3. CHARACTERIZATION OF DIFFERENT FORMS OF ORGANIC MATTER IN UPPER CRETACEOUS LEVELS FROM CERRO DE LA MESA (MADRID, SPAIN)

C. ALVAREZ-RAMIS[1] and G. ALMENDROS[2]

1. Dep./UEI de Palaeontología, Instituto de Geología Económica (CSIC) Facultad de Ciencias Geológicas (UCM), E–28040 Madrid, Spain, 2. Centro de Ciencias Medioambientales (CSIC), Serrano 115 dpdo., E–28006 Madrid, Spain

Abstract

In addition to the palaeobotanical study of the Cretaceous levels from Cerro de la Mesa (Madrid), the most representative types of organic matter have been analyzed by pyrolysis – gas – chromatography-mass spectrometry. Both megarests and palynomorphs suggested a warm humid forest including large diversity of Angiosperms, Araucariaceae, Taxodiaceae and Cheirolepidiaceae the latter represented mainly by well-preserved cuticles of *Frenelopsis oligostomata.* The main pyrolysis products from these cuticles were alkyl-substituted polycyclic aromatic molecules such are naphthalenes, anthracenes, and phenanthrenes, as well as some aliphatic hydrocarbons. This pyrolysis pattern was considered to reflect vascular plant remains altered by intense maturation processes. The lignitiferous levels showed, after pyrolysis, similar qualitative composition, but yielded greater amounts of hydroxylated derivatives (phenols, catechols, naphthalenols and biphenylols) and only traces of alkanes and fatty acids, which point to the terrestrial origin of the organic matter. The greatest amounts of the latter two products, as well as of hydroaromatic molecules (tetralins, fluorenes and indenes) and heterocyclic molecules (dibenzofurans and xanthenes) were obtained from the layers consisting of carbonaceous marls, which – in agreement with the palaeobotanic results – could correspond to heavily carbonized material with the most significant input of aliphatic molecules from microorganism and algal biomass, and/or to an early diagenesis in aquatic environment.

Key words: Cretaceous flora, palynomorphs, *Frenelopsis,* pyrolysis, kerogen, Spain.

Introduction

The Upper Cretaceous basement in Cerro de la Mesa (Madrid, Spain) contains one of the nicest paleobotanical samples of the Mesozoic microflora. This formation includes a number of plants with well-preserved cuticles, especially in the mummified specimens. In addition, the sediments are very rich in palynomorphs.

The present study is included into the Spanish-Hungarian Project of the Dirección General de Cooperación Científica y Técnica del Ministero de Asuntos Exteriores (1992) entitled "Estudio de diversos aspectos paleobotánicos del Cretácico superior del Cerro de la Mesa (Norte de la Provincia de Madrid)", the financial support being provided by the DGICYT Project PB92–0101 (Estudio palinológico de las Angiospermas primitivas halladas en el Cretácico superior del Borde Sur de la Sierra de Guadarrama).

The palaeontological characteristics were studied in the laboratorio de Paleobotánica, Departamento de Paleontología, and in the Instituto de Geología Económica (CSIC), whereas the chemical analyses were studied in the laboratorio de Química del Humus del Centro de Ciencias Medioambientales del CSIC. The relative richness of organic remains, mainly plants, found throughout the lithostratigraphic series of Cerro de la Mesa, has been the subject of several palaeontological, stratigraphic and palaeoecological studies, the results of which being reported elsewhere (ALVAREZ-RAMIS, 1981, ALVAREZ-RAMIS and FERNÁNDEZ MARRÓN, 1993 and ALVAREZ-RAMIS et al., 1994a and b).

From the viewpoint of the organic geochemistry analyses, the most representative materials in the stratigraphic series are found in the gray marls and in the lignitiferous levels.

LOCATION AND GEOLOGICAL FEATURES OF CERRO DE LA MESA QUARRY

The samples studied were taken from a quarry located in the neighbourhood of Guadalix de la Sierra village (Madrid, Central Spain), that is currently exploited in the extraction of calcareous building blocks.

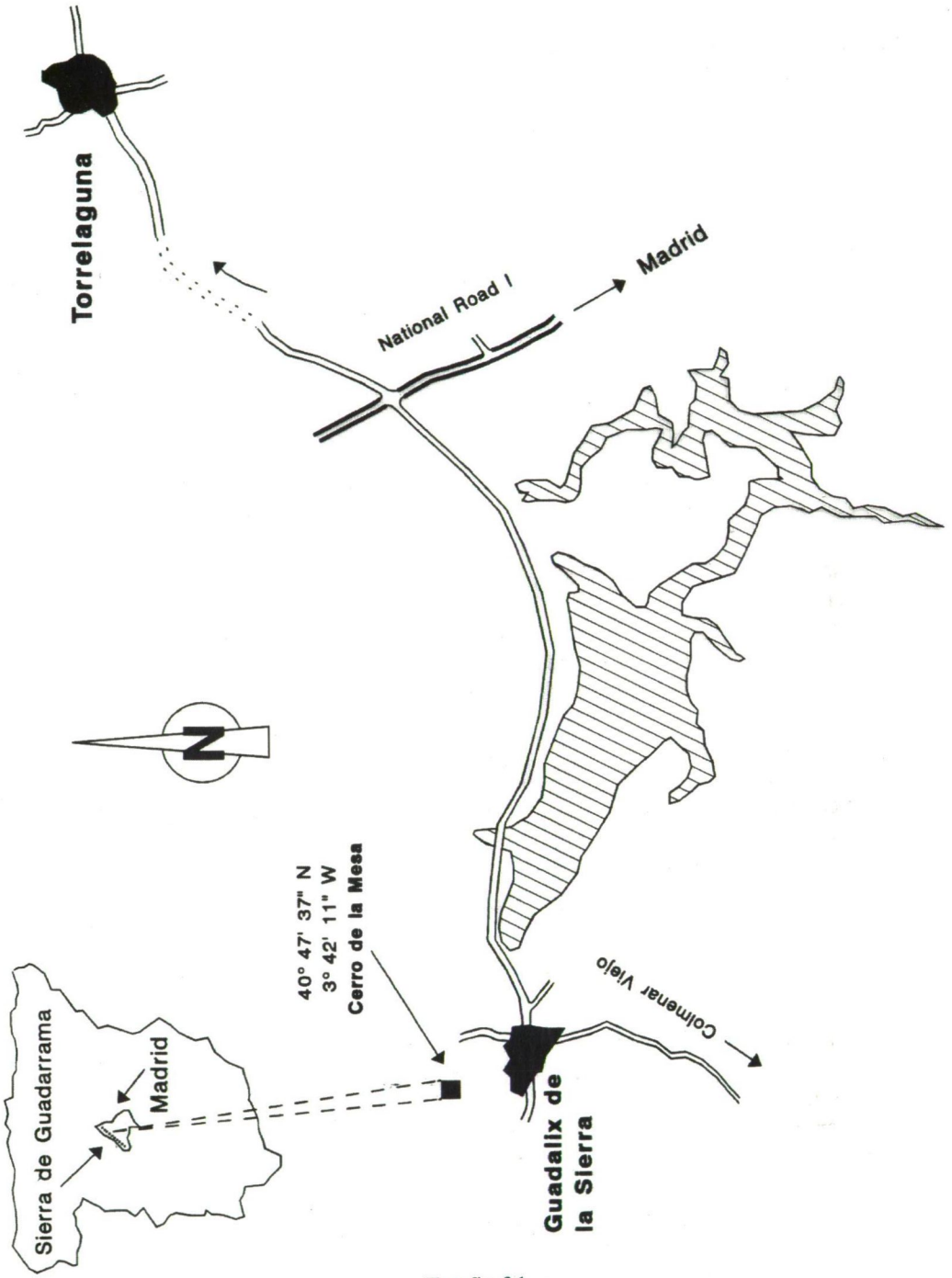
The coordinates of the basement correspond to 40° 47' 37" N and 3° 42' 11" W (Greenwich), the access to which being provided by two independent ways, ie., the road between the villages of Colmenar Viejo and Guadalix de la Sierra, or the road from Guadalix de la Sierra to Torrelaguna (Text-fig. 3.1.). The rock exploitation in the quarry has brought into light the different types of materials of the lithological series in the Upper Cretaceous, characteristic for the Southern side of the Sierra de Guadarrama (Central System of Spain). Plate 3.1. corresponds to a partial view of the quarry, showing the lithological features.

Basically, the materials consist of limestones and marls, more or less compacted and sandy, in cyclic alternance with dolomitized limestones and some small and irregular lignitiferous levels. The marly and carbonaceous levels are very rich in fragmented and coalified plant remains.

LITHOSTRATIGRAPHIC FEATURES

The lithostratigraphic series we have studied in Cerro de la Mesa consists of eight members. The marly material dominates in the lower part (members 8 and 6); whereas the most frequent material in the upper parts are limestones, in some cases dolomitized, and subjacent marly sandy limestones (member 4) include lignite layers of small thickness and irregular distribution (Text-fig. 3.2.).

The eight levels studied from the palynological viewpoint (ALVAREZ-RAMIS and FERNÁNDEZ MARRÓN, 1990, 1993, ALVAREZ-RAMIS et al., 1994a, 1994b) are shown at the right side of Text-fig. 3.2. The position of the three levels sampled for the organic matter studies are presented at the left side. The samples were taken from the 4th member, basically consisting of sandy limestones, and in the lowest level of lignites (L). One sample (CM), was taken in the calcareous marls (6th member) in



Text-fig. 3.1.
Location of the site studied in Cerro de la Mesa.

Plate 3.1.
Partial view of the Cerro de la Mesa quarry.

a point placed between levels 2–3. Just below it, a branch of *Frenelopsis* included into compact marls was isolated for analysis (F) (ALVAREZ-RAMIS, 1981, ALVAREZ-RAMIS et al., 1982).

PALAEONTOLOGICAL FEATURES

The megaflora identified (ALVAREZ-RAMIS et al., 1989) come almost exclusively from the marl layers in member 6. Nevertheless, plant remains dominate on the lignite layers in member 4, but they are difficult to classify due to their large coalification and fragmentation. The main forms correspond to the following para-taxons, included in Gymnosperms and Angiosperms:

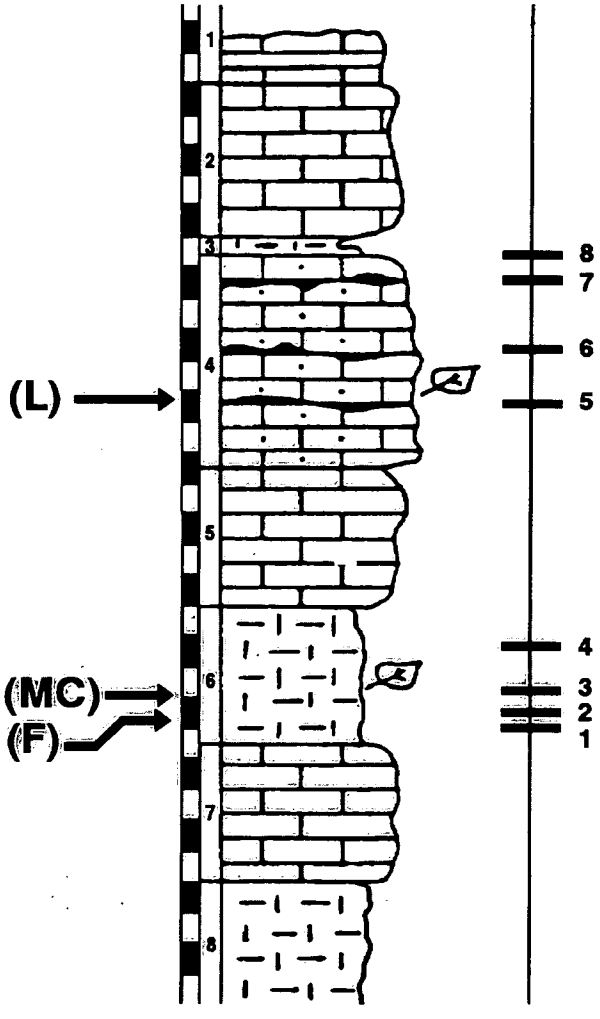
Gymnosperms	Angiosperms
Araucariacites fspp.	aff. *Banksia tenuifolia* BERRY
Frenelopsis oligostomata (ROM.) ALVIN	*Caesalpinites* fsp.
Sequoia fsp.	*Dewalquea* fsp.
	Eucalyptus geintzi HEER ?
	Myrica fsp.
	Lauraceae

The greatest number of megaremains corresponds to Gymnosperms, the most abundant being Araucariaceae, Taxodiaceae, and Cheirolepidiaceae. In the case of Angiosperms, there are a scarce number of megarests, but they show large diversity. As expected, the remains of reproductive structures, especially of Conifers, are abundant.

Concerning the microrests, the results of the analysis of palynomorphs are in agreement with the species of the above megarests. The most frequent forms are *Araucariacites, Inaperturopollenites, Classopollis* and mainly Normapolles (ALVAREZ-RAMIS and FERNÁNDEZ MARRÓN, 1990, 1993, ALVAREZ-RAMIS and DOUBINGER, 1994, ALVAREZ-RAMIS et al., 1994a and 1994b). The dominant palynomorphs correspond to the Plant Kingdom. Amongst them (ca. 60%), the most frequent are pollens from primitive Angiosperms (Normapolles), mainly *Interporopollenites, Papillopollis* and *Triatriopollenites,* and less proportion of *Vacuopollis, Complexiopollis* and *Atlantopollis.* The pollen grains from Gymnosperms amount ca. 25%, and the spores from vascular Cryptogams represent ca. 9%. There are additional amounts (2–8%) of sporomorphs from the Protista, Fungi and Animalia Kingdoms, with a dominance of cysts from Dinoflagellates.

PALAEOENVIRONMENTAL AND STRATIGRAPHIC NOTES OBTAINED FROM PALAEOBOTANIC STUDIES

The dominance of Angiosperms as regards the other groups, mainly of Conifers, suggests a warm humid climate in the site studied during the Upper Cretaceous. Nevertheless, the large diversity of their forms contrasts with their reduced amount, suggesting an allochthonous origin for the remains. This is in agreement with a large amount of remains, and a low proportion of arid or/and xerophytic species,



Text-fig. 3.2.

Calcareous series of Cerro de la Mesa bed, with indication of the material studied: *Frenelopsis oligostomata* (ROMARIZ) ALVIN (F) included into marls, calcareous marls (MC) (both in member 6), and lignites (L) in the lowest levels of member 4.

such are Cheirolepidaceae, and other plants adapted to saline conditions, frequent in coastal environments (Taxodiaceae).

The coastal location during the Upper Cretaceous of Cerro de la Mesa, is reinforced by the presence of internal lodges of Foraminiferae, Dinocysts and euryhaline elements such as Botryococcaceae. From palynological studies of ALVAREZ-RAMIS et al., (1994b) the age of Cerro de la Mesa is attributed to the Campanian-Maastrichtian interval.

Material and Methods

For chemical analyses, the geological samples are subjected to different pretreatments. The *Frenelopsis* (F, Text-fig. 3.2., and Plate 3.2.) are scrapped from the rock, grounded in an agate mortar, washed with 0.5M HCl to remove carbonates, and finally washed on a 0.1 mm screen. The same is used for the lignite material (L).

In order to concentrate the organic matter in sample MC, the grounded material is decarbonated with HCl and dried, and an organic matter-rich fraction is separated by flotation in the $CHBr_3$–CH_3CH_2OH mixture of density 1.9.

The analysis of the organic fraction is carried out by pyrolysis-gas-chromatography-mass spectrometry in the experimental conditions reported elsewhere (ALMENDROS et al., 1993). The pyrolysis products released at 500°C are condensed in liquid nitrogen and injected in a HEWLETT-PACKARD 5890 gas chromatograph, and the compounds are identified from their 70 eV mass spectra. For quantitative comparisons, the integration routine of the instrument is used on the single ion chromatograms corresponding to the molecular ions of the different homologues series of compounds, except in the case of alkanes and fatty acids, where the ions 85 and 83 are used, respectively. Such data are referred as percentages of the total ion counts in the chromatogram.

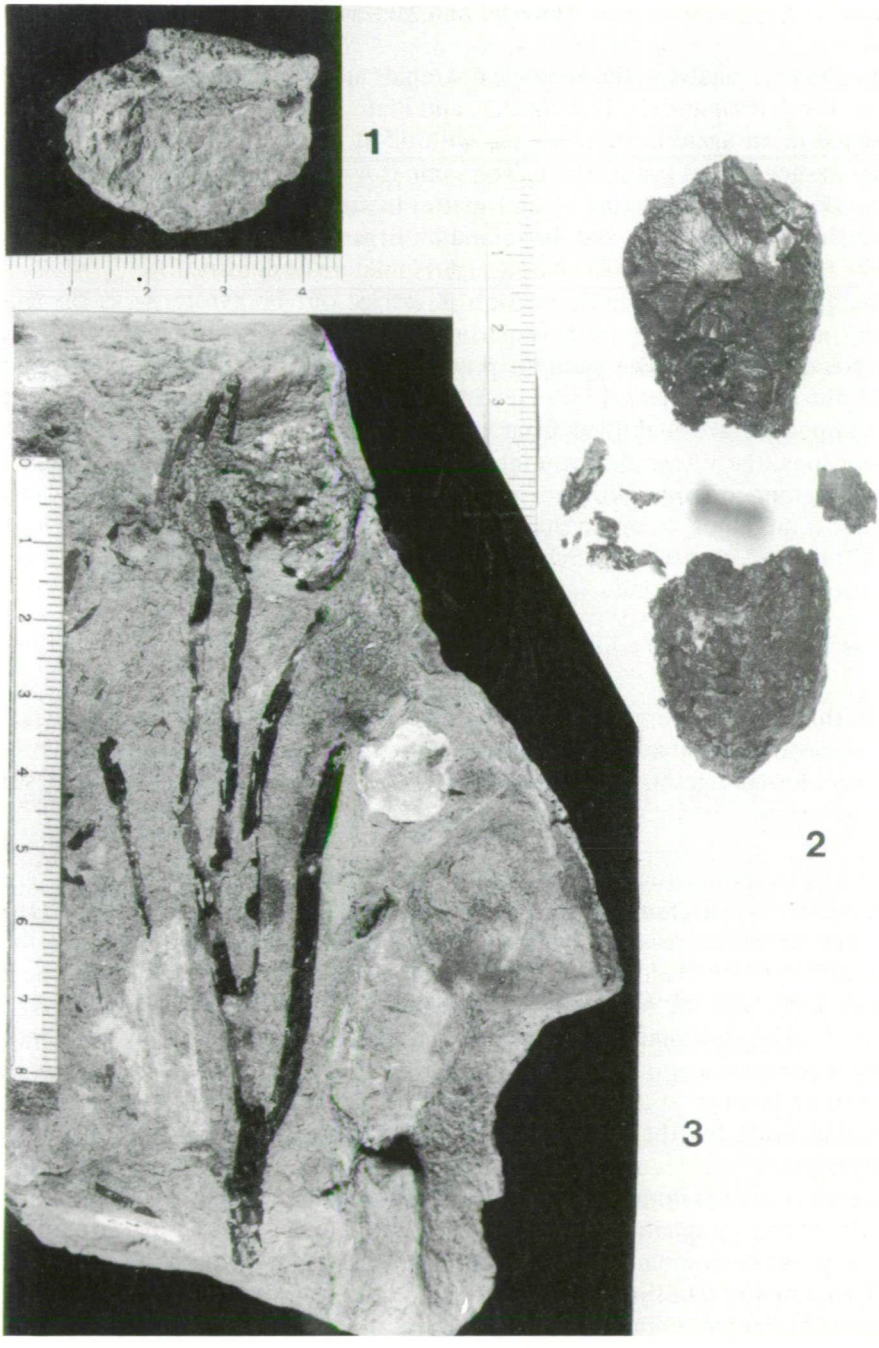
Results and Discussion

The three forms of organic matter studied in Cerro de la Mesa yield quite different qualitative and quantitative compound assemblages after analytical pyrolysis. The gas chromatograms show about 200 major peaks, the most frequent series being shown in Text-fig. 3.3.

Most of the pyrolysis products correspond to alkyl-substituted polycyclic aromatic hydrocarbons (naphthalenes, anthracenes, phenanthrenes, and pyrenes), some including hydroaromatic rings (tetralins, fluorenes and indenes) or heterocyclic rings (dibenzofurans and xanthenes) as well as some of their OH-substituted derivatives (phenols, catechols, naphthalenols, and biphenylols). In general the lack of fatty acids, and the low yields of aliphatic hydrocarbons point to a terrestrial origin of the organic matter. As expected, no traces of typical carbohydrate-derived pyrolysis products are found in the three materials studied. In general, the products obtained are similar to those reported by SCHULTEN et al., (1991) after pyrolysis of soil humic acids, but the present patterns showed greater proportion of polycyclic products.

Sample (L) yields dominant series of OH-substituted mono- and polycyclic compounds, whereas aliphatic molecules are practically lacking. The major chromatographic peaks correspond to cresols. Such patterns, in addition to the presence of small amounts of vanillyl and syringyl-type ketones similar to those produced by pyrolysis of lignins, point to an origin from the accumulation of vascular plant remains altered by intense diagenetic and catagenetic process.

By contrast, the organic matter in sample (MC) yields no methoxyl-containing ketones, and shows reduced amounts of oxygen-containing molecules. The domi-


1
2
3

nant products are alkyl-substituted polycyclic aromatic hydrocarbons (1 to 4 benzenic rings) in addition to aliphatic series consisting of alkanes and olefins. Such pattern could correspond to heavily carbonized organic matter with the most significant input of aliphatic molecules from microorganism and algal biomass, and/or to an early diagenesis in aquatic environment. This coincides with the paleobotanical results, that showed the presence of rests from the Protista and Fungi Kingdoms.

Finally, the composition of the organic matter remaining in *Frenelopsis* rests should be interpreted as the result of large maturation of an original material consisting of aromatic and lipid biopolymers (ALMENDROS et al., 1982, 1985, ALVAREZ-RAMIS et al., 1984). There are considerable diversity of aromatic and hydroaromatic oxygen-containing structures, and moderate amounts of ketones, alkanes, and olefins, some of them being similar to those formed during the pyrolysis of lignins or cutins from extant and fossil Gymnosperms.

In general, the relatively large maturity of the fossil organic matter in Cerro de la Mesa precludes more detailed palaeobiochemical considerations, as corresponds to the transformation of most of the diagnostic fossil biomarker molecules.

References

ALMENDROS, G., ALVAREZ-RAMIS, C. and POLO, A. (1982): Estudio paleobioquímico de la materia orgánica de restos fosilizados de *Frenelopsis* procedentes del supracretácico de Torrelaguna (Madrid). – Revista de la Real Academia de Ciencias Exactas, Físicas y Naturales *76,* 285–302.

ALMENDROS, G., MARTIN, F., GONZÁLEZ-VILA, F. J. and ALVAREZ-RAMIS, C. (1985): Caracterización de las distintas formas de materia orgánica fósil de dos canteras del Cretácico superior de la provincia de Madrid. – Anales de Edafología y Agrobiología *44,* 1–121.

ALMENDROS, G., MARTIN, F., GONZÁLEZ-VILA, F. J. and DEL RIO, J. C. (1993): The effect of various chemical treatments on the pyrolytic pattern of peat humic acid. – Journal of Analytical and Applied Pyrolysis *25,* 137–147.

ALVAREZ-RAMIS, C. (1981): Estudio de *Frenelopsis oligostomata* (ROMARIZ) ALVIN, procedente del Cretácico superior de Torrelaguna (Madrid). – Estudios Geológicos *37,* 83–87.

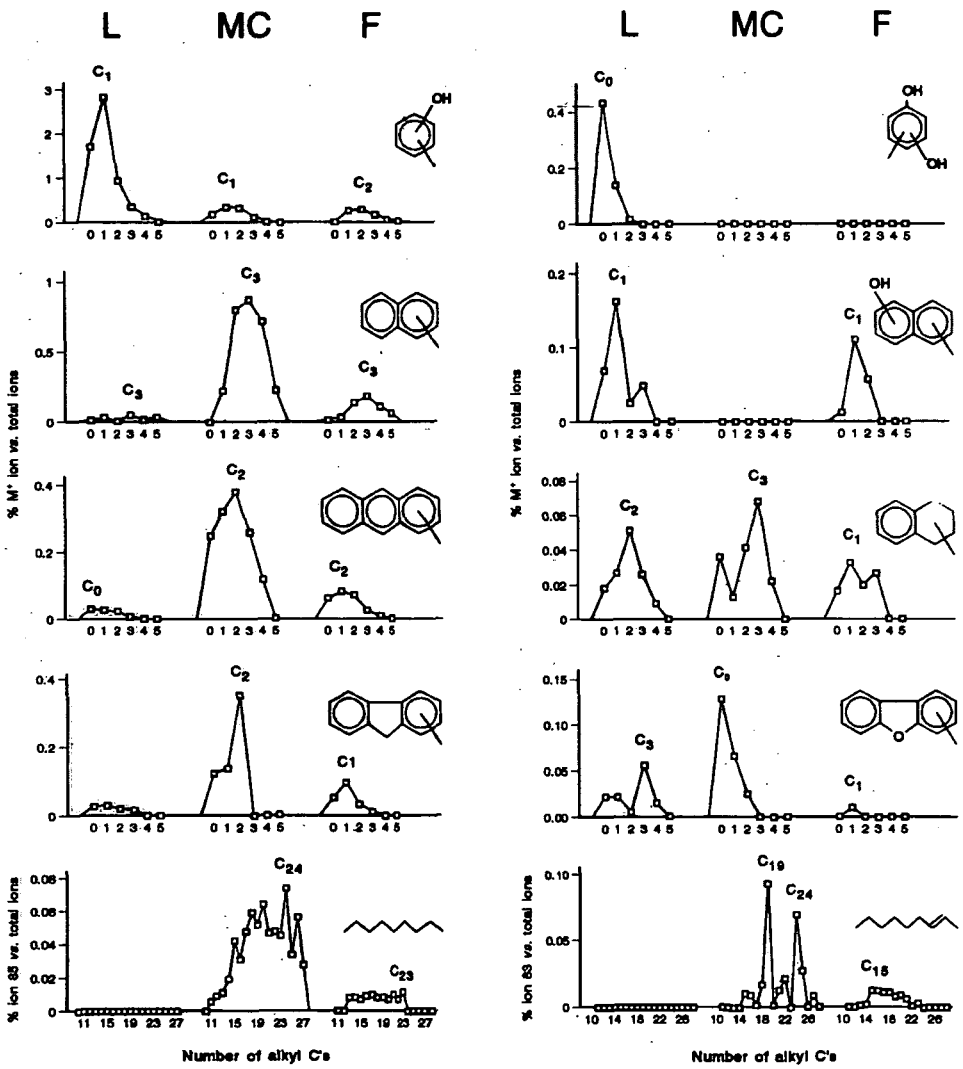
ALVAREZ-RAMIS, C., ALMENDROS, G. and POLO, A. (1982): Sur la présence du genre *Frenelopsis* dans le gisement de Guadalix de la Sierra (Madrid, Espagne). – Sciences (M. E. N.) *1,* 85–95.

ALVAREZ-RAMIS, C., ALMENDROS, G. and POLO, A. (1984): Precisiones histológicas y bioquímicas acerca de los ejemplares de *Frenelopsis* procedentes de Torrelaguna (Madrid). – Estudios Geológicos *40,* 107–113.

ALVAREZ-RAMIS, C. and DOUBINGER, J. (1994): Contribución al conocimiento de la palinoflora cretácica de la provincia de Madrid. Los Alcores, Guadalix de la Sierra. – Revista Española de Micropaleontología *26,* 1–18.

◄ Plate 3.2.

1. Fragment of gray calcareous marl including different fossil impressions, from member 6 of the local series of Cerro de la Mesa (MC).
2. Fragments of compact lignites, including plant tissues remains and seeds isolated from member 4 (L).
3. Very compact limestone, rich in macrofossils, showing a mummified conifer rest of *Frenelopsis oligostomata* (ROMARIZ) ALVIN, in member 6 (F).



Text-fig. 3.3.

Series of homologues compounds released by pyrolysis on the main forms of organic matter from Cerro de la Mesa: L = lignites, MC = carbonaceous marls, F = fossil rests of *Frenelopsis oligostomata*. Left to right, top to bottom: phenols, catechols, naphthalenes, naphthalenols, C_{14}-tricyclic aromatic hydrocarbons (anthracenes + phenanthrenes), tetralins, fluorenes, dibenzofurans, alkanes and olefins.

ALVAREZ-RAMIS, C. and FERNÁNDEZ MARRÓN, T. (1990): Caracterización palinológica del Cretácico superior del Cerro de la Mesa (Guadalix de la Sierra, Madrid). – 8. Simposio de Palinología A. P. L. E., Tenerife (Islas Canarias), 24/28. Septiembre 1990, Resúmenes.

ALVAREZ-RAMIS, C. and FERNÁNDEZ MARRÓN, T. (1993): Estudio palinológico preliminar de los niveles terminales del Cretácico superior del Cerro de la Mesa (Guadalix de la Sierra, Madrid). – In: Polen y esporas: Contribución a su conocimiento, ed: I. DE LA SERNA, 315–322.

ALVAREZ-RAMIS, C., FERNÁNDEZ MARRÓN, T. and GÓMEZ PORTER, P. (1989): Avance del estudio macropaleobotánico de la flora supracretácica del Cerro de la Mesa (Sierra de Guadarrama, Madrid). – II. European Palaeobotanical Conference, Madrid, September 1989, Abstracts, 15.

ALVAREZ-RAMIS, C., KEDVES, M. and FERNÁNDEZ MARRÓN, T. (1994a): Asociaciones esporopolínicas del Cretácico superior del Cerro de la Mesa (Guadalix de la Sierra, Provincia de Madrid). – Botánica Macaronésica.

ALVAREZ-RAMIS, C., KEDVES, M. and FERNÁNDEZ MARRÓN, T. (1994b): Consideraciones en torno a las asociaciones esporopolínicas del Cretácico superior del Cerro de la Mesa (Guadalix de la Sierra, Madrid). – Plant Cell Biology and Development (Szeged) *5,* 34–45.

SCHULTEN, H.-R., PLAGE, B. and SCHNITZER, M. (1991): A chemical structure for humic substances. – Naturwissenschaften *78,* 311–312.