic transition in the Badia Valley (Southern Alps, Italy). *Palaeogeography, Palaeoclimatology, Palaeoecology* 138, 85–113.
- Durand, B., Espitalié, J., 1976. Geochemical studies on the organic matter from the Douala Basin (Cameroon). II. Evolution of kerogen. *Geochimica et Cosmochimica Acta* 40, 801–808.
- Espitalié, J., Marquis, F., Barsony, I., 1986. Use of  $T_{max}$  as a maturation index for different types of organic matter. Comparison with vitrinite reflectance. In: Burrus, J. (Ed.), *Thermal modelling in sedimentary basins* Editions Technip, Paris, pp. 475–496.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthod rapide de caractérisation des roches mères de leur potentiel pétrolier et de leur degré d'évolution. *Revue de l'Institut Français du Pétrole* 32, 23–42.
- Halleux, A., de Greef, H., 1963. Extraction of a vitrinite and chemical analysis of the fractions. *Fuel* 42, 185–202.
- Hayatsu, R., Scott, R.G., Moore, L.P., Studier, M.H., 1975. Aromatic units in coal. *Science* 257, 378–381.
- Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P., Studier, M.H., 1977. Oxidative degradation studies of coal and solvent refined coal. *Preprints of the American Chemical Society. Division of Fuel* 22 (5), 156–168.
- van der Heijden, E., 1994. A combined anatomical and pyrolysis mass spectrometric study of peatified plant tissues. Ph.D. thesis, University of Amsterdam, The Netherlands.
- Heredy, L.A., Wender, I., 1980. Model structure for bituminous coal. *Preprints of the American Chemical Society. Division of Fuel* 25, 38–45.
- Kessler, T., Raymond, R., Sharkey Jr., A.G., 1969. Composition of pyridine extracts from reduced and untreated coals as determined by high resolution mass spectrometry. *Fuel* 48, 179–186.
- Kohnen, M.E.L., Sinnighe Damsté, J.S., Rijpstra, W.I.C., de Leeuw, J.W., 1990. Alkylthiophenes as sensitive indicators of palaeoenvironmental changes: a study of a Cretaceous oil shale from Jordan. In: Orr, W.L., White, C.M. (Eds.), *Geochemistry of sulfur in fossil fuels* ACS symposium

- series, 249 American Chemical Society, Washington, pp. 444–485.
- Koopmans, M.P., Sinninghe Damsté, J.S., Lewan, M.D., de Leeuw, J.W., 1995. Thermal stability of thiophene biomarkers as studied by hydrous pyrolysis. *Organic Geochemistry* 23, 583–596.
- Kruege, M.A., Stankiewicz, B.A., Crelling, J.C., Montanari, A., Bensley, D.F., 1994. Fossil charcoal in Cretaceous-Tertiary boundary strata: evidence for catastrophic fire-storm and megawave. *Geochimica et Cosmochimica Acta* 58, 1393–1397.
- Pastorova, I., Botto, R.E., Arisz, W., Boon, J., 1994. Cellulose char structure: a combined analytical Py–GC–MS, FTIR and NMR study. *Carbohydrate Research* 262, 27–47.
- Püttmann, W., Hagemann, H.W., Merz, C., Speczik, S., 1988. Influence of organic material on mineralization processes in the Permian Kupferschiefer Formation, Poland. Mattavelli, L., Novelli, L. (Eds.) *Advances in Organic Geochemistry* 1987 (special issue). *Organic Geochemistry* 13, 357–363.
- Siskin, M., Kitritzky, A.R., 1991. Reactivity of organic compounds in hot water: geochemical and technological implications. *Science* 254, 231–237.
- Visscher, H., Brugman, W.A., 1986. The Permian-Triassic boundary in the southern Alps: a palynological approach. *Società Geologica Italiana, Memoire* 34, 121–128.
- White, C.M., Lee, M.L., 1980. Identification and geochemical significance of some aromatic components of coal. *Geochimica et Cosmochimica Acta* 44, 1825–1832.
- Williams, J.A., Bjørøy, M., Dolcater, D.L., Winters, J.C., 1986. Biodegradation in South Texas Eocene oils—Effects on aromatics and biomarkers. Leythaeuser, D., Rullkötter, J. (Eds.) *Advances in Organic Geochemistry* 1985 (special issue). *Organic Geochemistry* 10, 451–461.
- Yew, F.F.H., Mair, B.J., 1966. Isolation and identification of C<sub>13</sub> to C<sub>17</sub> alkylnaphthalenes, alkylbiphenyls and alkyldibenzofurans from the 275 to 305°C dinuclear aromatic fraction of petroleum. *Analytical Chemistry* 38, 231–237.