

## TERRESTRIAL MOLECULAR FOSSILS IN A TYPICAL LACUSTRINE TYPE I BOTRYOCOCCUS-RICH OIL SHALE FROM GANDARELA BASIN, BRAZIL.<sup>1</sup>

Araujo, C.V.\*; Loureiro, M.R.B.\*\*; Barbanti, S.M.B.\*;  
Gonçalves, F.T.T.\*; Miranda, A.C.M.L.\*\* & Cardoso, J.N.\*\*

\* PETROBRAS/CENPES, Cidade Universitária, Quadra 7, Rio de Janeiro, Brasil, 21949-900; \*\* UFRJ, Instituto de Química, Bloco A, Cidade Universitária, Rio de Janeiro, Brasil, 21949-900.

**ABSTRACT** - An oil shale sample from the Gandarela Basin, Minas Gerais State, Brazil, was studied by organic petrography and geochemistry techniques. The sample has a TOC content of 30% and a hydrogen index of 887 mgHC/gTOC. Microscopic examination revealed dominance of orange fluorescent amorphous kerogen and yellow fluorescent *Botryococcus*-type alginite. Microscopic features together with the high hydrogen index point to a type I organic matter. The contribution of *B. braunii* is supported by the release of homologous series of *n*-alkanes and alkylbenzenes when the kerogen is submitted to hydrous pyrolysis. GC-MS and GC-MS-MS analyses of the aliphatic fraction isolated from the organic extract showed the absence of biomarkers derived from *Botryococcus* type-algae, the presence of *n*-alkanes from C<sub>15</sub> up to C<sub>35</sub>, with odd over even predominance maximizing at C<sub>31</sub>, a high relative abundance of *des*-A-lupane and the occurrence of a series of *des*-A-ferrenes. In the aromatic fraction, hydrocarbons with oleanane, lupane and arborane/fernane skeletons were identified. So, the biomarker fingerprint pointed to a dominant higher plant input which is unexpected for a sample mostly composed of fluorescent amorphous kerogen and remains of *Botryococcus*-type algae. The results show that the combination of visual, bulk and pyrolytic analyses of the kerogen with free lipids data is essential for the complete characterization of the depositional environment.

**RESUMO** - Uma amostra de folhelho negro da Bacia de Gandarela, localizada no Estado de Minas Gerais, Brasil, foi estudada utilizando-se técnicas de petrografia e geoquímica orgânica. Os resultados obtidos revelaram um teor de carbono orgânico de 30% e alto índice de hidrogênio, 887 mg HC/g COT. Ao microscópio foi observado o predomínio de matéria orgânica amorfa com fluorescência laranja e alginite do tipo *Botryococcus* com fluorescência amarela. Estas características permitiram classificar a matéria orgânica como sendo do tipo I. A contribuição de *B. braunii* foi confirmada pela liberação de séries homólogas de alcanos e alquilbenzenos ao se submeter a amostra à hidropirólise. A análise por CG-EM e CG-EM-EM da fração de hidrocarbonetos alifáticos isolada do extrato orgânico, por sua vez, mostrou a ausência de botriococano e outros biomarcadores típicos de algas do tipo *Botryococcus*; presença de *n*-alcanos de C<sub>15</sub> até C<sub>35</sub>, com predominância dos homólogos ímpares e com máximo em C<sub>31</sub>; alta abundância relativa de *des*-A-lupano e a presença de uma série de *des*-A-ferrenes. Na fração de hidrocarbonetos aromáticos foram identificados compostos com esqueletos de oleanano, lupano e arborano/fernano. As características apresentadas pelos biomarcadores são, portanto, típicas da contribuição de vegetais superiores, o que não seria esperado para uma amostra composta, predominantemente, por matéria orgânica amorfa com fluorescência e algas do tipo *Botryococcus*. Os resultados mostram que a combinação de métodos de análise do querogênio com a distribuição dos lipídeos livres é essencial para a descrição do ambiente deposicional.

**KEY WORDS** - oil shale organic, petrography, organic geochemistry, *Botryococcus*, kerogen, *hydrous pyrolysis*.

### INTRODUCTION

The recognition of biological markers in ancient and recent sediments provides valuable information regarding the origin of the deposited organic matter (Seifert & Moldowan, 1981). For instance, the contribution of bacteria is often indicated by the presence of hopanoid compounds (Ourisson *et al.*, 1979), whereas the occurrence of tetracyclics and pentacyclics with oleanane, ursane

and lupane skeletons is taken as an indication of angiosperm-derived organic matter (Stout, 1992).

*Botryococcane* represents a particularly diagnostic biomarker for the assessment of paleoenvironments. This C<sub>34</sub> isoprenoidal alkane is considered to be derived from *botryococcane*, a compound known to exist only in *Botryococcus braunii*, which is widely distributed in freshwater lakes. Thus, the identification of *botryococcane* in oils and sediments indicates the contribution of *B. braunii* to the depositional environment. However, despite the quite widespread presence of *Botryococcus* remains in type I kerogen, this

<sup>1</sup> Presented at the 5th Latin-American Congress of Organic Geochemistry (Cancun, Mexico, 1996)

specific biomarker was only detected in a few extracts and oils, such as Sumatran oils (Moldowan & Seifert, 1980; Seifert & Moldowan, 1981), Australian coastal bitumen (McKirdy *et al.*, 1986) and Maoming oil shale (Brassell *et al.*, 1986). This observation may be explained, at least in part, by the fact that of the three modern chemical races of *B. braunii* (A, B and L; for a review see Metzger *et al.*, 1992), only race B produces botryococcene. Therefore, the absence of botryococcene cannot be interpreted as proof of the lack of a *Botryococcus* contribution to the biomass. Derenne *et al.* (1988), for example, demonstrated the lack of botryococcene in bitumens from several torbanites (kerogen-rich oil shales mainly composed of an algal residue similar to an extant *B. braunii*).

The Tertiary Gandarela Basin oil shale is a good example of a *Botryococcus*-rich sediment in Brazil. In order to reach a better understanding of the relationships between bulk kerogen features and biomarker distributions in this kind of sediments, an outcrop sample from this basin was investigated through organic petrography, Rock-Eval pyrolysis and hydrous pyrolysis of the kerogen, and GC-MS and GC-MS-MS analyses of the bitumen.

The Gandarela Basin, with an area of 9 km<sup>2</sup>, is located in the Quadrilátero Ferrífero region, southeastern Brazil (Fig. 1). The sedimentary column comprises a sequence of lacustrine and fluvial-deltaic sandstones, siltstones, claystones and lignites (Fig. 2), ranging in age from late Eocene to early Miocene (Pinto & Regali, 1990). The origin of the basin is related to extensional stresses, which have controlled both the tectonic framework and sediment deposition (Maizatto & Castro, 1993). Recent palynological studies indicate a transition from tropical humid climate during the late Eocene, to semi-arid conditions in the Oligocene/Miocene (Maizatto, 1997).

## EXPERIMENTAL

### Preparation of Samples

The oil shale sample was demineralized with 50% HCl and analysed for TOC content using a WR-12 LECO apparatus. Pyrolysis analysis was performed using the Rock-Eval method (Espitalié *et al.*, 1985).

For visual kerogen investigation, one slice of the sample was polished to be analysed by fluorescence microscopy. A slice of the same sample was crushed and treated with HCl and HF and mounted on strewn slides to be analysed in both transmitted white light and fluorescence

microscopy. The analyses were performed using a Zeiss standard microscope equipped with a high pressure mercury lamp (HBO 100W). The strewn slide was qualitatively analysed at 160X magnification. A point counting was carried out in the polished section under blue light excitation and for this purpose a line perpendicular to the stratification was scanned with an average stepwidth of 1mm using a 40X magnification oil objective. Photomicrographs were taken using an image analysis system coupled to a Zeiss Axiophot Microscope, model MPM 400. Reflected light and fluorescence images were obtained with a 50X magnification objective and oil immersion. For fluorescence analyses an excitation filter G 395-440 and a high pressure mercury lamp HBO 100W were used.

### Extraction, Fractionation and Analysis of the Bitumen

The crushed sample was extracted in a Soxhlet apparatus (CH<sub>2</sub>Cl<sub>2</sub>, 48h) and the aliphatic and aromatic hydrocarbons were isolated from the extract by medium pressure liquid chromatography (MPLC; hexane as eluent). Gas chromatography-mass spectrometry (GC-MS) and GC-MS-MS biomarker analyses were carried out using Hewlett-Packard 6890 series and TSQ-70 Finnigan MAT systems. GC conditions: DB-5 fused silica capillary column, 60m, 0.25 mm film thickness; injector temperature (splitless injection), 300°C; temperature program: 70°C (2 min) to 150°C at 20°C/min, 150°C to 320°C at 5°C/min and isothermal for 20 min. GC-MS-MS parent mode, monitoring the transitions m/z 448 -> 154 and m/z 448 -> 110, was used in the search of botryococcene.

### Hydrous Pyrolysis of the Kerogen

Hydrous pyrolysis was carried out by sealing 3g of finely ground (80 mesh), solvent extracted shale and 2ml of distilled water in an a glass tube purged with nitrogen for 20min. The tube was placed inside a reactor with 2ml of water and the reactor was placed in an oven at 330°C for 72h. After heating, the tube was cooled and opened. The remaining water was evaporated and the reaction products were isolated by extraction with dichloromethane.

### Identification of Pyrolysis Products

The separation of saturate and aromatic hydrocarbons of the pyrolysate was carried out by medium pressure liquid chromatography using *n*-hexane as a solvent. The saturate fraction was

analysed by GC and both saturate and aromatic fractions were analysed by GC-MS full scan (m/z 40-500) and selective ion monitoring modes using Hewlett-Packard 6890 gas chromatograph-mass spectrometer system. GC conditions : DB-5 fused silica capillary column, 60m, 0.25mm film thickness; injector temperature (splitless injection), 300°C; interface temperature 310°C; carrier gas helium; temperature program: 55°C (2min) to 150°C at 20°C/min, 150°C to 320°C at 1.5°C/min and isothermal for 25 min.

## RESULTS

### Bulk Analyses and Organic Petrography

The Gandarela oil shale sample is rich in organic matter, presenting an average TOC content of 30% and high S<sub>1</sub> and S<sub>2</sub> peaks from Rock Eval pyrolysis (20 and 266 mg HC/g rock, respectively). The high hydrogen index (887 mg HC/g TOC) along with the very low oxygen index (41 mg CO<sub>2</sub>/g TOC) indicate a type I kerogen.

The microscopy analyses of the organic matter under blue-light excitation showed the predominance of orange-fluorescing amorphous kerogen (74%) associated with bright yellow-fluorescing telalginite (17%, Table 1; Plate 1a). This is typical of *Botryococcus* algae which is often related to lacustrine freshwater depositional environments (Tyson, 1995). The algal colonies present an average size of 20µm (Plates 1a,b). A total of 1445 points were counted and the results are presented in Table 1.

Some particles of the amorphous kerogen show a distinctive lamellar shape (in strewn slides of demineralized kerogen preparation) characteristic of lamalginite (Hutton, 1990). Amorphous kerogen and lamalginite present a weaker fluorescence than telalginite. This feature was also observed by Hutton (1990) in low-rank Australian oil shales, where lamalginite and telalginite occurred in the same samples. Despite the strong fluorescence, telalginite (*Botryococcus* colonies; Plates 1a,b) tends to present a poorly preserved structure,

suggesting microbial activity in the depositional setting. Sporinite, presenting a yellow fluorescence, is less abundant than alginite (Plate 1c). Non-fluorescing grains, comprising vitrinite, inertinite and minerals, reach up to 9% of the total kerogen. Reflected light observation revealed the occurrence of abundant pyrite and rare vitrinite phytoclasts (Plate 1d).

In terms of thermal evolution, both a spore coloration index (SCI) of 2.0 and a Tmax of 427°C from pyrolysis, point to a very incipient thermal evolution stage.

### Bitumen Analysis

Liquid chromatography of the Gandarela bitumen showed a dominance of NSO compounds (81%) over aliphatic (13%) and aromatic (6%) hydrocarbons.

The GC-MS total ion current traces of the aliphatic and aromatic fractions are reproduced in Figs. 3 and 4, respectively. Identifications were usually based on comparison of mass spectra with published data and relative GC retention times. The structures recognized are presented in the Appendix. In the case of compounds I and II, structures were confirmed by GC co-injection with the standards.

The study of the aliphatic fraction revealed a low relative abundance of isoprenoids and the presence of *n*-alkanes from C<sub>15</sub> up to C<sub>35</sub>, with a predominance of odd-numbered homologues around C<sub>31</sub>, usually considered to derive from epicuticular waxes of higher plants (Tissot & Welte, 1984).

As already pointed, the microscopic examination has shown a high abundance of *Botryococcus*-type alginite in the Gandarela kerogen. *B. braunii* algae biosynthesize large amounts of hydrocarbons whose structures depend on the race: the A race produces *n*-alkadienes and trienes, the B race, botryococenes and the L race, a single C<sub>40</sub> isoprenoidal compound, lycopadiene (Metzger *et al.*, 1992). A careful search for biomarkers derived from such algae was

Fluorescing amorphous O.M. (including lamalginite)	<i>Botryococcus algae</i> (telalginite)	Non-fluorescing particles *	Total
1064	254	127	1445
74%	17%	9%	100%

**Table 1.** Data from point-counting, under blue-light excitation, of a line perpendicular to stratification on the polished section. \*vitrinite+inertinite+minerals

undertaken in the Gandarela aliphatic hydrocarbon concentrate but no botryococcane or compounds structurally related to alkadienes/trienes and lycopadiene were in fact detected.

Steranes were detected in minute amounts, observation that may be explained by the fact that sterols are insignificant constituents of *B. braunii* (McKirby *et al.*, 1986).

The aromatic fraction is characterized by the presence of mono-, di- and tri-aromatic polycyclic hydrocarbons. The geochemical significance of these biomarkers, as well as the tetra- and pentacyclic compounds identified in the aliphatic concentrate, is discussed below.

#### ***Lupane and Oleanane Derivatives***

Among the cyclic aliphatic hydrocarbons (Fig. 3), one of the most abundant components - compound 1 - was identified as *des*-A-lupane (Corbet, 1980).

In the fraction of aromatic hydrocarbons (Fig. 4), the lupane family is represented by compounds II and IV, corresponding to mono- and tri-aromatic pentacyclic structures, respectively (Saptorahardjo, 1985 and Chaffee & Fooks, 1988).

The tetracyclic hydrocarbon I and the pentacyclic III, both oleanane-derived (Spyckerelle, 1975; Chaffee and Fooks, 1988), have also been characterized in the Gandarela aromatic fraction.

The above mentioned structures are thought to arise from 3-oxygenated pentacyclic triterpenes (Fig. 5), which are important constituents of plants (especially angiosperms). In this way, their presence in geological samples is generally taken to be indicative of a terrigenous contribution to the biomass (e.g., Stout, 1992; ten Haven *et al.*, 1992).

#### ***Arborane/Fernane Derivatives***

Compounds 2 and 3, one of them a prominent component in the aliphatic fraction of the Gandarela extract fraction, belong to a tetracyclic series tentatively identified by Loureiro (1989) as *des*-(A)-fermenes (Fig. 6).

One tetracyclic (compound V) and two pentacyclic hydrocarbons (compounds VI and VII; Loureiro & Cardoso, 1990; Hauke *et al.*, 1992a) also related to the arborane/fernane skeleton, were detected in the aromatic concentrate (Fig. 4). The mass spectra of compounds VI and VII, the dominant constituents in the aromatic fraction, are reproduced in Fig. 7. Compound VII has a mass spectrum identical to that of 24, 25-dinorarbora-1,3,5,7,9-pentaene reported by Hauke *et al.* (1992a). In the case of compound VI, its fragmentation features

present close resemblance with those of 24,25-dinorarbora-1,3,5(10),9(11)-tetraene, also characterized by Hauke *et al.* (1992a). Taking into account that this structure is considered to be a direct precursor for the diaromatic pentacyclic VII confidently identified in the same fraction of Gandarela sample, it is reasonable to tentatively assign this arborane/fernane derivative for compound VI; the differences between the mass spectrum of compound VI and the data from literature may be due to different conditions in the mass spectrometric analysis.

These compounds could derive from the arborane or fernane families of triterpenes in a pathway like that proposed in Fig. 5. As far as the origin of arborane/fernane compounds is concerned, there is a range of opinions in the literature. During some time, their presence in sediments was generally interpreted as an indication of a higher plant input to the biomass, especially of Graminae (see, for instance, Nishimoto *et al.*, 1968). Hauke *et al.* (1992a,b) interpreted the presence of such structures in lacustrine sediments as indicative of a bacterial source, based, among other facts, on the carbon isotopic composition of these compounds. More recently, on the basis of petrological evidence, the occurrence of arborane/fernane hydrocarbons in coal samples has been used to propose a higher plant (gymnosperm) origin for these compounds (Vliex *et al.*, 1994).

#### ***Hopane Derivatives***

The distribution of hopanoids in the aliphatic fraction is dominated by  $\beta\beta$  isomers (Fig. 3), especially 17 $\beta$ (H)-trisnorhopane and 17 $\beta$ (H),21 $\beta$ (H)-homopane, as expected for an immature oil shale.

Among the aromatic hopanoids, compounds VIII (Greiner *et al.*, 1977) and IX (Schaeffer *et al.*, 1995) are the more important biomarkers found in the Gandarela bitumen (Fig. 4).

Compound VIII is probably derived from unsaturated natural precursors such as diploptene - a C<sub>30</sub> hopene widespread in living organisms, especially microorganisms -, via a sequential aromatization process spreading from ring D to A (Greiner *et al.*, 1976).

Compound IX is the C<sub>31</sub> homologue of a novel series of benzohopanes only more recently characterized in the geosphere (Schaeffer *et al.*, 1995); contrary to the regular benzohopanes, these biomarkers are derived from bacteriohopanoids by cyclization at C (16), and not at C (20) position.

#### ***Hydrous pyrolysis***

*n*-Alkanes ranging from C<sub>12</sub> to C<sub>42</sub> and maximizing at C<sub>17</sub> dominate the aliphatic fraction obtained from the Gandarela hydrous pyrolysate (Fig. 8).

The release of linear alkanes has been previously reported in the pyrolysis of *Botryococcus*-rich sedimentary samples. In a torbanite pyrolysate, for instance, Derenne *et al.* (1988) have identified *n*-alkanes extending up to C<sub>31</sub>. According to these authors, the maximum observed at *n*-C<sub>18</sub> may simply reflect the loss of lower molecular weight hydrocarbons during the separation procedure. Homologous series of *n*-alkanes (and *n*-alk-1-enes) up to C<sub>34</sub> and with maximum at C<sub>10</sub> dominate in the flash pyrolysate of the kerogen of Ribesalbes oil shale (Spain, Tertiary; Sinninghe Damsté *et al.*, 1993). The flash pyrolysis of a coorongite sample also revealed homologous series of *n*-alkanes (C<sub>6</sub> to C<sub>30</sub>, maximum at C<sub>9</sub>) and *n*-alk-1-enes as important products (Gatellier *et al.*, 1993).

In the aromatic fraction isolated from the Gandarela hydrous pyrolysate, series of long-chain (up to C<sub>34</sub>) alkylbenzenes and alkyltoluenes have been identified, on the basis of mass spectral characteristics and retention behavior, as the most prominent components (Fig. 9).

Accordingly, both series were recorded in the pyrolysates of kerogens comprised mainly of fossilized *B. braunii*; they extend up to C<sub>34</sub> in the Ribesalbes sediment (Sinninghe Damsté *et al.*, 1993) and to C<sub>30</sub> in a torbanite sample (Derenne *et al.*, 1988). Alkylated benzenes (up to C<sub>19</sub>) and toluenes (up to C<sub>21</sub>) have been detected among the pyrolysis products of a coorongite sample (Dubreuil *et al.*, 1989). Allan *et al.* (1980) propose the cyclization and aromatization of olefins during pyrolysis as a possible origin for these alkylbenzenes.

## DISCUSSION

The organic matter in the Gandarela oil shale is derived mainly from remains of the lacustrine alga *Botryococcus braunii*. Evidence for this conclusion is based on organic petrography and hydrous pyrolysis experiments on the kerogen. Surprisingly, however, the biomarker fingerprint of the Gandarela bitumen points to an important higher plant input and to the absence of chemical fossils derived from *B. braunii*.

A similar bias of the biomarker composition is apparent from the literature data on sedimentary rocks believed to be chiefly composed of *B. braunii* remains. Derenne *et al.* (1988), for instance, could not detect any traces of botryococcane in the bitumens isolated from four different torbanites.

Instead,  $\alpha\beta$  hopanes are prevalent in the branched/cyclic hydrocarbon fractions, followed by pristane, phytane and alkylcyclohexanes. In the same way, no *Botryococcus*-derived biomarkers were identified in the Ribesalbes oil shale bitumen (Sinninghe Damsté *et al.*, 1993). According to Derenne *et al.* (1988), the absence of botryococcane-related compounds in the torbanites may be explained, at least in part, by the removal of the precursors through microbiological processes during sedimentation under partly oxic conditions.

Other features were recognized by some authors who studied the lipid compositions of *Botryococcus*-rich kerogens. Lichtfouse *et al.* (1994), for instance, observed in a Pliocene oil shale C<sub>25</sub>-C<sub>35</sub> *n*-alkanes with a marked odd predominance and proposed that the odd carbon-numbered alkadienes found in *B. braunii* race-A (Metzger *et al.*, 1992) would be, at least in part, their precursors through diagenetic reduction. In this way, the presence of *n*-alkanes exhibiting a similar distribution in the Gandarela sample (see Fig. 3), a feature which normally would be attributed to a terrestrial input to the depositional setting, could also be due to the contribution of these algae.

The high hopane/sterane ratio of the Gandarela bitumen is in accordance with low content of sterols in *B. braunii* (McKirdy *et al.*, 1986).

## CONCLUSIONS

Both petrographic and hydrous pyrolysis data provide evidence for an expressive contribution of botryococcoid alga to the organic matter of the Gandarela oil shale. Indeed, visual kerogen analyses show a major contribution of alginite and a minor contribution of higher plants.

Biomarker composition, on the other hand, evidenced a strong odd/even predominance of *n*-alkanes in the range C<sub>27</sub>-C<sub>33</sub>, a fact that together with the high relative abundance of lupane, oleanane and fernane/arborane derivatives in the aliphatic and aromatic fractions, could be in principle attributed to a higher plant input.

So, the presence of significant higher plant derived biomarkers and the absence of *Botryococcus*-related molecular fossils in the Gandarela bitumen, indicate that relative proportions of the free lipids do not necessarily reflect the relative importance of the original organisms which contributed to the biomass. These results show that visual, bulk and pyrolytic analyses of the kerogen associated to biomarkers data are indispensable to characterize the depositional

environment, and reinforce the observation that free lipids from higher plants are better preserved than those from algae.

**Acknowledgements** - The authors wish to thank J.M. Moldowan (Stanford University) for his critical comments and help in improving this paper. Helpful suggestions from W. Kalkreuth (UFRGS) are also acknowledged.

## REFERENCES

- Allan J., BJOROY M. and DOUGLAS A. G. (1980) A geochemical study of the exinite group maceral alginite, selected from three Permo-Carboniferous Torbanites. In *Advances in Organic Geochemistry 1979* (Ed. Douglas A.G. and Maxwell J.R.), 599-618. Pergamon Press, Oxford.
- Brassell S.C., Eglinton G. and Mo F.J. (1986) Biological marker compounds as indicators of the depositional history of the Maoming oil shale. In *Advances in Organic Geochemistry 1985* (Ed. D. Leythaeuser and J. Rullkötter) Vol.10, 927-941
- Chaffee A.L. and Fookes R.J. (1988) Polycyclic aromatic hydrocarbons in Australian coals, III. Structural elucidation by proton nuclear magnetic resonance spectroscopy. *Org. Geochem.*, Vol.12, 261-271.
- Corbet B. (1980) Origine et transformation de triterpenes dans des sediments recents. Ph.D. Thesis - Université Louis Pasteur de Strasbourg (France).
- Derenne S., Largeau C., Casadevall E. and Connan J. (1988) Comparison of torbanites of various origins and evolutionary stages. Bacterial contribution to their formation. Cause of the lack of botryococcane in bitumens. *Org. Geochem.*, Vol.12, 43-59.
- Dubreuil C., Derenne S., Largeau C., Berkaloff C. and Rousseau B. (1989) Mechanism of formation and chemical structure of Coorongite-I. Role of the resistant biopolymer and of the hydrocarbons of *Botryococcus braunii*. Ultrastructure of Coorongite and its relationship with Torbanites. *Org. Geochem.*, Vol.14, 543-553.
- Espitalié J., Deroo G. and Marquis F. (1985) La pyrolyse Rock-Eval et ses applications. *Revue de L'Institute Français du Pétrole*. Vol.40, 563-579.
- Gatellier J.P.L.A., de Leeuw J.W., Sinninghe Damsté J. S., Derenne S., Largeau C. and Metzger P. (1993) A comparative study of macromolecular substances of a Coorongite and cell walls of the extant alga *Botryococcus braunii*. *Geochim. Cosmochim. Acta*, Vol.57, 2053-2068.
- Greiner A. Ch., Spycykerelle C. and Albrecht P. (1976) Aromatic hydrocarbons from geological sources; I. New naturally occurring phenanthrene and chrysene derivatives. *Tetrahedron*, Vol.32, 257-260.
- Greiner A. Ch., Spycykerelle C., Albrecht P. and Ourisson G. (1977) Aromatic hydrocarbons from geological sources. Part V. Mono- and di-aromatic hopane derivatives. *J. Chem. Research (M)*, 3829-3871.
- Hauke V., Graff R., Wehrung P., Trendel J.M. and Albrecht P. (1992a) Novel triterpene-derived hydrocarbons of arborane/fernane series in sediments, Part I. *Tetrahedron*, Vol.48, 3915-3924.
- Hauke V., Graff R., Wehrung P., Trendel J.M., Albrecht P., Riva A., Hopfgartner G., Gülaçar F.O., Buchs A. and Eakin P.E. (1992b) Novel triterpene-derived hydrocarbons of arborane/fernane series in sediments: Part II. *Geochim. Cosmochim. Acta*, Vol.56, 3595-3602.
- ten Haven H.L., Peakman T.M. and Rullkötter J. (1992) Early diagenetic transformation of higher-plant triterpenoids in deep-sea sediments from Baffin Bay. *Geochim. Cosmochim. Acta*, Vol. 56, 2001-2024.
- Hutton A. (1990) Classification, organic petrography and geochemistry of oil shales. *Eastern Oil shale symposium*, 163-172.
- Lichtfouse E., Derenne S., Mariotti A. and Largeau C. (1994) Possible algal origin of long chain odd *n*-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. *Org. Geochem.* Vol.22, 1023-1027.
- Loureiro M.R.B. (1989) Marcadores biológicos do xisto do Vale do Paraíba (Formação Tremembé). Ph.D. Thesis - Universidade Federal do Rio de Janeiro (Brazil).
- Loureiro M.R.B. and Cardoso J.N. (1990) Aromatic hydrocarbons in the Paraíba Valley oil shale. *Org. Geochem.*, Vol.15, 351-359.
- Maizatto J. R. (1997) Análise paleoecológica e bioestratigráfica dos sedimentos cenozóicos da Bacia do Gandarela, Quadrilátero Ferrífero, Minas Gerais, com base nos aspectos palinológicos e sedimentares. M.Sc. Thesis, Universidade Federal de Ouro Preto (Brazil)
- Maizatto J.R. and Castro P.T.A. (1993) Origem e evolução na Bacia de Gandarela-Quadrilátero Ferrífero, Minas Gerais. Anais do IV Simpósio Nacional de Estudos Tectônicos, Núcleo Minas Gerais, 325-329.
- McKirdy D.M., Cox R.E., Volkmann J.K. and Howell V.J. (1986) Botryococcane in a new class of Australian non-marine crude oils. *Nature*,

- Vol.320, 57-59.
- Metzger P., Largeau C. and Casadevall E. (1992) Lipids and macromolecular lipids of the hydrocarbon-rich microalga *Botryococcus braunii*. Chemical structure and biosynthesis. Geochemical and Biotechnological Importance. In *Progress in the chemistry of organic natural products*. (ed. W. Herz *et al.*), Vol.57, 1-70. Springer.
- Moldowan J.M. and Seifert W. (1980) First discovery of botryococcane in petroleum. *J. C. S. Chem. Comm.*, 912-914.
- Nishimoto K., Ito M., Natori S. and Ohmoto T. (1968) The structures of arundoin, cylindrin and fernenol, triterpenoids of fernane and arborane groups of *Imperata cylindrica* Var. *koenigii*. *Tetrahedron*, Vol.24, 735-752.
- Ourisson G., Albrecht P. and Rohmer M. (1979) The hopanoids paleo chemistry and biochemistry of a group of natural products. *Pure Appl. Chem.*, Vol. 51, 709-729.
- Pinto A.D.P. and Regali M.S.P. (1990) Palinoestratigrafia dos sedimentos terciários da Bacia de Gandarela, Minas Gerais - Brasil. *Rev. Esc. Minas*, Vol.44, 10-15.
- Saptorahardjo A. (1985) Diagenèse précoce de la matière organique dans la série sédimentaire du delta de la Mahakam, Indonésie, aspects moléculaires. Ph.D. Thesis - Université Louis Pasteur, Strasbourg (France).
- Schaeffer P., Adam P., Trendel J.M., Albrecht P. and Connan J. (1995) A novel series of benzohopanes widespread in sediments. *Org. Geochem.*, Vol.23, 87-89.
- Seifert W.K. and Moldowan J.M. (1981) Paleoreconstruction by biological markers. *Geochim. Cosmochim. Acta*, Vol.45, 783-794.
- Sgarbi G.N.C., Fantinel L.M. and Masotti F.S (1992) Geologia dos sedimentos lacustres da Bacia Terciária de Gandarela. *R. Esc. de Minas, Ouro Preto*, Vol.45 (1 e 2), 118-122.
- Sinninghe Damsté J. S., de las Heras F.X.C., van Bergen P.F. and de Leeuw J.W. (1993) Characterization of Tertiary Catalan lacustrine oil shales: discovery of extremely organic sulphur-rich Type I kerogens. *Geochim. Cosmochim. Acta*, Vol. 57, 389-415
- Spyckerelle C. (1975) Constituants aromatiques des sédiments. Ph.D. Thesis - Université Louis Pasteur, Strasbourg, (France).
- Stout S.A. (1992) Aliphatic and aromatic triterpenoids in a Tertiary angiospermous lignite. *Org. Geochem.*, Vol.18, 51-66.
- Trendel J.M. (1985) Dégradation de triterpènes dans les sédiments, Aspects photochimiques et microbiologique. Ph.D. Thesis, Université Louis Pasteur de Strasbourg (France).
- Tissot B.P. and Welte D.H. (1984) *Petroleum Formation and Occurrence*. Springer, Berlin.
- Tyson R.V. (1995) *Sedimentary Organic Matter: organic facies and palynofacies*. Chapman & Hall, London.
- Vliex M., Hagemann H.W. and Pütmann W. (1994) Aromatized arborane/fernane hydrocarbons as molecular indicators of floral changes in Upper Carboniferous/Lower Permian strata of Saar-Nahe Basin, southwestern Germany. *Geochim. Cosmochim. Acta*, Vol.58, 4689-4702.

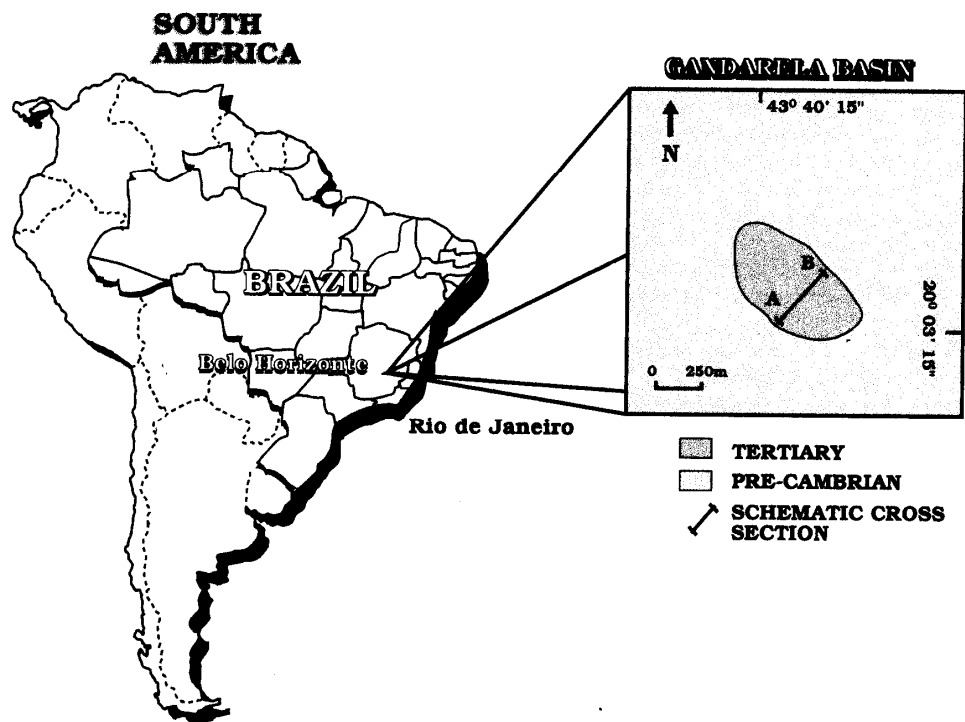


Fig. 1 - Location map of the Gandarela basin (Modified from Sgarbi et al., 1992)

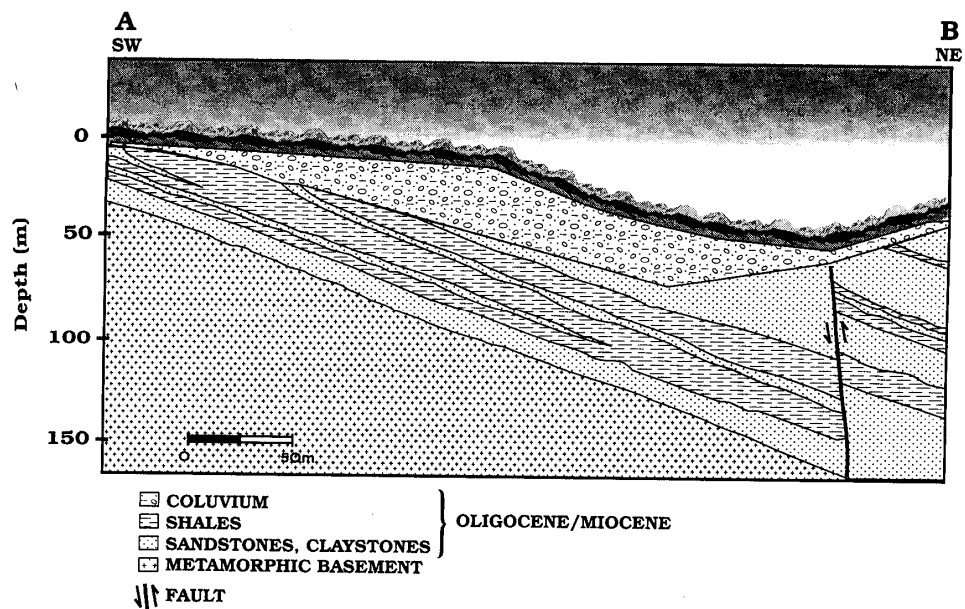


Fig. 2 - Schematic cross section through the Gandarela basin. See location on Fig. 1 (Modified from Sgarbi et al., 1992)



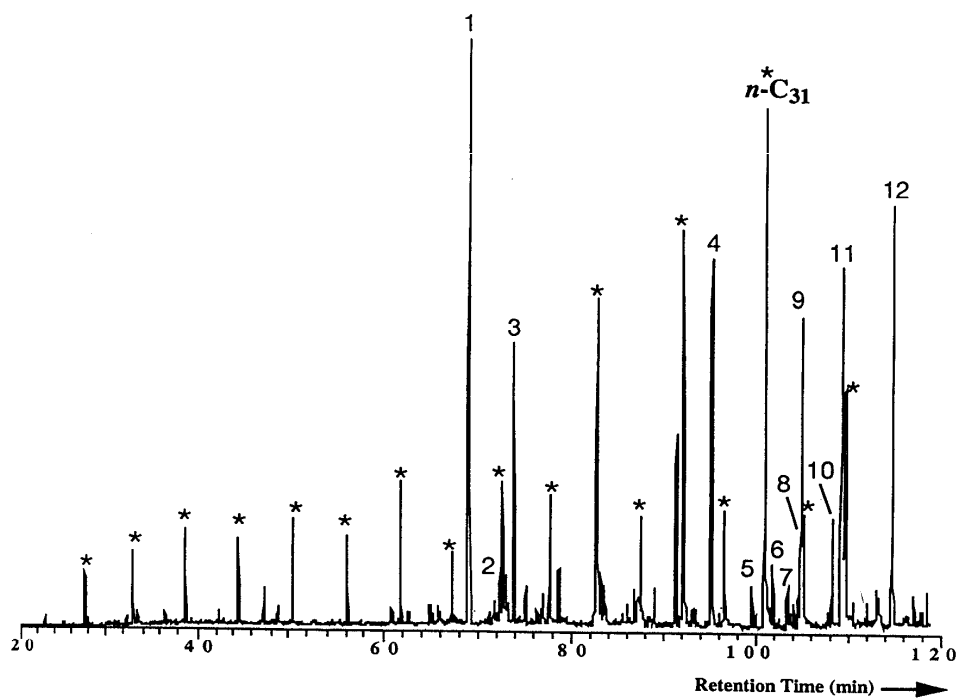


Fig. 3 - Total ion chromatogram of the aliphatic fraction detected in the Gandarela bitumen showing n-alkanes (\*);

*des-A-lupane (1); des-A-ferrenes (2,3); C<sub>27</sub> 17β(H)-hopane (4); C<sub>29</sub>-C<sub>31</sub> 17α(H), 21β(H)-hopanes (5,7,10); C<sub>29</sub>-C<sub>30</sub> 17β(H), 21α(H)-hopanes (6,8) and C<sub>29</sub>-C<sub>31</sub> 17β(H), 21α(H)-hopanes (9,11,12) (for structures 1,2 and 3 see Appendix)*

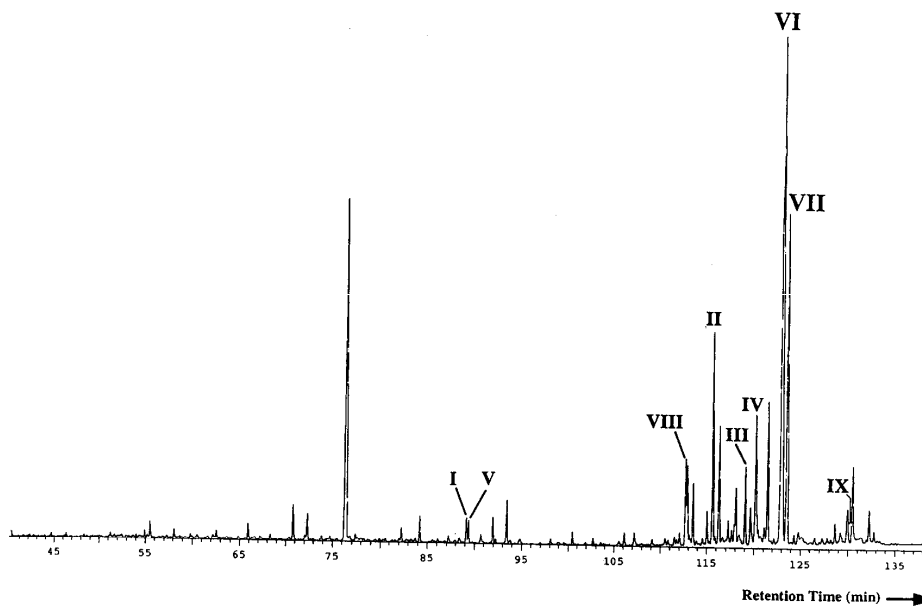


Fig. 4 - Total ion chromatogram of the aromatic fraction detected in the Gandarela bitumen (for peak identification see Appendix)

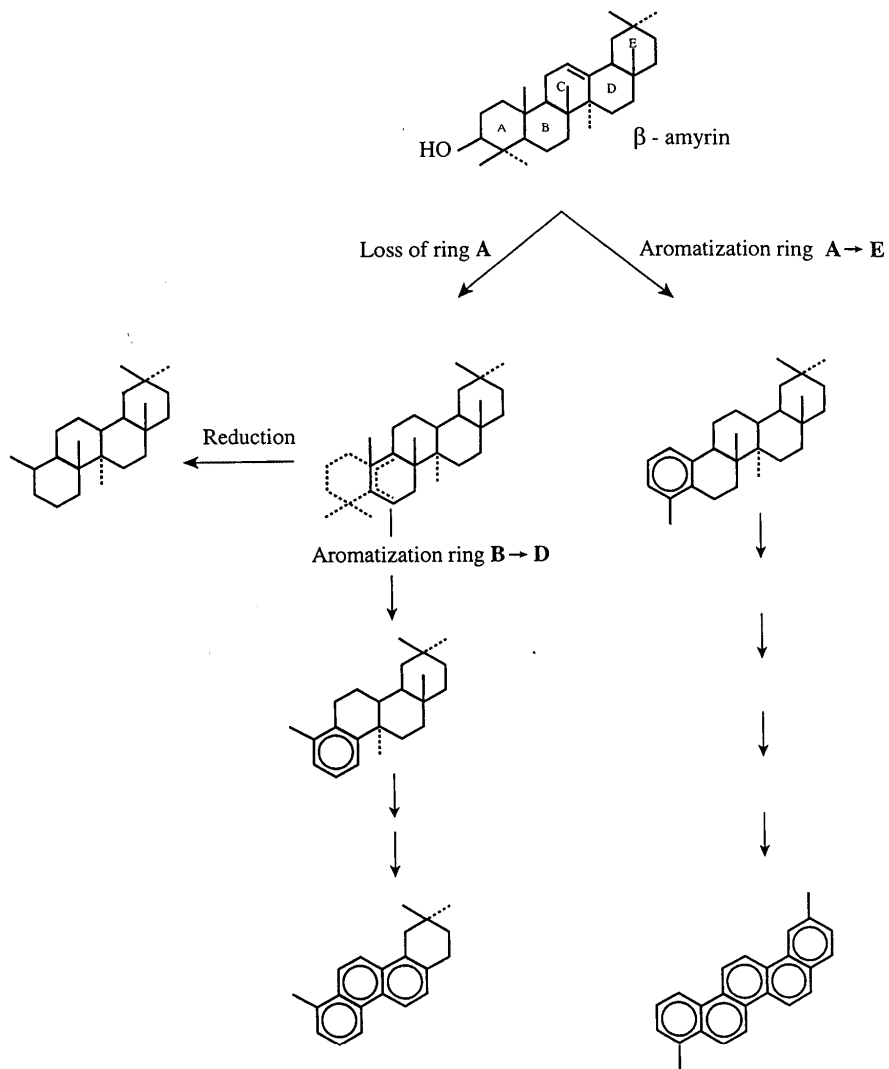


Fig. 5 - Hypothetical diagenetic pathways of  $\beta$ -amyrin (oleanane skeleton) (after Trendel, 1985). Similar schemes can be devised for the lupane, ursane and fernane/arborane derivatives, from the respective C-3 oxygenated pentacyclic triterpenoid precursors

FERNENES

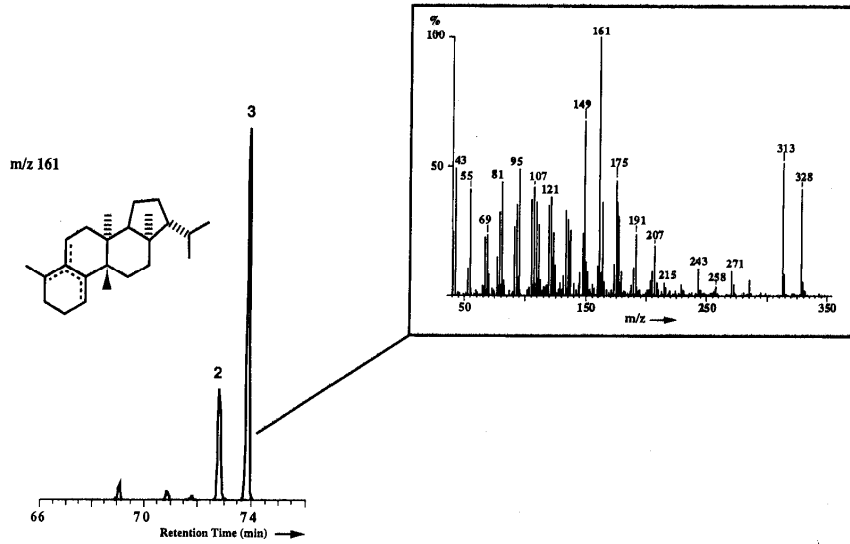


Fig. 6 - Partial mass chromatogram m/z 161 of aliphatic fraction from Gandarela bitumen showing the distribution of des-A-farnenes and the mass spectrum of compound 3

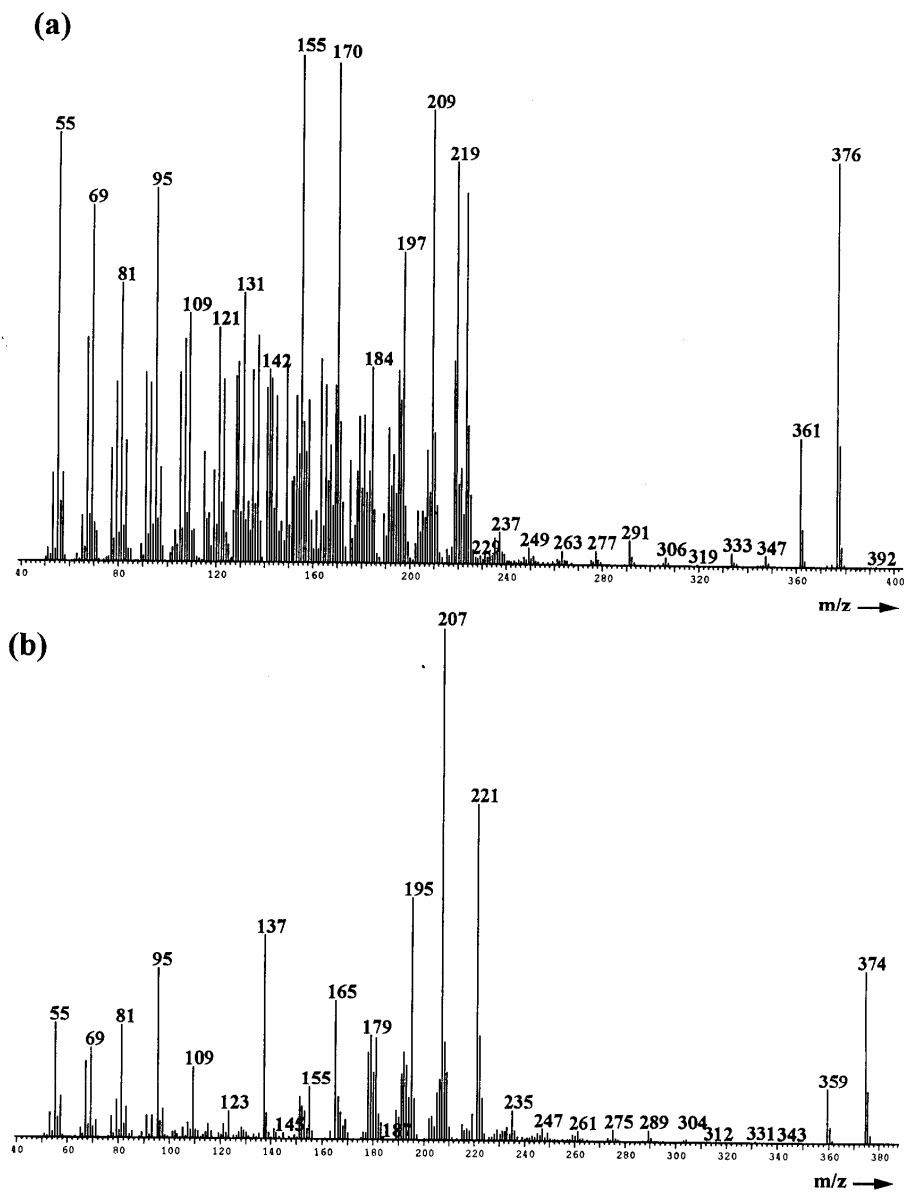


Fig. 7 - Mass spectra of compounds VI (a) and VII (b)

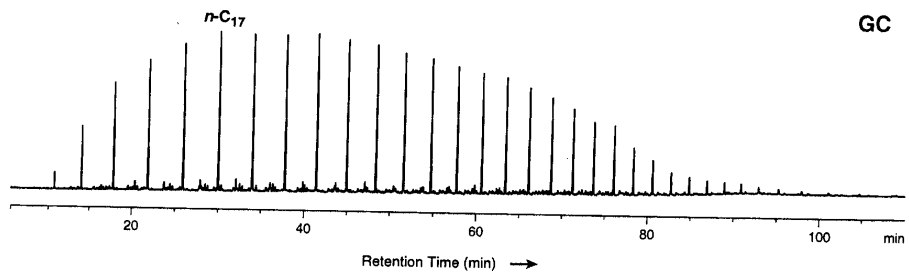


Fig. 8 - Gas chromatogram of aliphatic fraction of pyrolysate of Gandarela kerogen

GC-MS

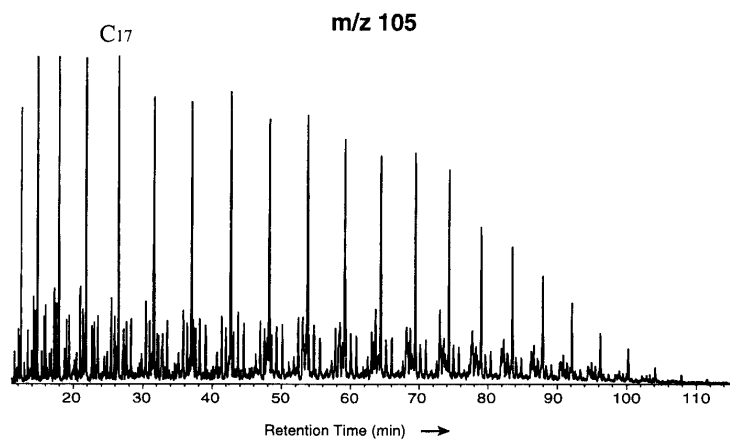
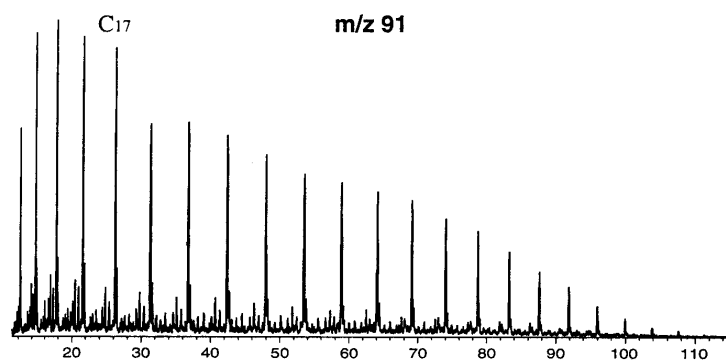
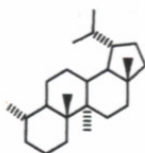


Fig. 9 -  $m/z$  91 and  $m/z$  105 mass chromatograms of aromatic fraction of the pyrolysate of Gandarela kerogen

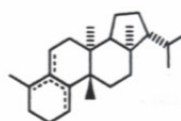
APPENDIX

Structures Cited in the Text

Aliphatic Hydrocarbons

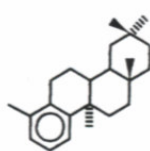


1

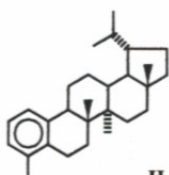


2 and 3

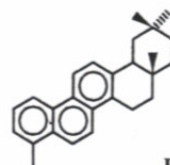
Aromatic Hydrocarbons



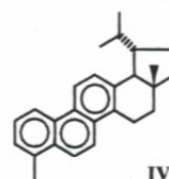
I



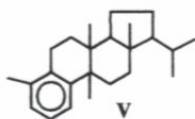
II



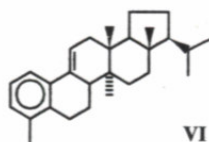
III



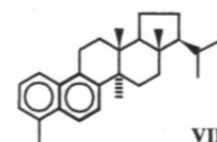
IV



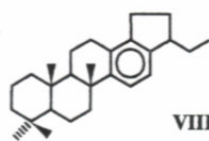
V



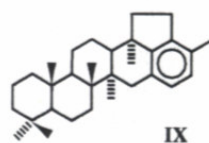
VI



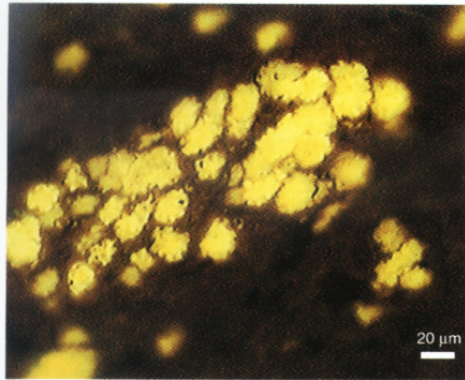
VII



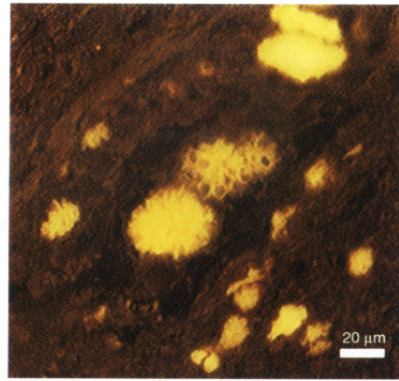
VIII



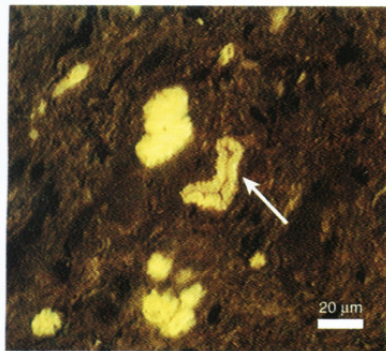
IX



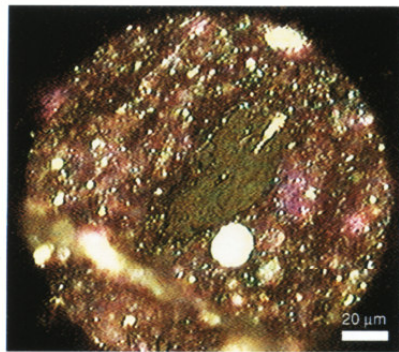
a



b



c



d

*Plate 1 - Photomicrographs showing: a) small Botryococcus-type algal colonies, fluorescing lemon-yellow; b) Botryococcus-type algae fluorescing lemon-yellow and amorphous kerogen fluorescing orange; c) sporinite fluorescing-yellow. Excitation filter G 395-440, 50X magnification objective, oil immersion; d) pyrite and a vitrinite phytoclast. Reflected light, 50X magnification objective, oil immersion*