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GEOCHEMICAL AND MOLECULAR STUDIES OF THE DEPOSITIONAL
ENVIRONMENTS OF SOURCE ROCKS AND THEIR DERIVED
OILS FROM THE BRAZILIAN MARGINAL BASINS.

BY

MARCIO ROCHA MELLO, B.Sc.

Thesis submitted to the University of Bristol

in partial fulfilment of the requirements for
the degree of doctor of Philosophy.

Organic Geochemistry Unit

School of Chemistry, University of Bristol

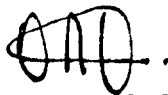
D. J. Johnson
J. Maxwell

TO LESLEY, MY MOTHER AND THE MEMORY OF MY FATHER.

Organic Geochemistry Unit
School of Chemistry, University of Bristol

MEMORANDUM

I certify that the work described in this thesis is my own
except where otherwise stated, and has not previously
been submitted for a degree at this, or any University.



MARCIO ROCHA MELLO

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ABSTRACT

A geochemical survey of Brazilian marginal basins using a wide selection of source rocks and oils, ranging from Lower Cretaceous to Tertiary in age, has been undertaken. The aims were to assess the palaeoenvironment of deposition of the source rocks, to correlate reservoir oils with their putative source rocks and to understand the effects of maturity on the composition and absolute concentrations of biological markers. The geochemical analyses included evaluation of organic carbon contents, Rock-Eval pyrolysis data, vitrinite reflectance measurements, determination of carbon isotope ratios, elemental and visual kerogen analysis, and molecular studies involving liquid and gas chromatography, qualitative and quantitative biological marker investigations using GC-MS, metastable GC-MS and GC-MS/MS for saturated and aromatic hydrocarbons, and UV/vis spectrophotometry, probe MS and HPLC for metalloporphyrins. The metastable ion GC-MS data were evaluated using principal component analysis.

Integration of the results with geological and paleontological data provides the recognition and differentiation of seven depositional regimes, namely lacustrine freshwater, lacustrine saline water, marine evaporitic, marine carbonate, marine deltaic with carbonate influence, open marine highly anoxic with a predominance of calcareous mudstone lithology, and open marine anoxic, with predominance of siliciclastic lithology.

The analyses of the oils reveal significant differences between groups which enable a correlation with putative source rocks laid down in five of the above depositional regimes: lacustrine freshwater; lacustrine saline water; marine evaporitic; marine carbonate and marine deltaic with carbonate influence.

The quantitative approach used to determine the effect of thermal maturity on the composition and concentration of the

biological markers shows that care must be taken in their use as maturity indicators, since source input and mineral matrix might play an important role. On the other hand, it also shows that the concentrations decrease considerably between the onset of petroleum generation and its peak. Thus, care must also be exercised when using biological marker concentration in palaeoenvironmental assessment

The metalloporphyrins in a selection of organic rich sediments have also been examined. The results suggest that their distributions can be a useful auxiliary tool in the characterisation of depositional environments of petroleum source rocks.

Finally, a combined geochemical and micropalaeontological study of Cenomanian to Maastrichtian pelitic sediments from the continental margin extends the occurrence of the recognised Cenomanian-Turonian and Santonian "oceanic anoxic events". As an extension, the presence of such events in the Coniacian is reported. In contrast, the Campanian-Maastrichtian appears to be a time interval when deposition under oxygenated conditions produced sediments with low organic carbon contents and poor hydrocarbon source potential.

In summary, biological marker characteristics of organic-rich sediments can distinguish different types of depositional environments, allow oil-source rock correlations, and the assessment of the depositional environment of the source rocks from analysis only of the oils. Thus, this thesis provides a framework of biological marker characteristics which can be compared with samples from other parts of the world.

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I would like to thank Drs. J.R. Maxwell and S.C. Brassell for the time, hard work, much help and good advice throughout this study. I am especially grateful to both Prof. G. Eglinton, Mrs. A.P. Gowar and Mrs. S.E. Trott for their kindly friendship and support, as well as many past and present members of the Organic Geochemistry Unit, particularly Drs. P. Farrimond, T. Peakman, G. Abbott, M.I. Chicarelli and P. Shaw and to R. Sleeman, B.J. Keely, L. Dyas, J. Robson and J. Waring. The technical assistance and advice of A. Gowar, L. Dyas was of fundamental importance to this work.

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INTRODUCTION

The differentiation and assessment of the features of palaeoenvironments of deposition of petroleum source rocks are gaining in importance. Recently it has been shown that saline lakes and restricted evaporitic environments such as in China and lacustrine freshwater on Australia, show diagnostic biological marker features. Organic-rich sediments from widely occurring and known environments of deposition, in the Brazilian marginal basins, provide an excellent opportunity to identify distinguishing features in their biological marker distributions and concentrations from a single geographical realm.

This work describes the use of a multidisciplinary approach (geochemical, geological, palaeontological and statistical) in the differentiation and assessment of the environments of deposition. Also, it addresses some key questions relating to the understanding of the effects of maturity on the composition and absolute concentration of biological markers, and provide a model for oil-source rock correlation using metastable ion GC-MS elution profiles and principal component analysis.

This research follows on from previous published work describing the application of the distribution and relative abundances of biological markers in petroleum geochemistry. Also, it extends earlier preliminary studies, of samples from some of the basins, carried out in the Petrobras Research Centre, Brazil. One key point is the application of an approach based on absolute concentrations of selected biological markers (ppm of extract and oil) in the characterisation of palaeoenvironment of deposition and in petroleum generation.

The flow diagram in Fig. 1 illustrates most of the analytical techniques and preparative steps.

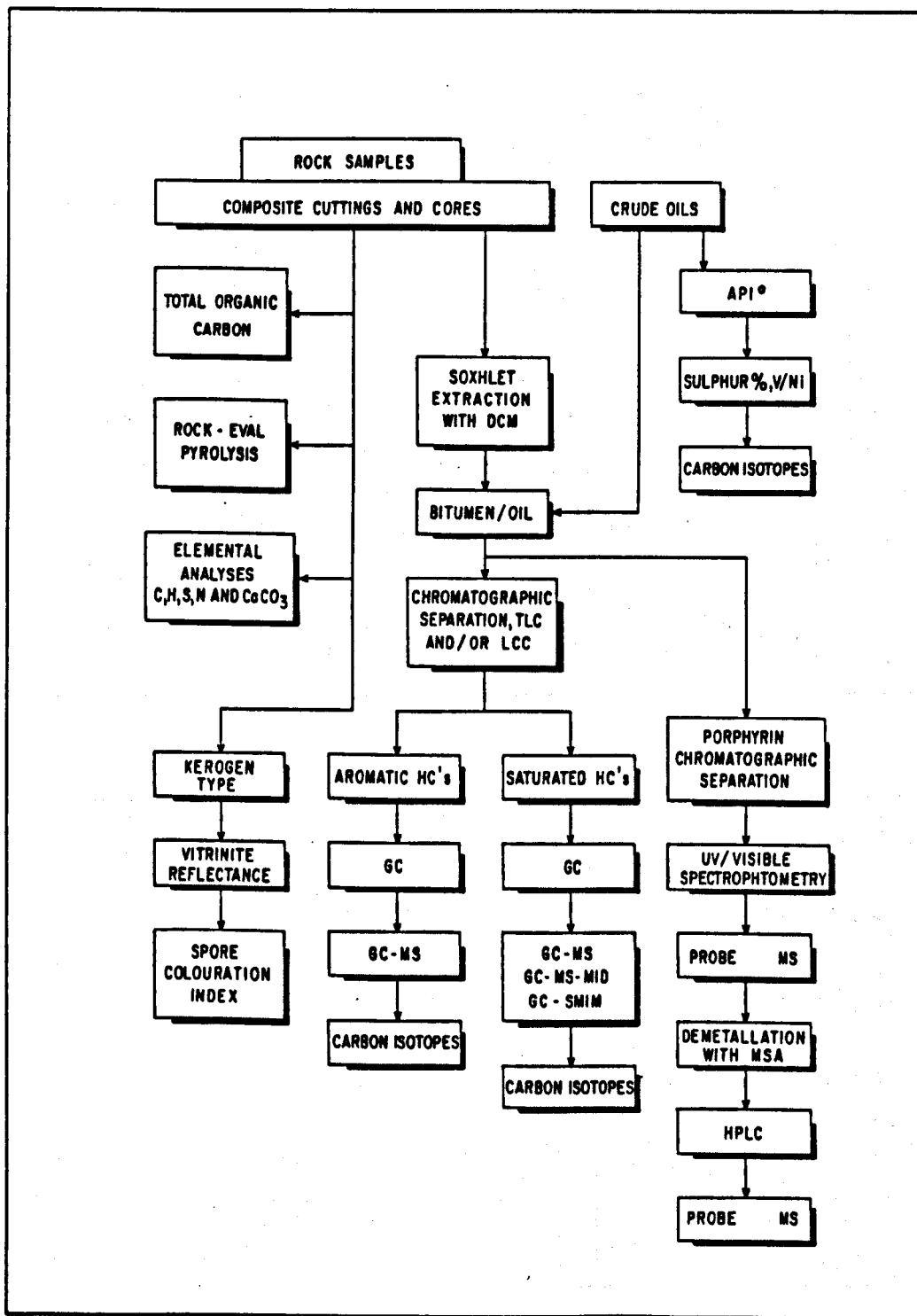


Figure 1- Flow diagram, analytical procedure.

In total, eighty oil samples and two hundred rock samples recovered from reservoirs and sedimentary successions respectively, ranging from lower Neocomian to Oligocene in age,

TABLE 1 - Rock Sample Types and Locations.

Sample No.	Well	Depth (m)	Basin	Type
1	BAS-18	2790	Bahia Sul	Cuttings
2	BAS-64	2250	Bahia Sul	Cuttings
3	BAS-32	2268	Bahia Sul	Core
4	CES-14	2511	Ceara	Cuttings
5	CES-37D	3501	Ceara	Cuttings
6	PTA-1	1731	Sergipe/Alagoas	Core
7	CS-1	1515	Sergipe/Alagoas	Core
8	CB-6	1800	Sergipe/Alagoas	Core
9	RNS-13	2598	Potiguar	Cuttings
10	RNS-35	2274	Potiguar	Core
11	RD-1	2895	Espirito Santo	Cuttings
12	ESS-43	2532	Espirito Santo	Core
13	IP-1	3370	Espirito Santo	Core
14	ESS-34	2310	Espirito Santo	Cuttings
15	RJS-101	4410	Campos	Core
16	RJS-71	3060	Campos	Core
17	RJS-76	4835	Campos	Cuttings
18	RJS-226	3597	Campos	Core
19	RJS-51	3318	Campos	Core
20	RJS-164	4260	Campos	Core
21	UPN-1	1337	Campos	Core
22	CES-7	2094	Ceara	Core
23	CES-41	2685	Ceara	Core
24	FGT-1	1557	Sergipe/Alagoas	Cuttings
25	RNS-15	2190	Potiguar	Cuttings
26	CES-42	3006	Ceara	Core
27	BAS-35	2400	Bahia Sul	Core
28	CAU-2	1510	Sergipe/Alagoas	Core
29	FGT-1	1938	Potiguar	Cuttings

Sample No.	Well	Depth (m)	Basin	Type
30	BAS-37	1653	Bahia Sul	Core
31	CES-42	3420	Ceara	Core
32	APS-29	4459	Cassipore	Core
33	BAS-35	2313	Bahia Sul	Core
34	CAU-3	1386	Sergipe/Alagoas	Cuttings
35	SES-14	1623	Sergipe/Alagoas	Cuttings
36	APS-31	4775	Cassipore	Cuttings
37	RJS-30	3348	Campos	Cuttings
38	FRG-1	1615	Espirito Santo	Core
39	ESS-23	2189	Espirito Santo	Core
40	ANG-1	1320	Sergipe/Alagoas	Core
41	ALS-11	1239	Sergipe/Alagoas	Cuttings
42	CES-56	1995	Ceara	Cuttings
43	APS-36	4230	Cassipore	Cuttings
44	MAS-10	3016	Maranhao	Cuttings
45	CES-50	1461	Ceara	Cuttings
46	CES-56	1710	Ceara	Cuttings
47	CES-19	1950	Ceara	Core
48	CES-28	1911	Ceara	Core
49	APS-29	4320	Cassipore	Cuttings
50	CAU-3	700	Sergipe/Alagoas	Cuttings
51	RJS-225	1902	Campos	Cuttings
52	ESS-46	3210	Espirito Santo	Cuttings
53	ESS-24	3264	Espirito Santo	Cuttings
54	CES-42	2550	Ceara	Core
55	ALS-30	1900	Sergipe/Alagoas	Cuttings
56	ALS-27	2301	Sergipe/Alagoas	Cuttings
57	RNS-15	1428	Potiguar	Core
58	CES-42	2400	Ceara	Core

TABLE 2 - Oil Sample Locations

Sample Number	Wells	Depth (m)	Basin
1	CES-8	1696	Ceara
2	BAS-48	2780	Bahia Sul
3	BAS-64	2340	Bahia Sul
4	PIR-4	1841	Sergipe/Alagoas
5	RNS-53	2289	Potiguar
6	RB-12	2306	Sergipe/Alagoas
7	AG-16D	2172	Potiguar
8	SE-1	1340	Potiguar
9	ESS-38	1947	Espirito Santo
10	LP-3	1524	Espirito Santo
11	RI-29	1047	Espirito Santo
12	ESS-26	2700	Espirito Santo
13	SM-35	1422	Espirito Santo
14	RJS-305	3166	Campos
15	RJS-49	2857	Campos
16	RJS-41	2210	Campos

Sample Number	Wells	Depth (m)	Basin
17	RJS-139	2814	Campos
18	GP-1	2680	Campos
19	RNS-10	1953	Potiguar
20	ARG-1	256	Potiguar
21	FZB-1	376	Potiguar
22	CES-8	1475	Ceara
23	CES-41	2764	Ceara
24	SES-77	1998	Sergipe/Alagoas
25	TM-5	999	Sergipe/Alagoas
26	BAS-11	1915	Bahia Sul
27	CP-678	623	Sergipe/Alagoas
28	APS-27	1107	Cassipore
29	MAS-5	2889	Maranhao
30	PAS-9	4291	Para
31	PAS-11	4289	Para

were analysed initially in relation to Chapters II - IV, and VI and VII. All these samples were investigated by Pyrolysis Rock-Eval, total organic carbon, organic petrography, carbon isotope and elemental analysis, gas chromatography and gas chromatography-mass spectrometry. The source rocks cover a range of maturity values (0.45 to 0.9% Ro) but only those with Ro values between 0.45 and 0.75% were selected for relative and absolute biological marker quantitation and porphyrin analysis, because of the effects of the increase of maturation on the concentrations of biological markers (Rullkötter *et al.*, 1984; cf. Chapter V). Similarly, only oils with medium to high API gravities and not severely affected by biodegradation were investigated. In summary, 58 representative organic-rich sediments (Table 1) ranging in age from lower Neocomian to Eocene and 31 oil samples (Table 2) from nine majors Brazilian marginal basins were selected to be examined by GC-MS using a synthesised deuteriated sterane standard in order to obtain an absolute concentrations of selected biological markers. In addition most were analysed by linked scan MS and GC-MS/MS. For the maturation study (Chapter V) an additional six samples were examined.

This work comprises of eight chapters. Each is divided into sections and subsections numbered sequentially. Compound assignments are shown in appendix I. Appendix II shows the measurement procedures for the concentrations and relative abundances of the biological markers. Structures are presented in appendix III. References are given after Chapter VIII.

Chapter I reviews and utilises some geological, palaeontological, sedimentological and geochemical aspects of the Brazilian marginal basins, in order to characterise the palaeoenvironments of deposition of a succession of organic rich sediments, ranging in age from lower Neocomian to Oligocene. For each of the proposed types of depositional environments, some bulk geochemical properties are included to assist in this characterisation. Chapter II provides an investigation of bulk, isotopic and molecular features of a

wide selection of source rocks from Brazilian marginal basins, ranging from Lower Cretaceous to Tertiary in age. Chapter III describes a combined geochemical, molecular and statistical characterisation of a wide selection of oils from the major Brazilian marginal basins. The distinction of the groups appears to reflect differences in the depositional environment of the source rocks of the oils. Each group is correlated with source rocks laid down in a specific depositional regime. Chapter IV provides a review of current knowledge about biological marker features used to assist in assigning the depositional palaeoenvironments of ancient organic-rich sedimentary rocks and petroleums by drawing on the literature and on the findings in Chapters II and III. Chapter V reviews and extends the application of bulk and biological marker properties to the assessment of the thermal maturity of a given sedimentary sequence. It aims to address some key questions relating to the understanding of the effects of maturity on the composition and absolute concentration of biological markers from organic-rich sediments. Chapter VI discusses the alkyl metalloporphyrin distribution and concentrations of a selection of the sediments in a preliminary study of the features of such compounds in relation to their characteristics for different depositional environments. Chapter VII illustrates a combined geochemical and micropalaeontological study of Cenomanian to Maastrichtian pelitic sediments from the Brazilian continental margin, aiming to characterise and extend the occurrence and distribution of the known worldwide Cenomanian-Santonian anoxic events "AOEs". Finally, chapter VIII describes the analytical procedures which were employed.

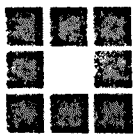
Several of the findings of this work are in press in three major journals:

1-M.R.MELLO, P.C.GAGLIANONE, S.C.BRASSELL & J.R.MAXWELL (1988). Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. In Marine and

Petroleum Geology. Butterworths and the Geological Society, London.

2-M.R.MELLO, N.TELNAES, P.C.GAGLIANONE, M.I.CHICARELLI, S.C.BRASSELL & J.R.MAXWELL (1988). Organic geochemical characterisation of depositional palaeoenvironments of source rocks and oils in Brazilian marginal basins. In Advances in Organic Geochemistry 1987 (Edited by Mattavelli, L. and Novelli, L.) Pergamon Journals, Oxford.

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CHAPTER I

CHAPTER I

GEOLOGY AND PALAEOENVIRONMENTAL ASSESSMENT
OF BRAZILIAN MARGINAL BASINS

This chapter reviews and utilises some geological, palaeontological, sedimentological and geochemical aspects of the Brazilian marginal basins, in order to characterise the palaeoenvironments of deposition of a succession of organic rich sediments, ranging in age from lower Neocomian to Oligocene. For each of the proposed types of depositional environments, some bulk geochemical properties are included to assist in this characterisation, although these properties are given and discussed in more detail in chapter II.

1.1 GENERAL GEOLOGY

The Brazilian marginal basins are directly related to the rupture of the African and South American plates. They originated as new accretionary plate boundaries, but once formed they ceased to be plate boundaries and now mark the junction between oceanic and continental crust within plate interiors. The almost 8000 Km long set of basins (Fig. 1) can be classified as components of a typical divergent, mature, atlantic-type continental margin (Ponte & Asmus, 1978; Ojeda y Ojeda, 1982; Estrella et al., 1984). Based on their tectono-sedimentary sequence, they can be linked to a single evolutionary geological history (Fig. 2), which can be divided in three main stages: pre-rift, rift and drift (gulf proto-oceanic and oceanic phases; Asmus, 1975).

The Late Jurassic/ Early Cretaceous pre-rift stage is associated with stretching of the continental crust and lithosphere. This phenomenon resulted in block faulting, sedimentary troughs and localized mafic volcanism associated with thinning of the underlying crust and mantle, and with an upwelling of the asthenosphere producing a thermal anomaly (Bott, 1976).

The Neocomian rift stage (Fig. 3A), as an evolutionary consequence of such processes, is a direct result of an overall subsidence produced by the thinning of the lithosphere. The rifting process is generally associated with a basement-involved block rotated faulting, and intense and widespread mafic volcanism (Bott, 1976; Mohriak & Dewey, 1987). As a result, a thick sedimentary succession comprising continental, fluvial and lacustrine siliciclastic and carbonate sediments was deposited. The section is mainly composed of fine to coarse clastics and carbonates deposited in freshwater to saline lacustrine environments (e.g. Viana et al., 1971; Bertani and Carozzi, 1984). In some areas it overlies, and is intercalated with volcanic rocks, which are mainly basalts. After rifting, tectonic activity appears to have been restricted to subsidence

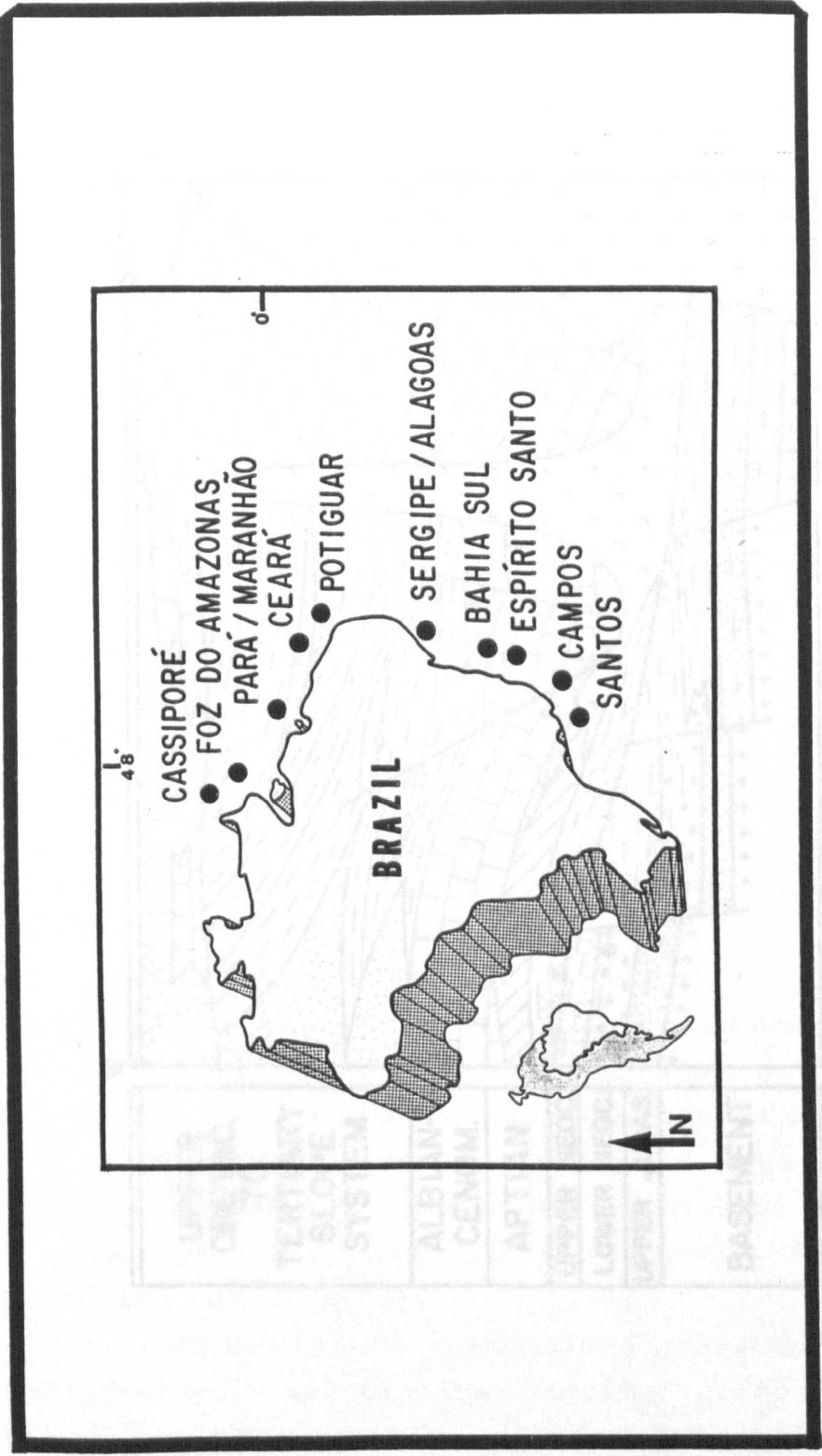
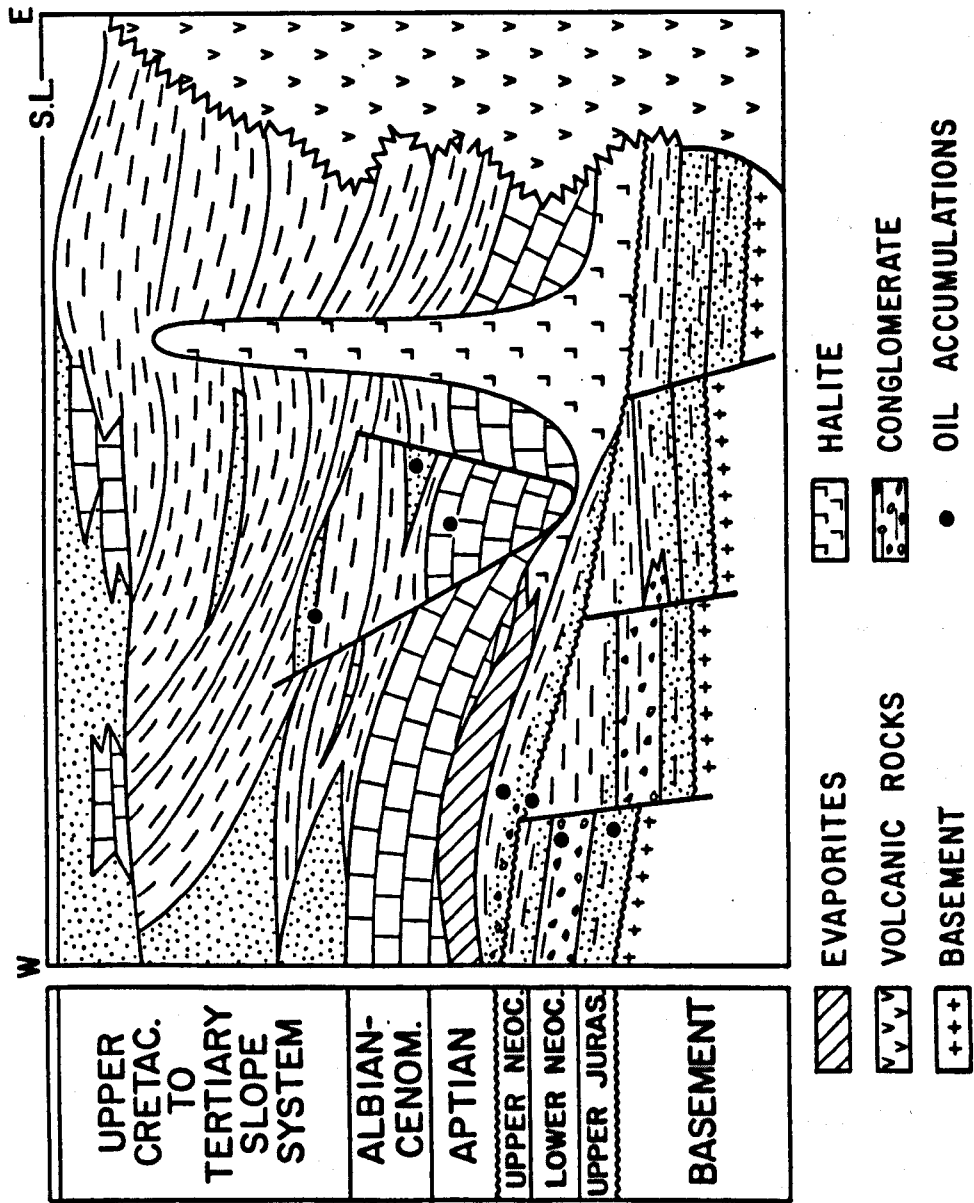


Figure 1- Location map of the Brazilian marginal basins.

Figure 2- Schematic stratigraphic and structural section for the Brazilian marginal basins.



UPPER CRETAC. TO TERTIARY SLOPE SYSTEM
ALBIAN-CENOM.
APTIAN
UPPER NEOC.
LOWER NEOC.
UPPER JURAS.
BASEMENT

- EVAPORITES
- VOLCANIC ROCKS
- BASEMENT
- HALITE
- CONGLOMERATE
- OIL ACCUMULATIONS

and basinward tilting, with the development of gravity sliding features (Falkenhein, 1981) and localized reactivation of faults (Ponte & Asmus, 1978).

The rifting phase ceased once sea floor spreading starts, with the succeeding drifting stage being characterized by flexural subsidence of the margin without conspicuous faulting. This phenomena is attributed to progressive cooling and contraction of the underlying lithosphere (Bott, 1976).

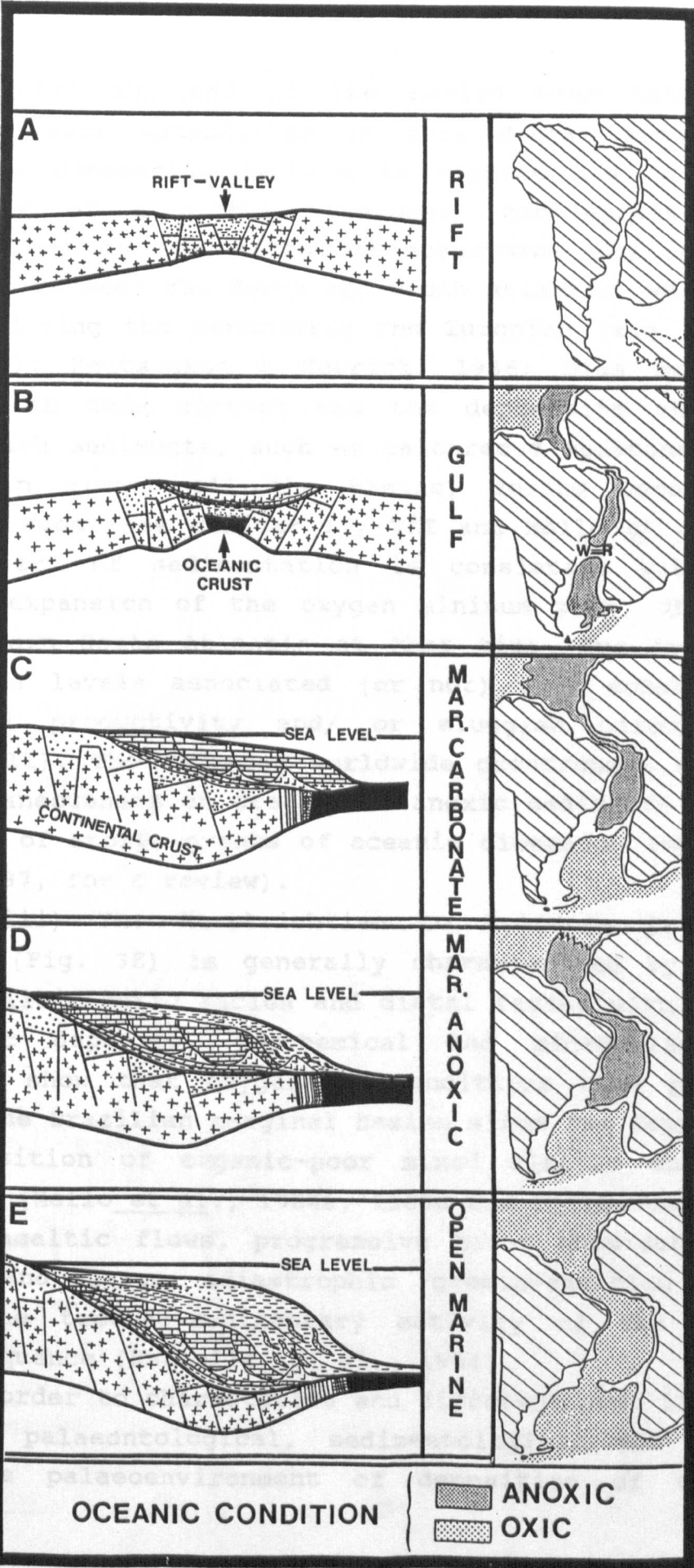
The resulting drift stage can be subdivided into two distinct phases: gulf proto-oceanic and oceanic. The gulf proto-oceanic phase (Fig. 3B) is associated with the first marine incursions into the coastal basins during the Aptian. The combination of tectonic quiescence, topographical barriers and arid climate led to a low clastic influx and restricted conditions appropriate for deposition of mixed carbonate and siliciclastic sediments together with evaporites in coastal, shallow continental to marine hypersaline environments (Asmus, 1975).

The oceanic phase (Fig. 3C) is a consequence of increasing sea floor spreading and the continuous subsidence of the Brazilian continental margin. Differences in palaeoenvironmental settings allow the subdivision of this phase into three major sequences:

i) The Albian marine carbonate sequence (Fig. 3C) is characterised mainly by platform and slope carbonate sediments deposited in a neritic to upper bathyal environment in a shallow and narrow epicontinental sea (Koutsoukos & Dias-Brito, 1987). This carbonate succession appears to have been linked with conditions of tectonic quiescence, with some adiastraphic tectonism often associated with listric detached faults soling out on the Aptian salt (Fig.2).

ii) The Cenomanian to Campanian/ Maastrichtian open marine shelf-slope sedimentary system (Fig. 3D), is characterised by predominantly siliciclastic and calcareous mudstone deposition in progressively deepening basins (e.g. Koutsoukos, 1987). The maximum water depths in this system took

Figure 3- Evolution of the Brazilian marginal basins through Cretaceous/ Tertiary times showing the distribution of depositional environments (modified from Tissot et al (1980) and Carozzi & Falkenhein (1985). W=R, Walvis Ridge.



place towards the end of the period when bathyal/abyssal conditions were established in more distal areas. In some areas, the Cenomanian section is missing and is probably a consequence of a global erosional/ non-depositional event brought about by the effective structural and oceanographic connection between the North and South Atlantic, which occurred sometime during the Cenomanian and Turonian (e.g. Koutsoukos, 1984, 1987; Koutsoukos & Merrick, 1986; Dias Brito, 1987). Important in this context was the deposition of widespread organic-rich sediments, such as calcareous mudstones and black shales, in almost all the basins, during Cenomanian to Santonian ages (see chapter II, VII and Mello et al., 1988c). This pattern of sedimentation is consistent with times of vertical expansion of the oxygen minimum zone, ubiquitous in the northern South Atlantic at that time, due to periods of rising sea levels associated (or not) with enhanced primary biological productivity and/ or sluggish circulation (cf. Chapter VII). The reported worldwide occurrences and apparent contemporaneousness of Cretaceous anoxic sediments have led to proposals of anoxic events of oceanic dimension (see Schlanger et al., 1987, for a review).

iii) The Maastrichtian to Holocene progradational sequence (Fig. 3E) is generally characterised by a proximal coarse siliciclastic facies and distal facies with pelitic and turbiditic deposits. Geochemical and micropalaeontological evidences show that oxygenated conditions have prevailed in most of the Brazilian marginal basins since the Campanian, with the deposition of organic-poor mixed clastic and carbonate sediments (Mello et al., 1984a, 1988c and references therein).

Local basaltic flows, progressive basin subsidence, tilting seaward and large adiasprophic growth-faulting structures marked the tectono-sedimentary activity of the whole open marine sequence (Estrella et al., 1984).

In order to characterise and differentiate, in accordance with the palaeontological, sedimentological and geochemical data, the palaeoenvironment of deposition of organic-rich

sediments found in the Brazilian marginal basins, each tectono-sedimentary stage is discussed separately, from a genetic point of view, in the following sections :

1.2 PRE-RIFT STAGE

The Upper Jurassic/ Lower Neocomian pre-rift stage in the Brazilian marginal basins is associated with a sedimentary succession made up of continental, fluvial and delta-lacustrine siliciclastic oxidized sediments (Fig. 2; Medeiros *et al.*, 1971; Schaller, 1969). Generally, this section is composed mainly of red beds of fine to coarse clastic sediments deposited, under highly oxygenated conditions in braided fluvial facies, associated with an eolic facies and shallow freshwater to saline lake environments (Fig. 4; Netto *et al.*, 1982; Azambuja, 1987). Due to those environmental conditions, the pelitic sediments show a very low organic carbon content (< 0.5%) comprised mainly of oxidized higher plant debris, and consequently were not studied further.

1.3 RIFT STAGE

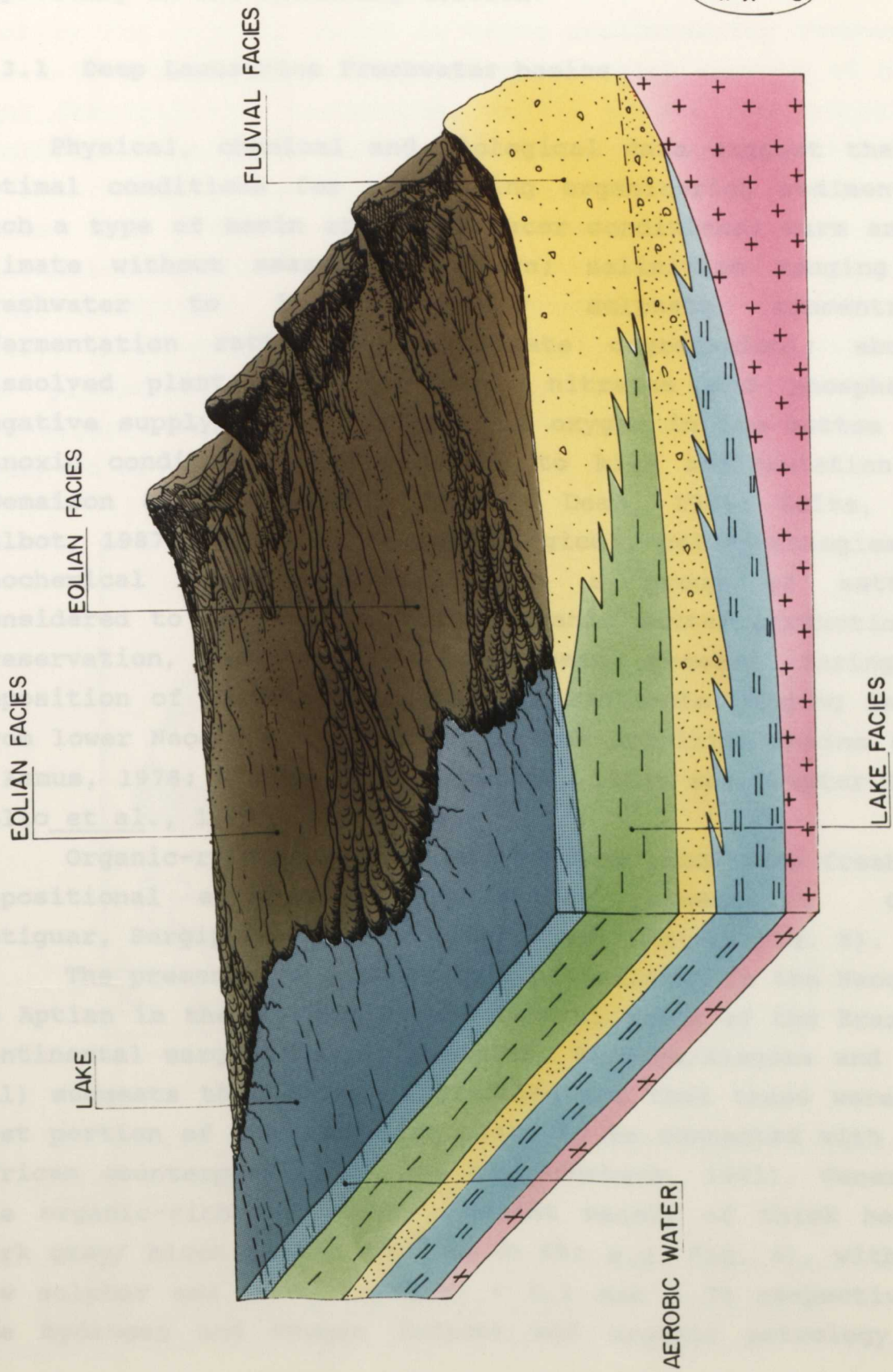
Palaeogeographical and geological evidence suggests that the organic-rich Neocomian rift-stage sedimentary succession was deposited in lacustrine environments. The formation and behaviour of such lacustrine systems are function of a number of physical processes whose relative importance is mainly influenced by tectonic setting, morphology, salinity and water chemistry and climatic conditions. Based upon sedimentological, palaeontological and geochemical data (see below and Chapter II) it is possible to differentiate two distinct organic-rich lacustrine systems in the rift stage:

i) A relatively large, deep lacustrine freshwater type of basins, ranging in age from Lower Neocomian to Aptian.

ii) A closed and shallow Upper Neocomian lake system, having saline to hypersaline waters of alkaline affinities. On

Figure 4- Schematic block diagram showing the sedimentary facies in a braided fluvial, eolic and shallow fresh to brackish water lacustrine depositional environments from the Pre-Rift stage in the Brazilian basins (modified from Medeiros & Ponte (1981)).

PRE-RIFT



the basis of such differences, each one is discussed separately in the following section.

1.3.1 Deep Lacustrine Freshwater basins

Physical, chemical and biological data suggest that the optimal conditions for producing organic-rich sediments in such a type of basin are: Deep water conditions; warm and wet climate without seasonal overturn; salinities ranging from freshwater to brackish; low sulphate concentration (fermentation rather than sulphate degradation); abundant dissolved plant nutrients (e.g. nitrates and phosphates); negative supply/ demand balance of oxygen in the bottom water (anoxic conditions) and moderate to high sedimentation rate (Demaison & Moore, 1980; Fouch & Dean, 1984; Kelts, 1987; Talbot, 1987). Based on sedimentological, palaeontological and geochemical interpretations, such a group of settings, considered to be favourable for organic matter production and preservation, appears to have been present during the deposition of lacustrine freshwater sediments ranging in ages from lower Neocomian to Aptian, in the Brazilian basins (Ponte & Asmus, 1978; Viana, 1980; Schaller, 1969; see Chapter II and Mello *et al.*, 1984a, 1988a, b).

Organic-rich sediments derived from lacustrine freshwater depositional environment are mainly present in Ceará, Potiguar, Sergipe/Alagoas and Bahia Sul basins (Fig. 5).

The presence of most of this palaeolakes in the Neocomian to Aptian in the Equatorial and Central areas of the Brazilian Continental margin (Ceará, Potiguar, Sergipe/Alagoas and Bahia Sul) suggests the timing of drifting and that these were the last portion of the Brazilian plate to be connected with their African counterpart (Fig. 3A; cf. Rohrback, 1981). Generally, the organic-rich sediments consist mainly of thick beds of dark grey/ black shales (TOC up to 6%; e.g. Fig. 6), with very low sulphur and CaCO_3 content (< 0.1 and $< 7\%$ respectively). The hydrogen and oxygen indices and organic petrology data

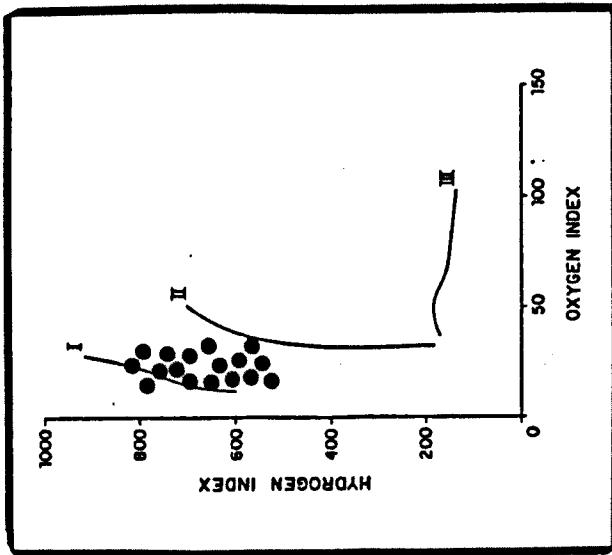
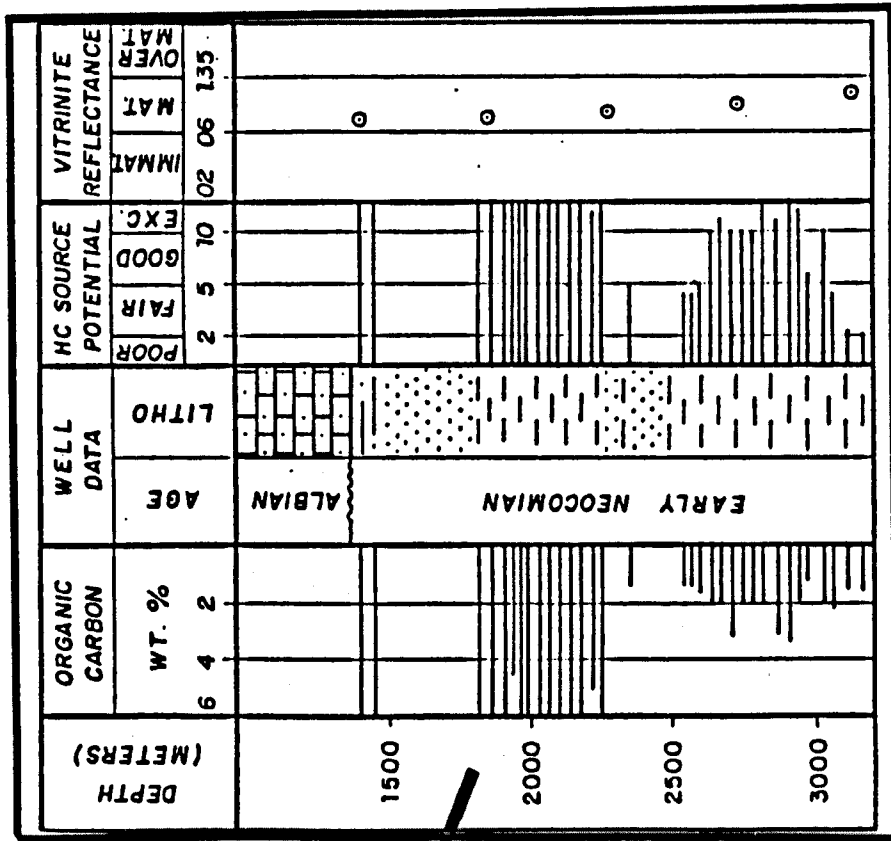
identify the organic matter as being predominantly composed of type I/II kerogen (e.g. Fig. 6), where high amounts of higher plant debris (25-35% herbaceous, mainly pollens and spores) are associated with lipid-rich (algal freshwater) organic matter (45-60%). These data suggest that algal blooms, higher plant debris and nutrient input in the photic and aerobic zone (shallow waters) enhanced anaerobic bacterial activity and anoxic conditions in the bottom waters (deep parts of the lakes), thus, creating ideal biological and chemical conditions for preserving organic matter (hydrogen index up to 600 mg HC/g organic carbon; hydrocarbon source potential up to 40 Kg of Hc/ton of rock; e.g. Fig. 6).



Fig. 5- Location map showing the basins where organic-rich lacustrine freshwater sediments occur.

The geochemical and biological marker data also support the anoxic freshwater sometimes brackish character of such sediments, and are discussed in detail elsewhere (Chapter II, see also Mello et al., 1988 a, b). The fossil biota are characterised by the presence of organisms typical of

Figure 6- Geochemical well log, showing the stratigraphic position for the lacustrine freshwater organic-rich sediments deposited during the early Neocomian and the hydrogen index (S₂/ TOC) vs oxygen index (S₃/ TOC), presented on van Krevelen type diagram.



freshwater lakes, such as ostracods, gastropods, conchostraceans, pelecypods, fishes, charophytes and reptils (Viana, 1980; Schaller, 1969; Ghignone & De Andrade, 1970). On the other hand, the inference of a deep water settings is supported by palaeontological data, e.g. shell ornamentation; ostracods with thin and delicately ornamented tests (De Deckker, 1987; Tölderer-Farmer et al., 1987), and the occurrence of particular sedimentary facies and structures, e.g. large turbidite deposits associated with deep water shales (Viana et al., 1971; Netto et al., 1982). The block diagram in Fig. 7, shows a proposed illustration of the main depositional facies of the deep lacustrine freshwater environment of the rift stage. The most organic rich and thickest deposits appear to have developed in an open lacustrine system, generally associated with the depocentre of the basin (deeper part of the palaeolakes). Detailed descriptions of a number of analogous ancient and contemporary deep freshwater systems have been reported. Noteworthy ancient examples include the Songliao and Shanganning basins in China (Powell, 1986; Wang Tieguan et al., 1988), Otway basin, Australia (Mckirdy et al., 1986). Analogous modern examples appear to be lakes Tanganyika and Kivu in the Eastern African Rift System (Demaison & Moore, 1980).

1.3.2 Shallow Saline to Hypersaline Lake Systems of Alkaline Affinities.

This type of lakes generally occur in areas of high evaporation (semi-arid/moist climates). The large amount of nutrients available in the highly saline waters, generally associated with alkaline springs, enhance the development of well adapted, limited aqueous species that, without competition, show prolific productivity. The result is a tremendous input of algal and bacterial organic matter within the lake.

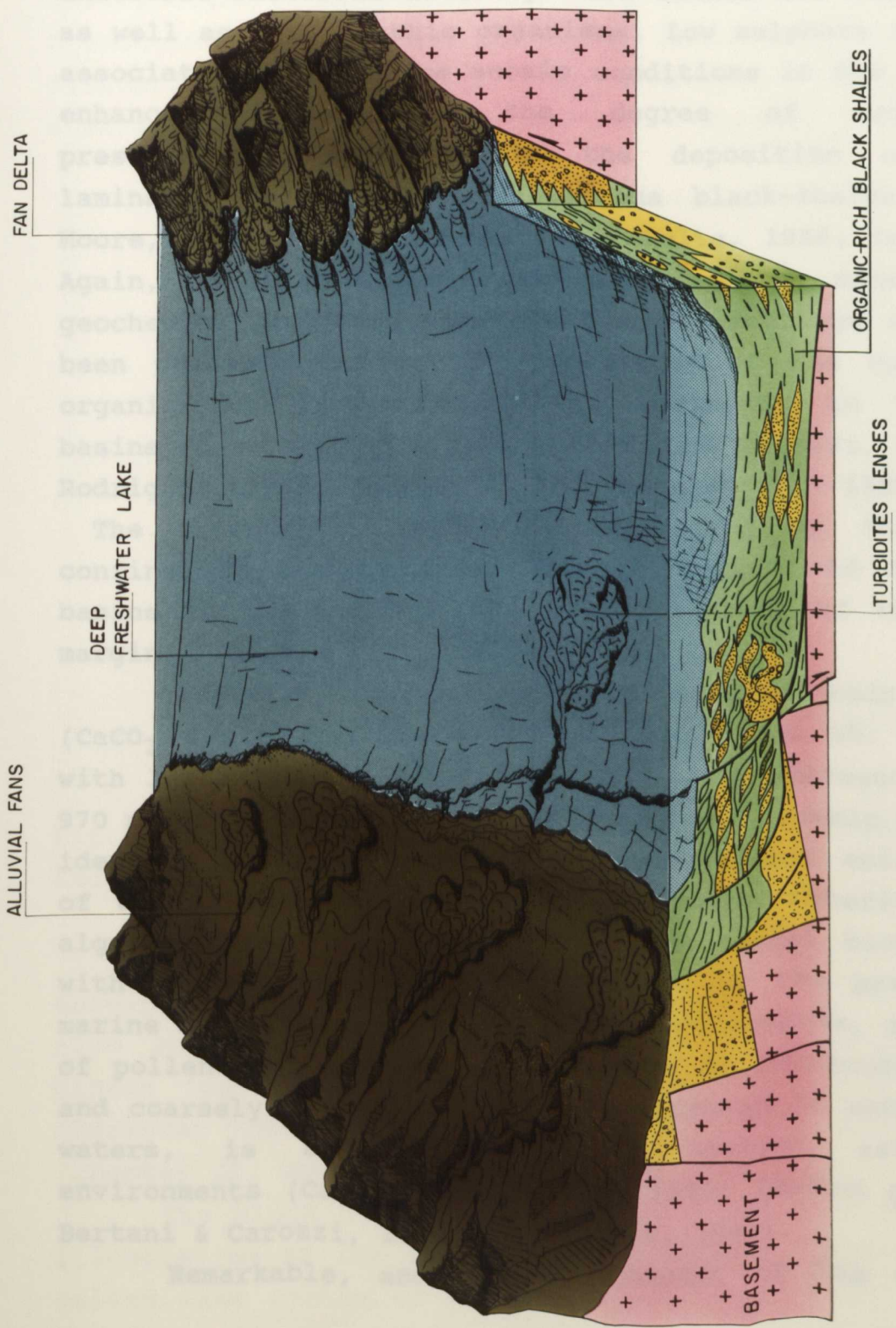
The differences in salinity between an upper aerobic, less

Figure 7- Schematic block diagram showing the sedimentary facies in a deep freshwater lake from the Rift stage in the Brazilian marginal basins (modified from Azambuja Filho (1987)).

LACUSTRINE FRESHWATER

saline layer and a lower anoxic, very saline, very rich layer (higher density) enhance the stability, leading to a... water anoxia. These conditions, without anaerobic bacterial activity are... as well as... associa... enhan... pre... ligni...

Des. Mattos



ANALOGOUS EXAMPLES

ANCIENT : SONGLIAO BASIN - CHINA,
EROMANGA BASIN - AUSTRALIA.

RECENT : LAKES TANGANIKA AND KIVU - EASTERN AFRICAN RIFT.

saline layer and a lower anaerobic, very saline and alkaline rich layer (higher density) enhance the water column stability, leading to stratification and permanent bottom water anoxia. These conditions, although they enhance anaerobic bacterial activity are lethal for macrolife forms, as well as for benthic organisms. Low sulphate concentrations associated with extreme anoxic conditions in the bottom waters enhances dramatically the degree of organic matter preservation, resulting in the deposition of well laminated, organic-rich calcareous black-shales (Demaison & Moore, 1980; Dean & Fouch, 1983; Kelts, 1988; Deckker, 1988). Again, sedimentological, palaeontological, mineralogical and geochemical evidence shows that such settings appear to have been present during the deposition of the Upper Neocomian organic-rich lacustrine saline sediments in the Brazilian basins (Castro et al., 1981 ; Bertani & Carozzi, 1984; Takaki & Rodrigues, 1984; Chapter II and Mello et al., 1988a, b).

The organic-rich sediments belonging to this group are confined to the Sergipe/Alagoas, Campos and Espirito Santo basins in the northern and southern areas of the continental margin (Fig. 8).

Generally, they are composed of thick beds of calcareous (CaCO_3 up to 18%) black shales (TOC up to 9%; e.g. Fig. 9), with low sulphur content (< 0.5). The hydrogen index (up to 970 mg HC/ g organic carbon; Fig. 9) and organic petrology data identify the organic matter as being almost entirely composed of type I kerogen, made up of amorphous material (lipid-rich algal and bacterially derived). The fossil biota, associated with these lakes are characterised by the presence of non-marine organisms such as ostracods, pelecypods, gastropods, and of pollens and spores. The presence of ostracods with thicker and coarsely reticulated shells, secreted in extreme saturated waters, is an indication of shallow saline alkaline environments (Castro & Azambuja, 1980; Castro et al., 1981; Bertani & Carozzi, 1984; De Deckker, 1988).

Remarkable, and also diagnostic of the shallow saline

alkaline character, is the mineralogical assemblage found; e.g. the widespread occurrence of gypsum and anhydrite moulds, the distribution of diagenetic minerals syndepositionally formed as trioctahedral smectites, dolomite, zeolites of the heulandite-clinoptilolite type, and some authigenic minerals such as stenvensite/talc/sepiolite (Bertani & Carozzi, 1984).

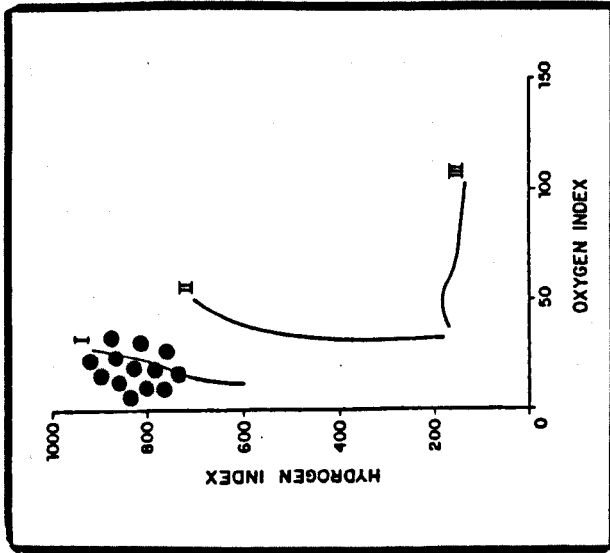
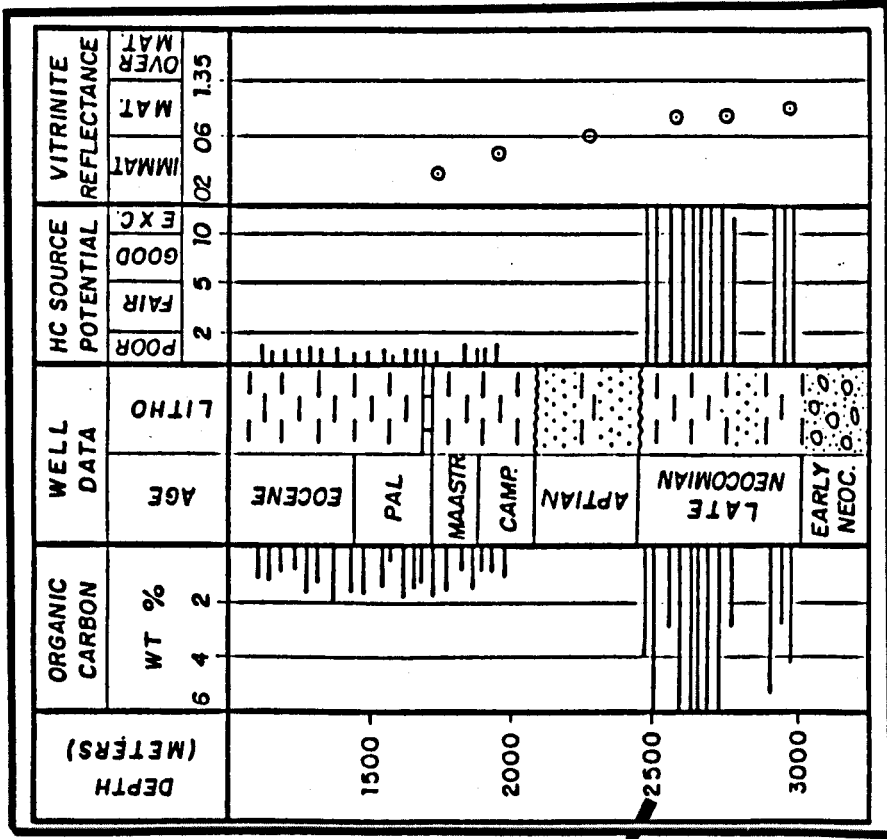


Fig. 8- Location map showing the basins where organic-rich lacustrine saline water sediments occur.

The isotopic composition data (carbonate of the fossils showing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between 1.0‰ and - 1.0‰), also suggest saline conditions (Takaki & Rodrigues, 1984). Others important diagnostic features that support the saline character came from geochemical and biological marker data (chapter II, see also Mello et al., 1988a, b).

The block diagram in Fig. 10 shows a proposed schematic illustration of the main sedimentological facies, of a shallow saline lake system of alkaline affinities that appear to have dominated the palaeoenvironment of deposition during the Upper Neocomian times in the rift stage of the Campos and Espirito

Figure 9- Geochemical well log, showing the stratigraphic position for the lacustrine saline water organic-rich sediments deposited during the late Neocomian and the hydrogen index (S_2 /TOC) vs oxygen index (S_3 / TOC), presented on van Krevelen type diagram.



Santo basins. As observed in the deep lacustrine freshwater basins, the thickest and most organic-rich deposits appears to be associated with an open lacustrine facies that generally correspond to the deeper parts of these shallow palaeolakes. It is noteworthy to mention, however, that in this case, conversely to the former, the depocentre of basin does not appear to correspond with the deep part of the lake where the organic-rich sediments were deposited.

Very few analogous examples of ancient shallow saline lake systems of alkaline affinities have been reported in the literature. The best comparisons to the Brazilian examples appear to be the well-studied Eocene Green River Formation in Uinta Basin, USA (Tissot *et al.*, 1978; Demaison & Moore, 1980; Dean & Fouch, 1983), Chaidamu and Jiangnan Basins in China (Changning *et al.*, 1984; Powell, 1986; Fu Jiamo *et al.*, 1986), and Officer Basin in Australia (McKirdy *et al.*, 1986). Modern examples appear to be lakes Nakuru, Magady and Bogoria in the Eastern African Rift System (Eugster, 1986; Vincens *et al.*, 1986; Degens & Michaelis, 1987).

1.4 DRIFT STAGE.

The drift stage can be subdivided into two distinct phases:

i) A gulf proto-oceanic evaporitic phase (Fig. 3B), normally associated with marine restricted conditions, and ideal for deposition of evaporitic sediments.

ii) An oceanic phase characterised mainly by platform and slope carbonate sediments deposited in a neritic to upper bathyal environment (Fig. 3C) and marine shelf-slope system (Figs. 3D, 3E), composed of predominantly siliciclastic and calcareous mudstone sediments deposited in neritic to bathyal conditions.

Figure 10- Schematic block diagram showing the sedimentary facies in a shallow saline to hypersaline lake with alkaline affinities from the Rift stage in the Brazilian marginal basins (modified from Eugster & Hardie (1975)).

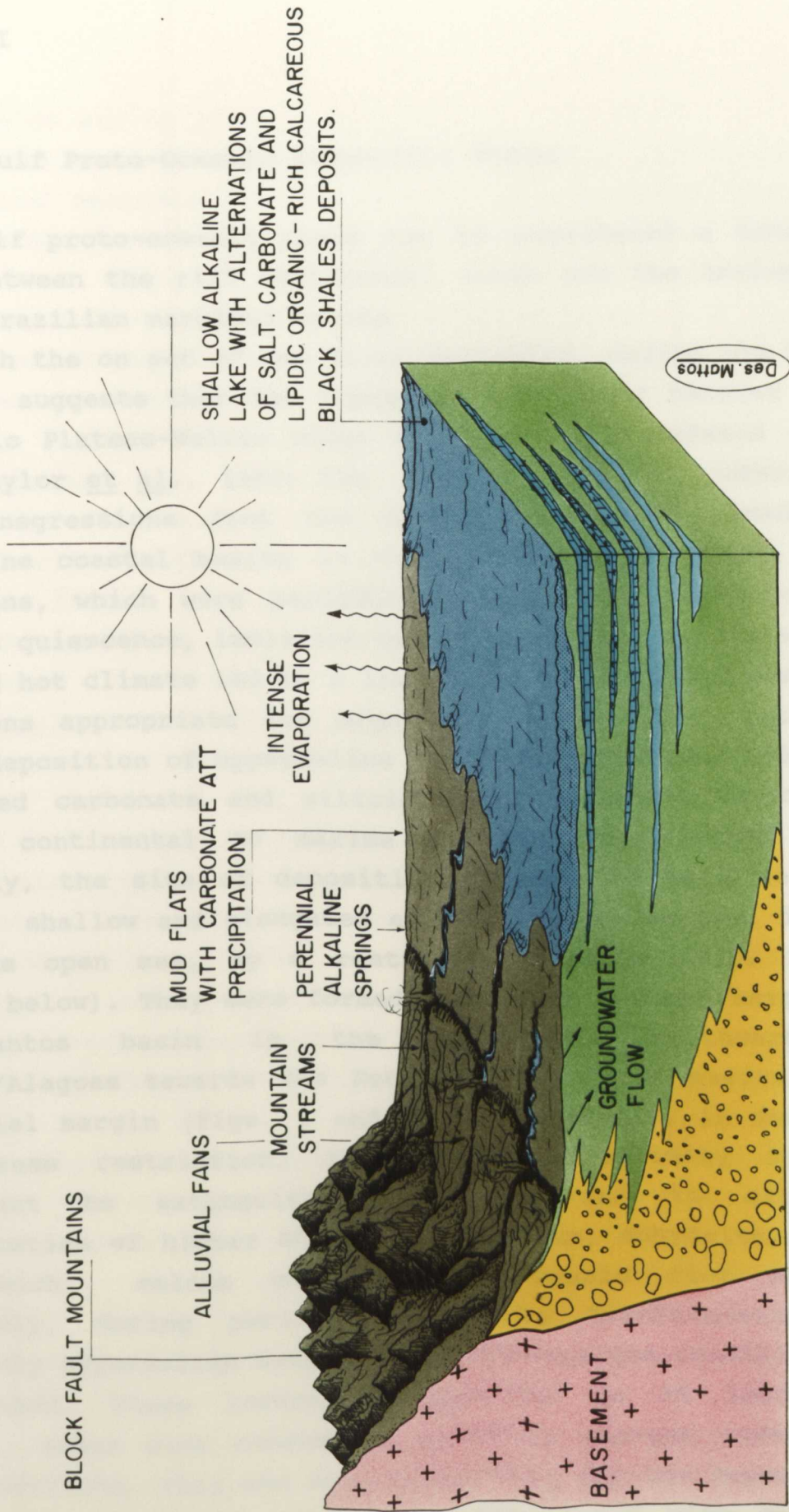
ANALOGOUS EXAMPLES

ANCIENT: GREEN RIVER - USA

GIANGHAN BASIN - CHINA

RECENT: LAKES MAGADI, BOGORIA AND NAKURO - KENYA

LACUSTRINE SALINE WATER ENVIRONMENT



1.4.1 Gulf Proto-Oceanic Evaporitic Phase.

The gulf proto-oceanic phase can be considered a transition phase between the rift continental stage and the marine phase in the Brazilian marginal basins.

With the on set of sea floor spreading, during the Aptian, evidence suggests that the topographic volcanic barrier of the São Paulo Plateau-Walvis Ridge complex was overpassed (Asmus, 1975; Taylor *et al.*, 1985; Fig. 3B). As a result, intermittent sea transgressions from the Southern Atlantic invaded the lacustrine coastal basins in the rift system. These marine incursions, which were periodically cut off, combined with tectonic quiescence, isolation by topographical barriers and an arid and hot climate led to a low clastic influx and restricted conditions appropriate for high evaporation, with subsequent cyclic deposition of hypersaline (halite, anhydrite, dolomite), and mixed carbonate and siliciclastic sediments in coastal, shallow continental to marine environments (Asmus, 1975). Typically, the site of deposition appears to be a series of narrow, shallow and elongated embayments or lagoons, isolated from the open sea, by a restricted passage (Fig. 3B; see diagram below). They were formed along the eastern margin from the Santos basin in the southeast, northwards via Sergipe/Alagoas towards the Potiguar and Ceará basins in the equatorial margin (Figs. 1 and 3B). Generally, in conditions of extreme restriction, the extensive salinity rise was sufficient to extinguish the fauna and to allow the precipitation of higher evaporites (gypsum, anhydrite, halite, etc) which seldom contain any organic rich material. Conversely, during periods of marine transgressions into previously hypersaline basins, less hypersaline conditions were established. These incursions resulted in an increase in basinal areas with consequent climatic changes towards less arid conditions. This was more favourable for the deposition of organic-rich sediments generally associated with calcareous

black shales and marls.

The occurrence of organic-rich sediments associated with hypersaline environments is due to the extensive supply of nutrients that can be provided to a selective number of adapted species that with little or no competition are able to thrive, producing a tremendous input of algal and bacterial organic matter to the lagoons. Furthermore, the high density of hypersaline waters (compared with normal sea water) results in water column stability, increasing the potential for stratification and permanent bottom water anoxia. These particular environmental conditions, lethal to macrolife forms and benthonic organisms, enhance dramatically the preservation of organic matter, resulting in the deposition of finely, well laminated organic-rich calcareous black-shales in highly anoxic environments (Demaison & Moore, 1980; Kirkland & Evans, 1981; Taylor et al., 1985; Katz et al., 1987)

Organic-rich sediments derived from this sequence occur mainly in the Ceará, Potiguar, Sergipe/Alagoas, Bahia Sul and Espirito Santo basins, localized along the central and eastern areas of the marginal basin (Fig. 11).

They were deposited during the Aptian and are characterised by a particular set of palaeontological, mineralogical and geochemical data that indicate a marine hypersaline depositional environment (Della Favera et al., 1984; Ojeda y Ojeda, 1982; chapter II and Mello et al., 1988a, b).

Usually, the calcareous black shales and marls, generally associated with the evaporites, contain few invertebrate marine fossils. Two possible explanations for this phenomenon are:

i) The extreme salinity of the evaporitic brines was so harsh that no normal marine fauna (e.g. dinoflagellates, calcareous nannoplankton and foraminifera) could survive and flourish.

ii) The marine waters which invaded the rift system from the south did not contain such fauna in abundance. Indeed, palaeontological and geochemical data, appear to suggest that

during the Aptian (when hypersaline and anoxic conditions existed also in the southern Atlantic) nannoplankton were few, benthic organisms occurred sporadically and planktonic foraminifers were extremely rare or absent (e.g. Magniez-Jannin et al., 1986).



Fig. 11- Location map showing the basins where organic-rich marine evaporitic sediments occur.

Whatever the explanation, the marine origin of this hypersaline succession is supported by palaeontological (rare occurrences of dinoflagellates and foraminifers in some areas) and mineralogical (e.g. massive presence of halite) evidence. This correlates well with classical, well-described marine hypersaline examples (Kendall, 1978; Friedman, 1980; Taylor et al., 1985). Further biological marker evidence for a marine origin is discussed in chapter II (see also Mello et al., 1988a, b).

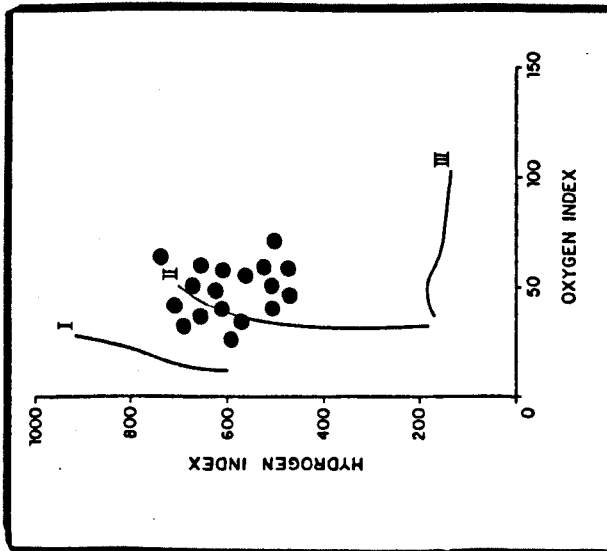
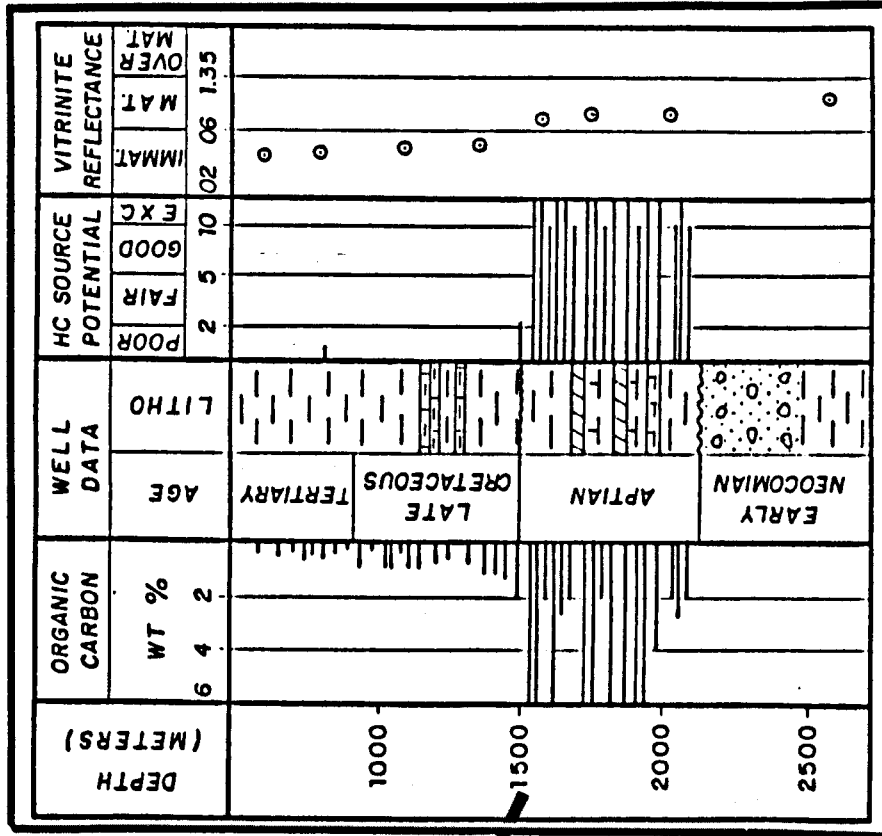
The sediments of this sequence are mainly composed of organic-rich (TOC up to 14%; e.g. Fig. 12) calcareous black shales and

marls (CaCO_3 up to 45%), generally rich in sulphur content (0.5 to 2.5%). Pyrolysis Rock-Eval data and organic petrology indicate a predominance of type II kerogen (hydrogen index up to 750 mg of HC/ g organic carbon; e.g. Fig. 12), mainly made up of a mixture of amorphous organic matter (45-60%) with herbaceous (15-25%) and woody plus coaly material (10-25%). Unexpected in such a prolific algal environment is the significant input of higher plant debris. One possible explanation for this phenomenon is the extreme salinity of these environments. In such conditions the suspended organic matter would tend to stay fluctuating in the water column due to the high water density. This would retard the settling rate of the organic matter, and prolong its exposure to anaerobic bacteria which would use the high amounts of sulphates, nitrates and phosphates to oxidize labile phytoplankton remains, thus causing a relative increase in the proportion of herbaceous and woody plus coaly organic matter (more resistant to oxidation processes; e.g. Katz et al., 1987).

The block diagram in Fig. 13, shows a proposed schematic illustration of the palaeoenvironment of deposition, that dominated the Brazilian margin, from Campos to Ceará basins, during the Aptian. This model assumes that intermittent incursions of sea water accounts for the filling of a pre-existing, deep topographic depressions (rift basins), with marine hypersaline (e.g. halite, anhydrite and dolomite), and mixed carbonate and siliciclastic sediments being formed in shallow water environments (broad embayments or lagoons).

As observed above, the most organic rich and thickest deposits appear to be associated within the deeper parts of these shallow lagoons. Few examples of analogous ancient marine evaporitic environments have been reported in the literature. The most appropriate appear to be the middle Miocene evaporites of Western Mediterranean (Hsu, 1972); the lower Cretaceous sediments from Gabon; the Pliocene-Pleistocene sediments of Dead Sea, Middle East; the Pleistocene of Danakil Basin, Ethiopia (Taylor et al., 1985); the Tyro (eastern

Figure 12- Geochemical well log, showing the stratigraphic position for the marine evaporitic organic-rich sediments deposited during the Aptian and the hydrogen index (S_2/ TOC) vs oxygen index (S_3/ TOC), presented on van Krevelen type diagram.



Mediterranean) and Messinian basins (northern Apennines), Italy (ten Haven, 1986; ten Haven et al., 1987; Tarragona basin, Spain (Albaiges et al., 1986), Camargue basin, southern France (Connan et al., 1987), Marl Slate member of the Zechstein, England (Gibbons, 1978), Gulf of Suez, Egypt and El Lajjun, Jordan (Barwise, 1987; Barwise & Roberts, 1984). There are no large marine evaporite basins in existence today, although there are several examples of small basins with hypersaline conditions of deposition, such as; the Red Sea in the Middle East (Friedman, 1980), Shark Bay in Western Australia (Dunlop and Jefferies, 1985) and Dead Sea in the Middle East (Taylor et al., 1985).

1.4.2 Oceanic phase

As a result of sea floor spreading and the progressive cooling and contraction of the underlying hot lithosphere, the environmental conditions became less restricted and near normal marine to open marine conditions prevailed within the marginal basins (Asmus, 1975; Ojeda y Ojeda, 1982).

Differences in palaeogeographical and environmental settings allow the subdivision of the oceanic phase into three distinct sequences:

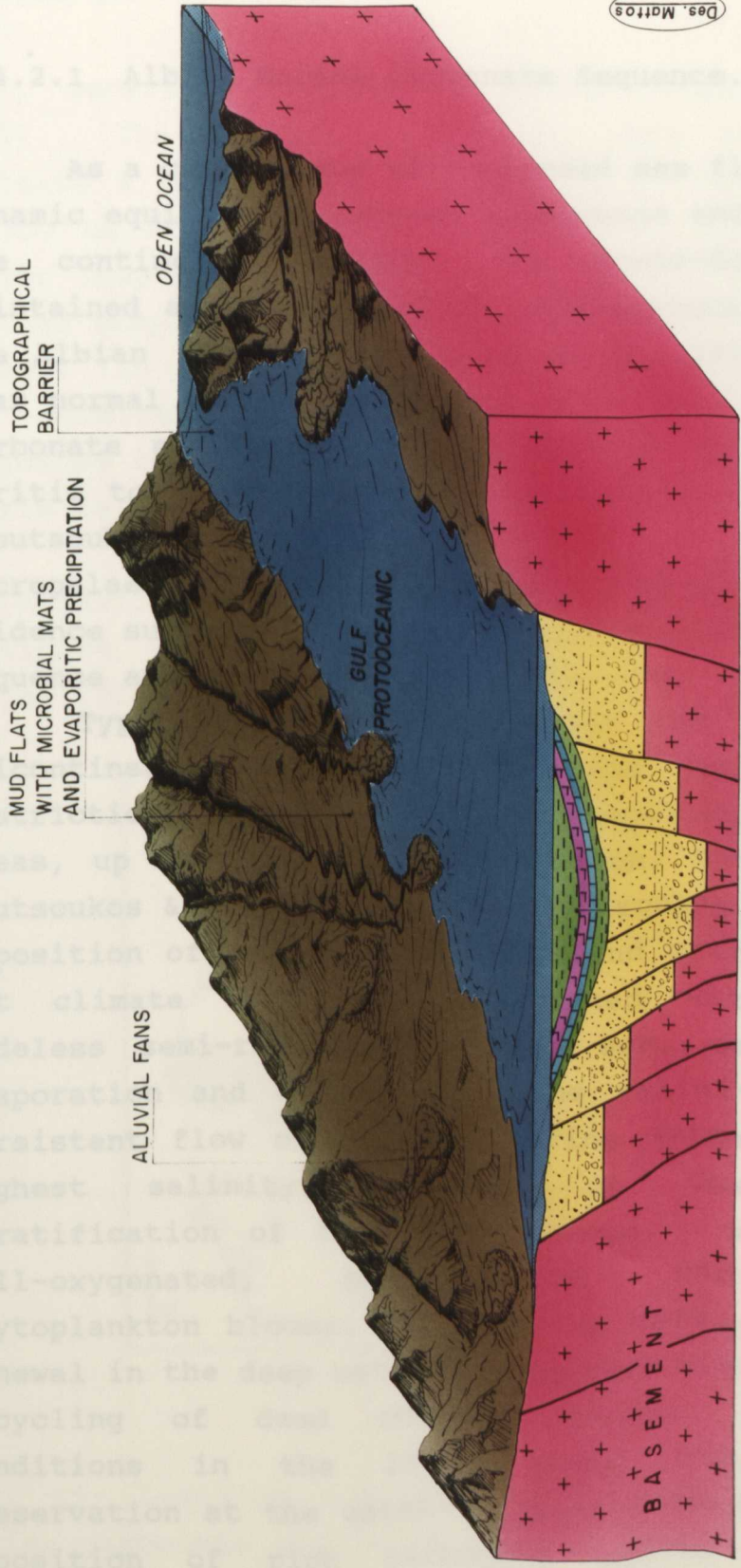
i) Albian marine platform and slope carbonate sequence (Fig. 3C) composed of mainly carbonate sediments deposited in semi-restricted neritic to upper bathyal environments.

ii) Cenomanian to Campanian open marine shelf-slope sequence (Fig.3D), characterised mainly by the deposition during late Cenomanian to Coniacian of organic-rich calcareous mudstone and siliciclastic sediments, in middle/ deep neritic and bathyal conditions (sequence of coastal onlap).

iii) Maastrichtian/ Holocene open marine shelf-slope sequence (Fig. 3E), characterised mainly by proximal siliciclastic facies and distal pelitic facies, and local deltaic deposits (progradational sequence of the continental margin).

Figure 13- Schematic block diagram showing the sedimentary facies in a marine evaporitic environment from the Brazilian marginal basins.

MARINE EVAPORITIC ENVIRONMENT



Des. Matros

SHALLOW HYPERSALINE GULF
WITH ALTERNATIONS OF EVAPORITES AND
CALCAREOUS BLACK SHALE VERY RICH IN
LIPIDIC ORGANIC MATTER

ANALOGOUS EXAMPLES

- ANCIENT : TARRAGONA BASIN – SPAIN
- PRINOS AND MESSINIAN BASIN – ITALY
- RECENT : RED SEA – MIDDLE EAST
- SHARK BAY – WESTERN AUSTRALIA

1.4.2.1 Albian Marine Carbonate Sequence.

As a consequence of increased sea floor spreading and the dynamic equilibrium between subsidence and sedimentation within the continental margin, the proto-South Atlantic Ocean maintained an almost uniform palaeogeographical setting during the Albian (Koutsoukos & Dias Brito, 1987). At that time, in near normal marine conditions (Fig. 3C), mainly fine to coarse carbonate sediments were accumulated under the predominantly neritic to upper bathyal environment of an epicontinental sea (Koutsoukos & Dias-Brito, *op. cit.*).

Micropalaeontological, sedimentological and geochemical evidence suggests similar environmental conditions between this sequence and the marine evaporitic one.

Typically, the Albian ocean was a narrow and shallow epicontinental sea, where hot and tropical climate, semi-restriction, and progressively deepening conditions (in some areas, up to upper bathyal; Beurlen, 1982; Dias Brito, 1982; Koutsoukos & Dias-Brito, 1987; Koutsoukos *et al.*, 1988), led to deposition of organic-rich marls and calcareous mudstones. The hot climate conditions associated with a stable, almost tideless semi-restricted Albian sea, enhanced the rates of evaporation and consequently the salinity of the water. The persistent flow of normal marine waters towards regions of highest salinity, resulted in thermal and salinity stratification of the water column, with the upper waters well-oxygenated, nutrient-rich and favourable for phytoplankton blooms. The lack of vertical mixing and oxygen renewal in the deep waters, together with deoxygenation due to recycling of dead organic matter, enhanced the anoxic conditions in the lower water column. This increased preservation at the water-sediment interface, resulting in the deposition of rich carbonate source rocks. They were deposited in mildly hypersaline, anoxic conditions (Dias-Brito, 1982; Koutsoukos *et al.*, 1988) and are mainly composed of organic-rich (TOC up to 4.0%; e.g. Fig. 14) marls (CaCO₃ up to

65%), generally possessing medium sulphur contents (0.3 to 1.7%). The pyrolysis Rock-Eval data and organic petrology indicate a predominance of type II kerogen (hydrogen index up to 550 mg HC/ g organic carbon; e.g. Fig. 14). The organic matter composition is very similar to the marine evaporitic derived samples, with a small increase in the woody plus coaly content (20-30%). As with the marine evaporitic environment, the occurrence of secondary oxidation processes can be suggested to explain the unexpected high input of higher plant debris to this marine carbonate environment (see above).

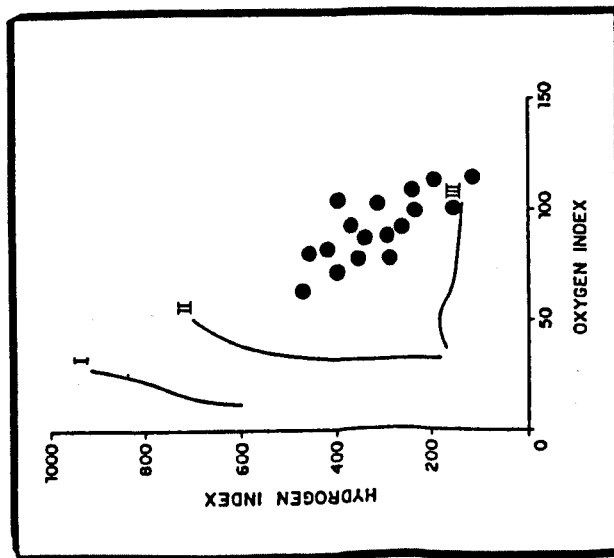
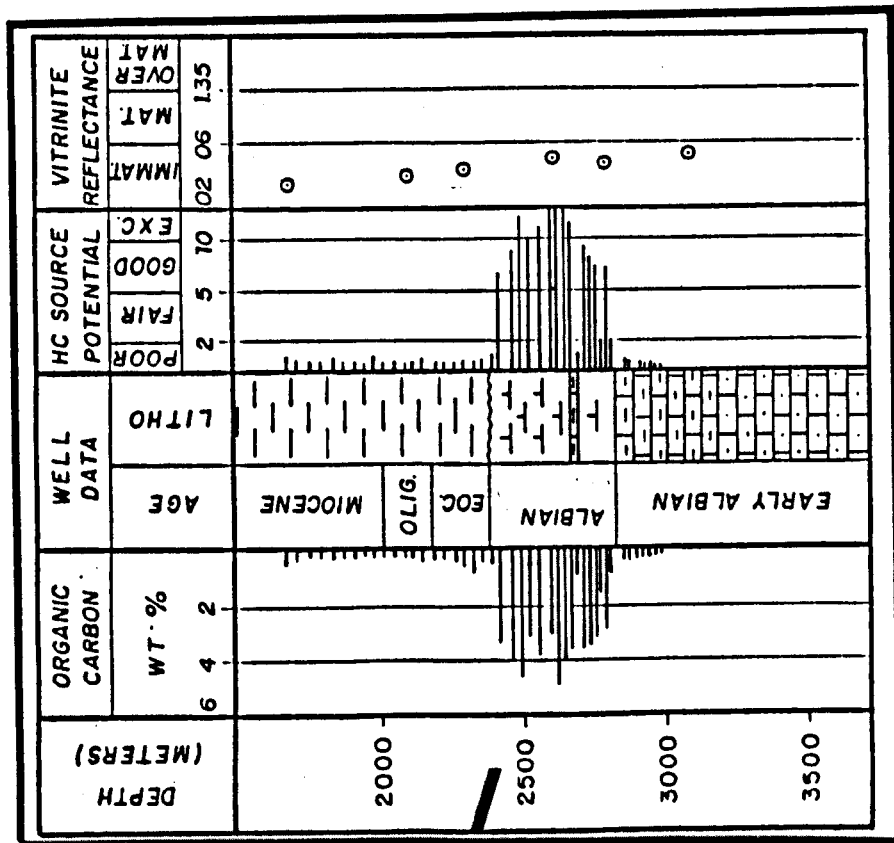
The organic-rich marine carbonate sediments occur mainly in the Cassiporé, Ceará, Sergipe/Alagoas, Bahia Sul and Espírito Santo basins (Fig. 15).



Fig. 15- Location map showing the basins where organic-rich marine carbonate sediments occur.

The block diagram shown in Fig. 16, is an idealized illustration of the marine carbonate palaeoenvironment of deposition, that is proposed to have existed in the Brazilian

Figure 14- Geochemical well log, showing the stratigraphic position for the marine carbonate organic-rich sediments deposited during the Albian and the hydrogen index (S_2/ TOC) vs oxygen index (S_3/ TOC), presented on van Krevelen type diagram.



margin, during the Albian. This model assumes that during the early-middle Albian extensive coarse carbonate deposits were primarily formed in upper to middle neritic environments. In the late Albian, a change in the oceanographic conditions, with consequent relative sea-level rise, resulted in a change in depositional environment to a lower neritic to bathyal one and allowed the deposition of pelitic organic-rich carbonate sediments (e.g. Koutsoukos & Dias-Brito, 1987; Koutsoukos et al., 1988; see chapter II and Mello et al., 1988a, b).

Analogous ancient marine carbonate environments have been reported from Cenomanian-Santonian marine carbonate sediments in La Luna and Querencual Formation, Venezuela (Cassani, 1986; Talukdar et al., 1986), Toolebuc Formation, Eromanga basin, Australia (Riley & Saxby, 1982; Saxby, 1983; Ozimic, 1986), Eastern Officer basin, Australia (McKirdy et al., 1984), Sunniland Formation, South Florida basin, USA (Palacas et al., 1984), Serpiano Shale, middle Triassic Grenzbitumenzone, Switzerland (Gransch & Eisma, 1966; Rieber, 1982; Premovic et al., 1986). Contemporary examples reported in the literature are very few. Worthy to mention are the continental margin of Southwestern Puerto Rico and of Northern Belize (Rafalska-Bloch & Cunningham Jr, 1986), and the Gulf of Aden, offshore Arabia (Pelet, 1981).

1.4.2.2 Cenomanian-Campanian Open Marine Sequence.

The Cenomanian to Campanian open marine shelf-slope sedimentary system, is characterised by alternation of siliciclastic and calcareous mudstone deposition in progressively deepening basins, leading ultimately to bathyal conditions in the more distal areas. The Cenomanian succession is generally missing in some offshore areas from the continental margin (e.g. Koutsoukos, 1987). Important in this context was the establishment of widespread anoxic conditions in the Brazilian marginal basins with the deposition of organic-rich sediments, such as calcareous mudstones or black

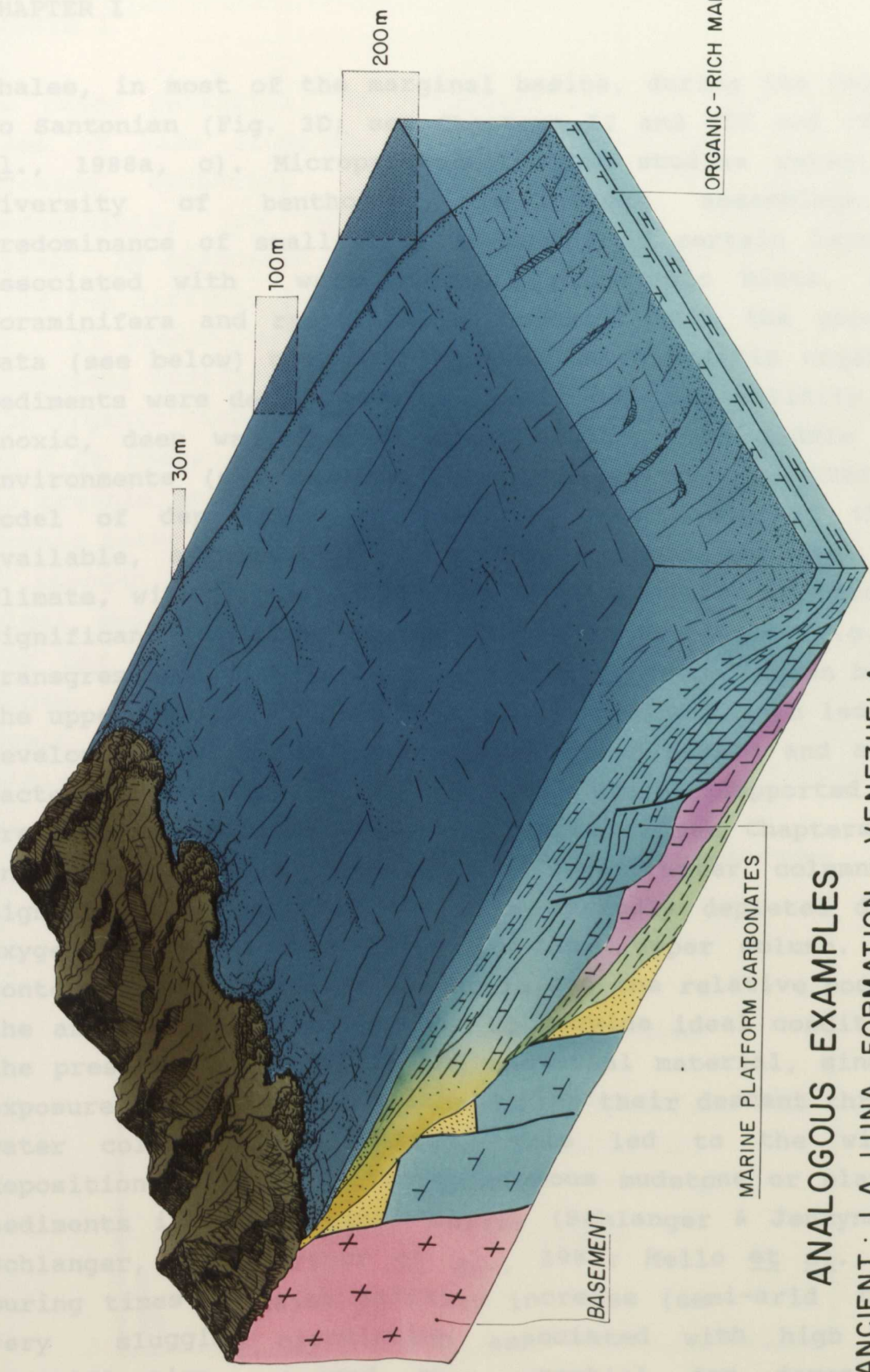
Figure 16- Schematic block diagram showing the sedimentary facies in a marine carbonate environment from the Drift stage in the Brazilian marginal basins.

MARINE CARBONATE ENVIRONMENT

CHAPTER 1

shales, in most of the original basins, to Santonian (Fig. 30 al., 1988a, c). Micro diversity of benthic predominance of shells associated with foraminifera and data (see below) anoxic, deep environment model of available, climates, significant transgression the upper back development of oxygen the pre-exposure water deposition sediments Schlanger During times very slugs stratification enhanced predominantly calcareous rich in siliceous and sulphur

Des. Mattos



ANALOGOUS EXAMPLES

ANCIENT : LA LUNA FORMATION - VENEZUELA,
 SOUTH FLORIDA BASIN - USA,
 EASTERN OFFICER BASIN - AUSTRALIA

RECENT : GULF OF ADEN - ARABIA
 SOUTHWESTERN PUERTO RICO

shales, in most of the marginal basins, during the Cenomanian to Santonian (Fig. 3D; see Chapters II and VII and (Mello et al., 1988a, c). Micropalaeontological studies reveal a low diversity of benthonic foraminifera assemblage, with predominance of small-sized specimens at certain layers, and associated with well-developed planktonic biota, such as foraminifera and radiolarians. Together with the geochemical data (see below) they suggest that these pelitic organic-rich sediments were deposited in slightly enhanced salinity, highly anoxic, deep waters from lower neritic to middle bathyal environments (see chapter II and Mello et al., 1988c). The model of deposition proposed, on the basis of the data available, assumes that an overall humid and warm equable climate, with periodic high sea level conditions, provided a significant increase in the supply of nutrients (e.g. marine transgressions flooding coastal areas). Phytoplankton blooms in the upper layers, coupled with sluggish circulation led to the development of salinity-stratified water masses and anaerobic bacterial activity in the bottom waters (supported by the presence of specific biological markers; see Chapters II, IV and VII). As a result, the lower water column became significantly more saline with markedly depleted dissolved oxygen content with respect to the upper column. In this context, both the degree of anoxia and the relative position of the anoxic water layer appear to provide ideal conditions for the preservation of algal and bacterial material, since their exposure to aerobic conditions during their descent through the water column was minimised. This led to the widespread deposition of organic-rich calcareous mudstone or black shale sediments in the marginal basins (Schlanger & Jenkyns, 1976; Schlanger, 1987; Arthur et al., 1987; Mello et al., 1988c). During times of major salinity increase (semi-arid climate), very sluggish circulation associated with high salinity stratification enhanced the potential for deposition of predominantly calcareous mudstone sediments, made up of kerogen rich in silica and sulphur (high level of dissolved silica and

low redox potential; cf. Chapters II and VII). Conversely, times of less sluggish circulation resulted in a salinity decrease, enhancing the potential for deposition of predominantly low sulphur siliciclastic sediments (black shales). As discussed above, these pelitic successions are made up of two distinct facies:

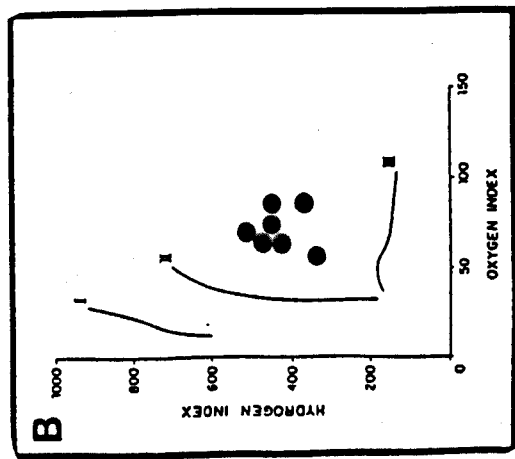
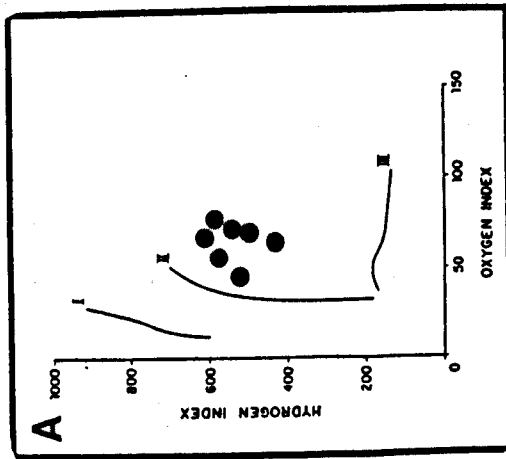
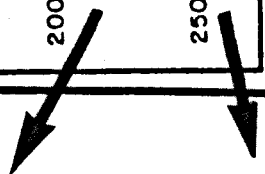
i) predominantly composed of light/ dark grey siliceous calcareous mudstones sediments (CaCO_3 from 11-40%), containing high organic carbon and low to medium sulphur contents (up to 5 and 0.6% respectively; e.g Fig. 17a). The pyrolysis Rock-Eval and organic petrology data (hydrogen index up to 500 mg HC/ g organic carbon) indicate organic matter composed mainly of type II kerogen (Fig. 17a), with the predominance of amorphous (algal and bacterially derived) organic matter (around 85%) over the herbaceous and woody plus coaly derived from higher plants. Organic-rich sediments from the open marine highly anoxic environment with dominance of calcareous lithology occur mainly in Cassiporé, Ceará, Potiguar, Sergipe/Alagoas, Bahia Sul, Espírito Santo and Campos basins (Fig. 18).



Fig. 18- Location map showing the basins where organic-rich open marine highly anoxic sediments with dominance of calcareous lithology occur.

Figure 17- Geochemical well log, showing the stratigraphic position for the open marine anoxic organic-rich sediments with dominance of calcareous (A) and siliciclastic (B) lithology deposited during the Santonian/ Turonian and the hydrogen index (S_2 / TOC) vs oxygen index (S_3 / TOC), presented on van Krevelen type diagram for both sections.

DEPTH (METERS)	ORGANIC CARBON		WELL DATA		HC SOURCE POTENTIAL			VITRINITE REFLECTANCE		
	WT %	LITHO	AGE	POOR	FAIR	GOOD	IMMAT	MAT	OVER MAT	
6	4			2						
4	2									
1000			MIOCENE							
1500			OLIG.							
1500			EOC.							
1500			PAL.							
2000			MAAST CAMP							
2000			SANT/TURON							
2500			APTIAN							



ii) predominantly composed of black shales (CaCO_3 up to 15%), containing high organic carbon and low sulphur content (up to 3 and up to 0.3% respectively; Fig. 17b). The pyrolysis Rock-Eval and organic petrology data (hydrogen index up to 400 mg HC/ g organic carbon), indicate organic matter being composed mainly of type II kerogen (Fig. 17b), with predominance of amorphous (algal and bacterially derived) organic matter (around 80%) over herbaceous and woody plus coaly derived from higher plants. Organic-rich sediments from open marine anoxic environment with dominance of siliciclastic lithology occur mainly in Ceará, Potiguar, Sergipe/Alagoas and Espírito Santo basins (Fig. 19).



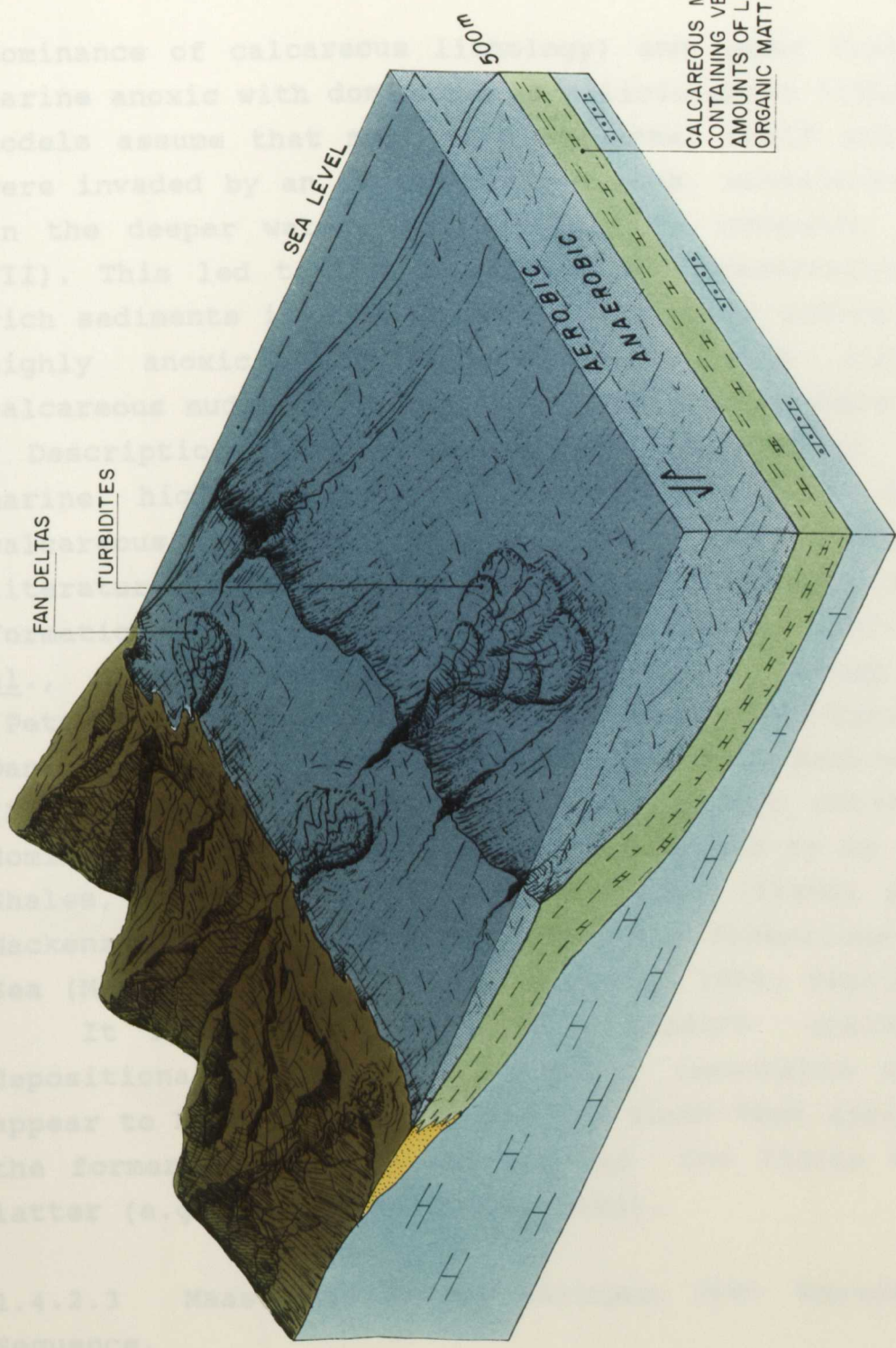
Fig. 19- Location map showing the basins where organic-rich open marine anoxic sediments with dominance of siliciclastic lithology occur.

The block diagrams in Figs. 20 and 21, shows a proposed schematic reconstruction, of the depositional palaeoenvironments in the Brazilian marginal basins during the latest Cenomanian-Coniacian (open marine highly anoxic with

Figure 20- Schematic block diagram showing the sedimentary facies in an open marine highly anoxic environment with dominance of calcareous mudstone lithology from the Drift stage in the Brazilian marginal basins.

dominance of calcareous marine anoxic with models assume that were invaded by in the deeper VII). This led rich sediments highly anoxic calcareous mudstones.

Des. Mattos



CALCAREOUS MUDSTONES CONTAINING VERY HIGH AMOUNTS OF LIPID-RICH ORGANIC MATTER

ANALOGOUS EXAMPLES

ANCIENT: MONTEREY FORMATION – USA
OUED BAHLLOUL – TUNISIA

RECENT: PERUVIAN UPWELLING – PERU
SOUTH – WEST AFRICAN SHELF

deposition appear to the former latter (a. 1.4.2.3 Sequence.

In general, the neritic to bathyal siliciclastic facies turbidite deposits

dominance of calcareous lithology) and upper Cretaceous (open marine anoxic with dominance of siliciclastic lithology). These models assume that most of continental shelf and upper slope were invaded by an oxygen minimum zone, occasionally depressed in the deeper waters and variable in intensity (cf. Chapter VII). This led to the deposition and preservation of organic rich sediments in a lower neritic to upper bathyal open marine highly anoxic/ anoxic environment with alternation of calcareous mudstone and siliciclastic (black shale) lithology.

Descriptions of several analogous examples of ancient open marine highly anoxic environments with a dominance of calcareous mudstone lithology have been reported in the literature. Noteworthy to mention are the well-known Monterey Formation in California, USA (Katz & Elrod, 1983; Curiale et al., 1985), Nakalagu Formation, Benue Trough in Nigeria (Petters & Ekweozor, 1982; the Cenomanian-Turonian of the Danish Graben in the North Sea and Oued Bahloul in Tunisia (Farrimond, 1987). Likewise, marine anoxic environments with dominance of siliciclastic lithology appear to be the Toarcian Shales, Paris Basin and Southern Alps (Tissot et al., 1971; Mackenzie, 1980; Farrimond, 1987), the Kimmeridge Shale, North Sea (Mackenzie et al., 1984; Demaison, 1984; Farrimond, 1987).

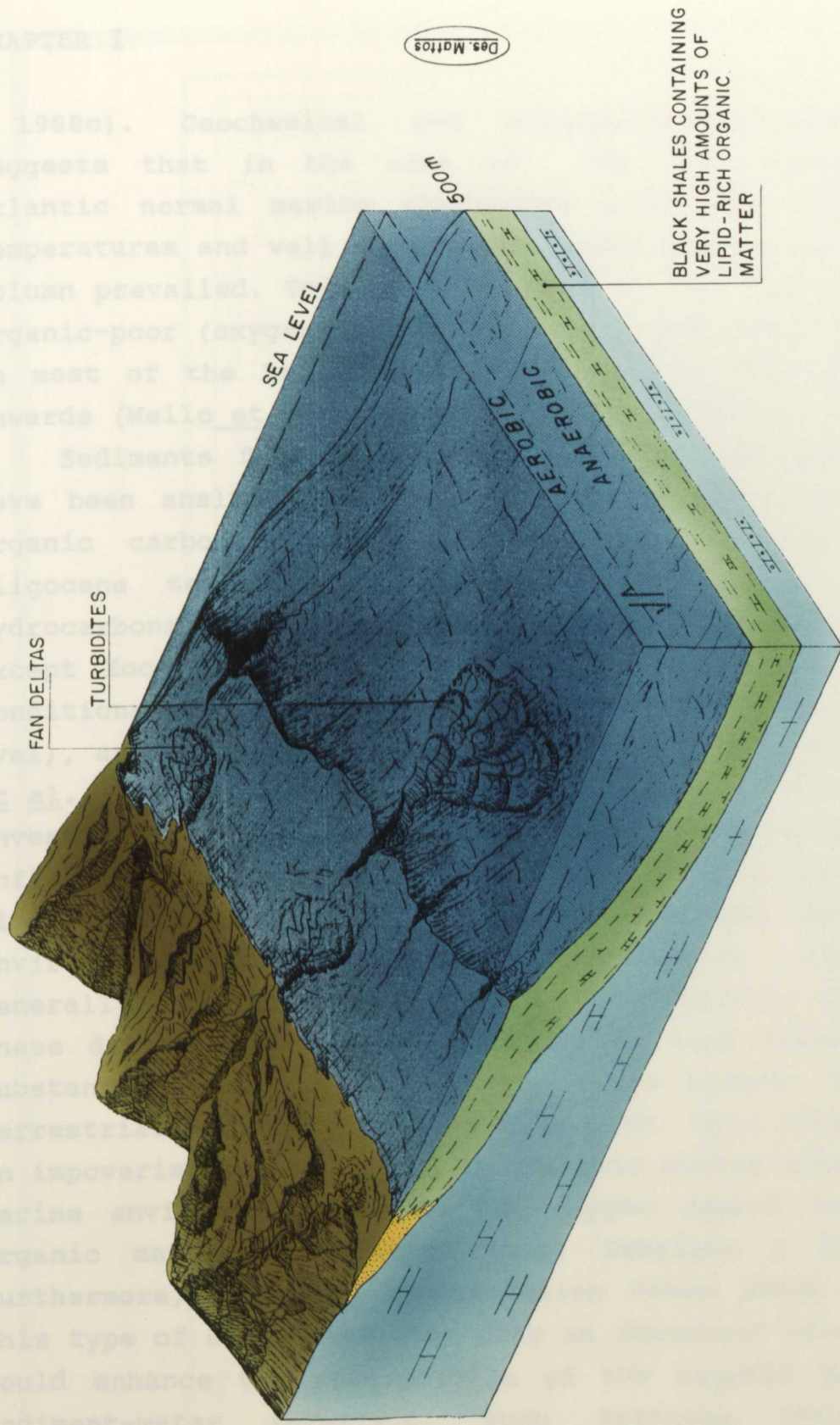
It is difficult to think of modern analogues of such depositional environments. However, reasonable approximations appear to be offshore Peru and the South-West African Shelf for the former and the black Sea and the Indian Ocean for the latter (e.g. Demaison & Moore, 1980).

1.4.2.3 Maastrichtian to Holocene Open Marine Shelf-Slope Sequence.

In general, the Maastrichtian to Holocene sequence, in the Brazilian margin, is characterised by the deposition, in neritic to bathyal environments, of a proximal coarse siliciclastic facies and distal facies with pelitic and turbiditic deposits (e.g. Koutsoukos, 1987; Mello et al.,

Figure 21- Schematic block diagram showing the sedimentary facies in an open marine anoxic environment with dominance of siliciclastic lithology from the Drift stage in the Brazilian marginal basins.

OPEN MARINE SILICICLASTIC ENVIRONMENT

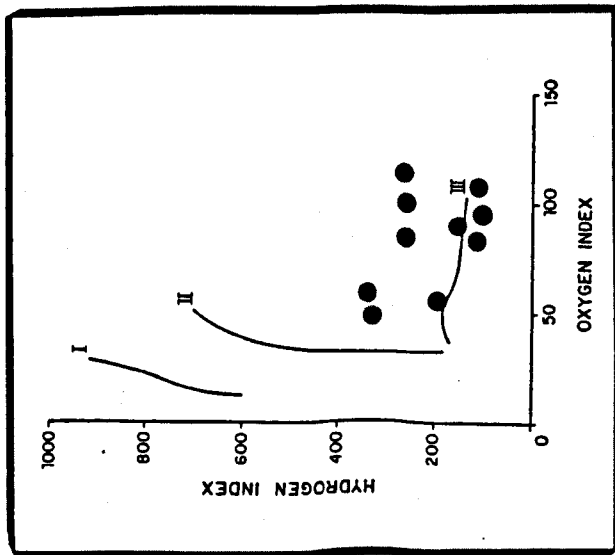
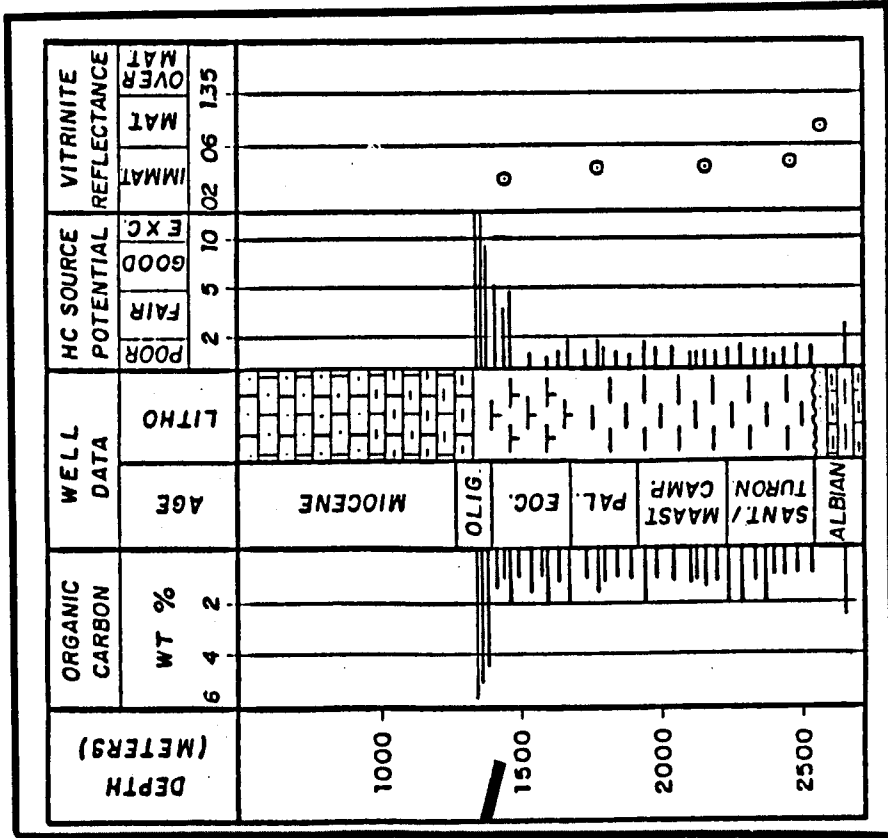


- ANALOGOUS EXAMPLES
- ANCIENT: PARIS BASIN - FRANCE
- KIMMERIDGIAN SHALE - NORTH SEA
- RECENT : INDIAN OCEAN AND BLACK SEA

1988c). Geochemical and micropalaeontological evidence suggests that in the case of the late Cretaceous South Atlantic normal marine conditions with warm tropical water temperatures and well oxygenated conditions in the whole water column prevailed. This is emphasized by the the deposition of organic-poor (oxygenated) mixed clastic and carbonate sediments in most of the Brazilian marginal basins from the Campanian onwards (Mello et al., 1984a, 1988c; cf. Chapter VII).

Sediments from this sequence in all the marginal basins have been analysed. Generally, they contain low to moderate organic carbon contents (up to 2%; e.g. Fig. 22 except oligocene section). However, their potential to generate hydrocarbons is extremely poor (type III kerogen; e.g. Fig. 22 except Eocene/ Oligocene sections). The prevalent oxygenated conditions are supported by high oxygen index (pyrolysis Rock-Eval), and normal and abundant benthonic foraminifera (Estrella et al., 1984; Mello et al., 1984a, 1988c). Whatever the area investigated, these sediments are characterised by the influence of well-oxygenated water conditions, being devoid of lipid-rich organic matter. Exceptions are marine deltaic environments that are associate with major river systems. Generally, the primary biological productivity offshore from these deltas tend to be exceptionally high since there is a substantial nutrient influx from these rivers. The input of terrestrial organic matter is also high. This situation causes an impoverishment of oxygen in the oxic bottom waters of normal marine environments due to the oxygen demand resulting from organic matter degradation (e.g. Demaison & Moore, 1980). Furthermore, the high sedimentation rates which characterise this type of environment may play an important role, since they would enhance the preservation of the organic matter at the sediment-water interface. Such features result in the deposition of marine sediments generally rich in terrestrial organic matter (type III kerogen; Demaison & Moore, 1980). This appears to have been the case for the organic-rich sediments deposited, during Eocene / Oligocene ages, in the area

Figure 22- Geochemical well log, showing the stratigraphic position for the marine deltaic with carbonate influence organic-rich sediments deposited during the Eocene/Oligocene and the hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram



offshore the Amazon River in Brazil (Mello et al., 1988a, b; see also below and Chapter II).

Geochemical and geological evidence suggests the establishment during the Eocene-Oligocene of deltaic environments associated with major river systems in several regions of the South Atlantic (e.g. Niger delta, Nigeria; Ekweozor et al., 1979a and b; Grantham et al., 1983), and Congo delta, Angola basin (Connan et al., 1988).

Organic-rich sediments associated with marine deltaic environment of deposition is confined in the northern area of the Brazilian continental margin (Fig. 23). The sediments arising from this type of depositional environment are mainly organic-rich (TOC up to 7%; Fig. 22) grey marls (CaCO₃ up to 70%), generally possessing medium sulphur contents (up to 0.4%). The pyrolysis Rock-Eval data and organic petrology indicate a predominance of type II/ III kerogen (hydrogen index up to 350 mg HC/ g organic carbon; Fig. 22), made up mainly of amorphous organic matter (up to 85%).

The block diagram shown in Fig. 24, is a proposed idealized illustration of the marine deltaic palaeoenvironment of deposition that appear to have developed in the northern area of the Brazilian margin, during Eocene/Oligocene times. This model assumes that during that time, thicker and extensive proximal coarse carbonate deposits were formed in upper to middle neritic environments. Conversely, in distal areas of a deep neritic to lower bathyal environment the deposition of pelitic carbonate rocks very rich in terrestrial organic matter occurred.

This resulted in the establishment of a marine deltaic environment over a marine carbonate platform system (see chapter II and Mello et al., 1988a, b). Similar ancient marine deltaic depositional environment, but with predominance of siliciclastic lithology has been reported from Eocene/Oligocene sequences from Niger delta, Nigeria (Ekweozor et al., 1979a and b; Grantham et al., 1983), Congo delta, Angola basin (Connan et al., 1988), Mahakam delta,

Indonesia (Grantham et al., 1983), and Beaufort-Mackenzie delta (Brooks, 1986).

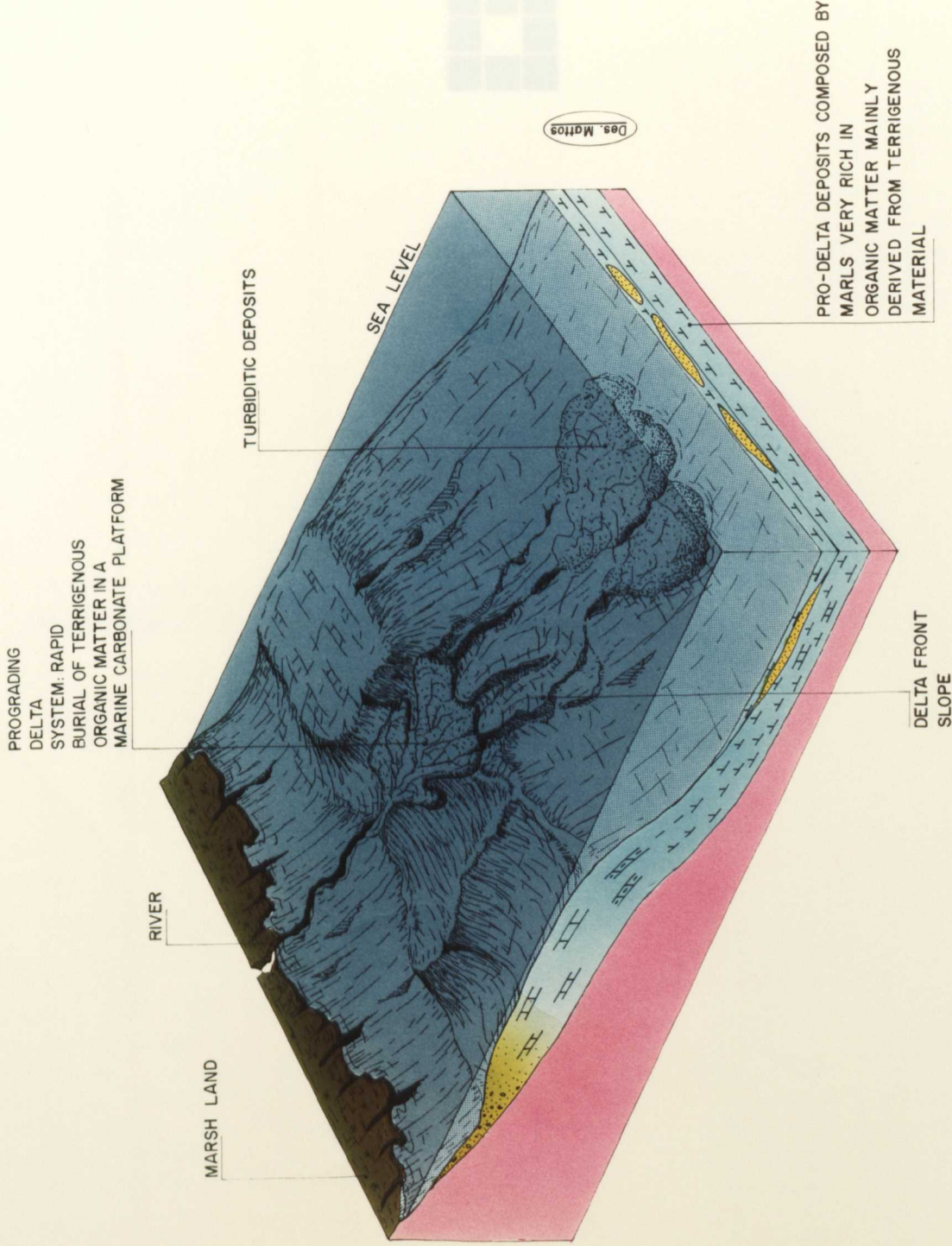


Fig. 23- Location map showing the basin where organic-rich sediments derived from marine deltaic depositional environment with carbonate influence occur.

Contemporary examples appear to be Niger delta, Nigeria; Indus and Ganges deltas, Indian Ocean; Amazon delta, Brazil, and Mississippi delta (Demaison & Moore, 1980), and Mahakam delta, Indonesia (Pilon et al., 1986).

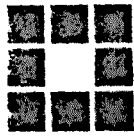
Figure 24- Schematic block diagram showing the sedimentary facies in a marine deltaic depositional environment associated with a marine carbonate platform from the Drift stage in the Brazilian marginal basins.

WITH CARBONATE PLATFORM



ANALOGOUS EXAMPLES

- ANCIENT: NIGER DELTA — NIGERIA
MAHAKAN DELTA — INDONESIA
- RECENT: MAHAKAN DELTA — INDONESIA
AMAZON DELTA — BRAZIL



CHAPTER II

CHAPTER II

GEOCHEMICAL AND BIOLOGICAL MARKER ASSESSMENT OF
PALAEOENVIRONMENT OF DEPOSITION OF ORGANIC-RICH SEDIMENTARY
ROCKS FROM BRAZILIAN MARGINAL BASINS.

This chapter provides an investigation of bulk, isotopic and molecular features of a wide selection of source rocks from Brazilian marginal basins, ranging from Lower Cretaceous to Tertiary in age. The results enable the recognition and differentiation of seven depositional regimes discussed in Chapter 1: lacustrine freshwater; lacustrine saline water; marine evaporitic; marine carbonate; marine deltaic with carbonate influence; open marine highly anoxic with a predominance of calcareous mudstone lithology, and open marine anoxic with dominance of siliciclastic lithology.

2.1 INTRODUCTION

The assessment and differentiation of the depositional palaeoenvironments of organic-rich sedimentary rocks using geochemical and biological marker parameters has increased greatly in the last few years. Recently, many authors have shown that both geochemical evidence and biological marker distributions can provide diagnostic criteria for the distinction of organic-rich sediments derived from source rocks deposited in a variety of environments, such as lacustrine freshwater, fresh-brackish water, saline and hypersaline in China (Brassell et al., 1988; Fu Jiamo et al., 1986; Wang Tieguan et al., 1988); freshwater in Australia, Sudan, Chad (McKirdy et al., 1986; Philp and Gilbert, 1986; Moldowan et al., 1985) freshwater and saline water in China and the USA (Powell, 1986); marine hypersaline in Spain, USA, Italy, and France (eg. Albaiges et al., 1986; ten Haven et al., 1987; Connan and Dessort, 1987); marine carbonate in Venezuela, Australia and Florida (Talukdar et al., 1986; McKirdy et al., 1984; Palacas et al., 1984) and marine deltaic in Nigeria, Indonesia and Canada (Hills and Whitehead, 1966; Grantham et al., 1983; Brooks, 1986).

This Chapter summarises a multidisciplinary approach (geochemical, geological, palaeontological and statistical) used to assess the depositional environments of source rocks in the major Brazilian marginal basins.

The work extends earlier preliminary studies of samples from some of the basins, carried out in the Petrobras Research Centre (Mello et al., 1984a, b; Estrella et al., 1984; Pereira et al., 1984; Cerqueira et al., 1984; Gaglianone et al., 1984; Babinski & Santos, 1987; Rodrigues et al., 1988; Mello et al., 1988 a, b, c). In the present study, two hundred rock samples recovered from sedimentary successions ranging from lower Neocomian to Oligocene in age were analysed initially. They cover a wide range of maturity values (0.45 to

0.90% Ro) but only those with Ro values between 0.45 and 0.75% are discussed because of the effects of the increase in maturation on the concentrations of biological markers (Rullkötter et al., 1984, cf. Chapter V).

In summary, bulk and biological marker ratio data were obtained for 120 rock samples. Table 1 in the "Introduction" shows the 58 representative rock samples types and locations, selected to be discussed in this Chapter. Biological marker concentration data and linked scan MS analyses were obtained for these samples, selected from 8 sedimentary basins in the continental margin.

2.2 RESULTS AND DISCUSSION

A distinct advantage in the examination of the geochemical and biological marker characteristics of petroleum source rocks is the availability of samples from a variety of depositional environments whose geological and palaeontological features are well described. The Brazilian marginal basins provide an ideal opportunity for such an investigation, since they contain a succession of sediments deposited in different environments within a single geographical realm (see Chapter I). Also, where assumptions have to be made from geological and palaeontological studies, previous geochemical and biological marker features of samples from well-defined depositional environments elsewhere provide a background for the present investigation.

Although some of the molecular parameters discussed herein are maturity dependent (e.g. the biological marker concentrations; cf. Chapter V), the availability of a variety of both immature and mature rock samples chosen to cover a relatively narrow maturity range(%Ro from 0.45 to 0.75%), still allows various features to be ascribed to a source dependence. In addition to the quantitative biological marker data obtained at Bristol (Tables 1-14), quantitative data (obtained using a metastable linked scan technique; Moldowan et al., 1985) from 35 oils

(Chapter III) and 60 source rocks (including most, but not all of those analysed quantitatively at Bristol) obtained at Norsk Hydro were also analysed there using supervised principal component analysis and class modelling (Wold, 1976; Fig. 1). For each sample, raw data (ion intensity versus retention-time) from 26 digitised biomarker metastable ion monitoring elution profiles were added sequentially into a new file.

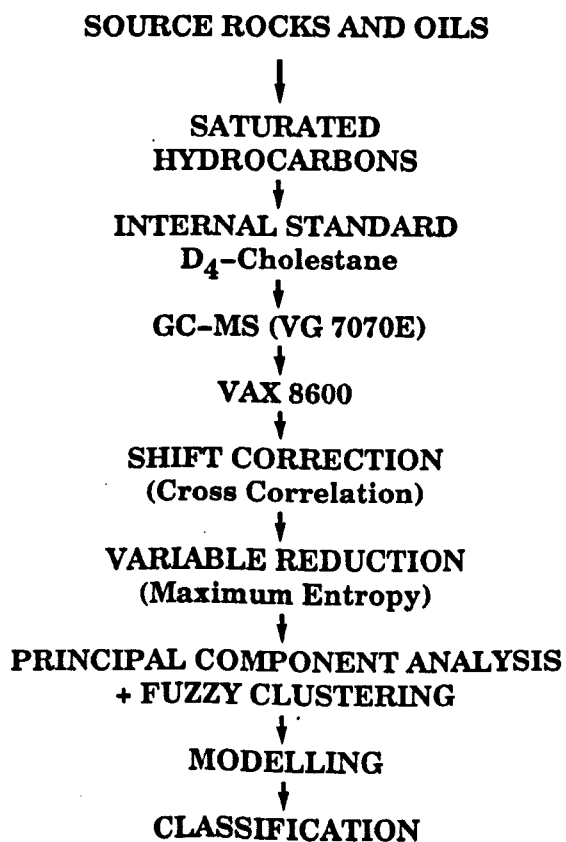


Figure 1- Flow diagram of multivariate analytical procedure.

The resulting 27,000 variables per sample (mass spectrometric cycle time 1 second, 26 transitions and retention time windows from 10 to 20 minutes) were shift-corrected to "normalise" retention times, the "background noise" being eliminated (Fig. 2), and reduced to 962 new variables by a maximum entropy method (Full *et al.*, 1984). This is a data reduction method that sums variables with little or no variance and thus retains

the most important information. The 962 new variables were then normalised to a deuteriated internal standard and used as input to a principal component analysis generating four new independent variables (principal components) which are linear combinations of the reduced biological marker elution profiles. These four principal components represent 95% of the variance in the reduced data. Data from each depositional environment were modelled using SIMCA (Soft Independent Modelling and Class Analogy; Wold, 1976).

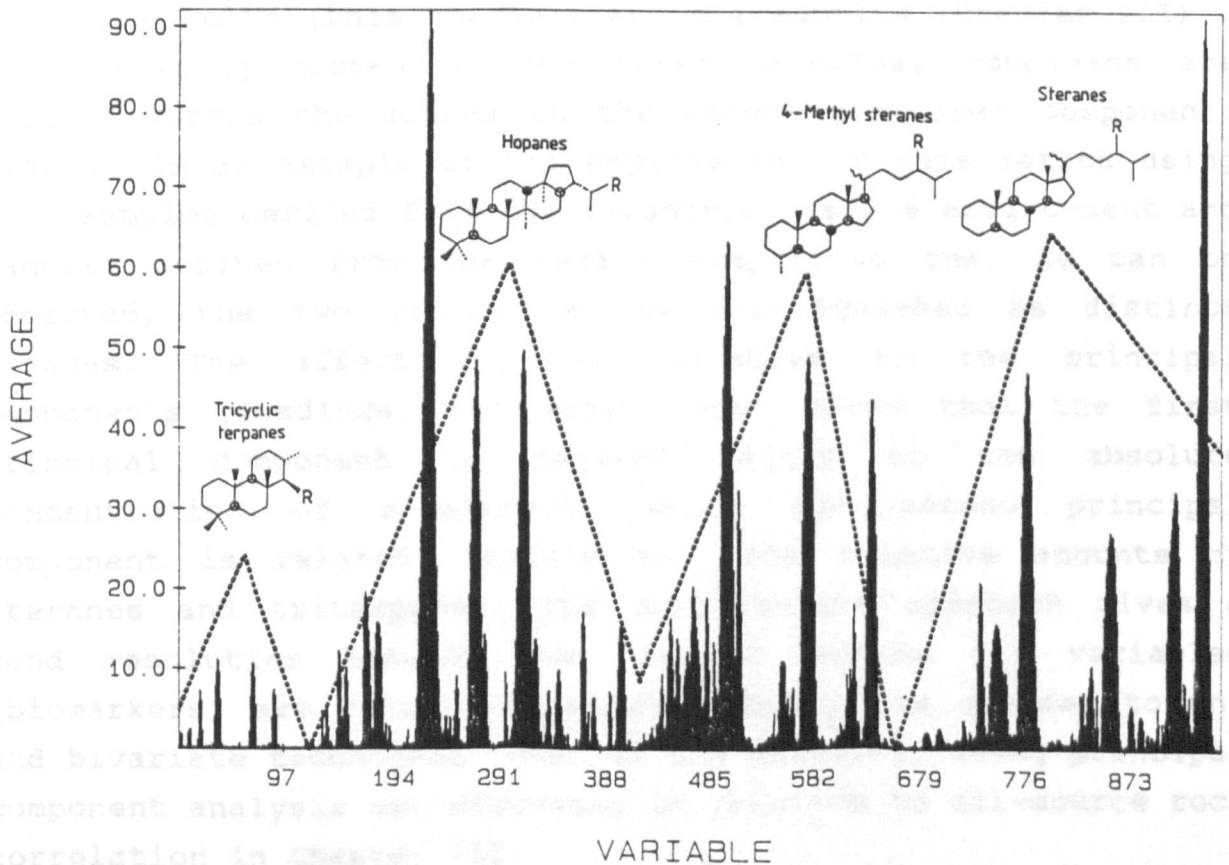


Figure 2- Metastable ion monitoring GC-MS reconstructed elution profile of 26 digitised biological markers added sequentially from transitions involving m/z 191, 231, and 217 respectively, for a rock extract derived from a marine evaporitic environment (CES-41).

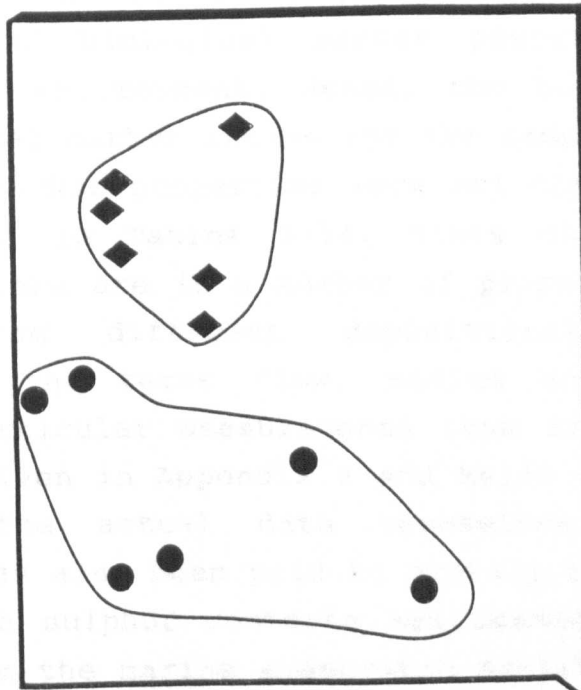
The modelling and discrimination powers of the 962 variables in each class (environment) were calculated and the most important 142 variables were selected on the basis of their discrimination power. These biomarker variables are the most significant in distinguishing the different depositional environments.

Since each class (depositional environment) contains a range of maturities, this selection procedure help to ensure a new set of variables which are primarily independent of maturity effects. These 142 variables were used as input to a new principal component analysis of environment classes represented by source rocks (this chapter) and oil samples (Chapter III) . The resulting scores on the first principal component are plotted versus the scores on the second principal component. Fig. 3 is an example of the application of this method using rock samples derived from the lacustrine saline environment and samples derived from the marine evaporitic one. As can be observed, the two groups can be distinguished as distinct classes. The effect of the variables on the principal components (loadings, not shown here) shows that the first principal component is related mainly to the absolute concentration of biomarkers, while the second principal component is related mainly to the relative amounts of steranes and triterpanes. The multivariate approach gives a good resolution between the classes because all variables (biomarkers) are considered simultaneously, as opposed to uni and bivariate techniques. Most of the examples using principal component analysis are discussed in relation to oil-source rock correlation in Chapter III.

The results below , taken with the principal component analyses, indicate that the bulk, elemental and biological marker distributions and concentrations for the organic-rich sediments allow differentiation of the seven distinct depositional regimes, discussed in Chapter 1: I-lacustrine freshwater; II-lacustrine saline water; III-marine evaporitic; IV-marine carbonate; V-marine deltaic with carbonate influence;

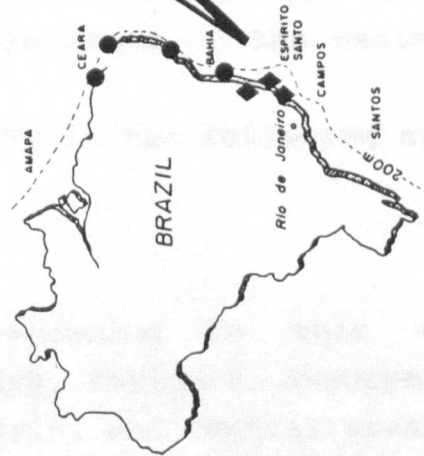
Figure 3- Scores of rock extracts derived from lacustrine saline and marine evaporitic depositional environments on principal component 1 vs scores on principal component 2.

LACUSTRINE SALINE X MARINE EVAPORITIC
SOURCE ROCKS



Component 1

◆ LACUSTRINE
● EVAPORITIC



Component 2

VI-open marine highly anoxic with a predominance of calcareous mudstone lithology, and open marine anoxic with dominance of siliciclastic lithology.

The samples in Tables 1-14 were chosen to represent not only typical organic-rich sediments from the respective depositional environments, but also to cover as far as practicable the whole range of variations in the bulk, elemental and biological marker properties found for each depositional environment. Hence, the bulk and elemental data and biological marker ratios for the samples whose quantitative biological marker properties were not obtained fall within the ranges given in Tables 1-14. Since the extremes have been included, there are in a number of properties overlaps between samples from different depositional environments. For convenience the terms "low, medium and high" are used to describe particular measurements (the ranges covered by these terms are given in Appendix 2 and Mello *et al.*, 1988a). Hence, not only the actual data themselves are considered but attention has also been paid to overall trends in the data. For example high sulphur contents are considered "typical" of the samples from the marine evaporitic environment, but of the ca. 25 samples examined three have contents of 0.3% (ie. low; Table 5) but are still classified in this group on the basis of the features as a whole.

Each regime is discussed separately in the following sections.

2.2.1 Lacustrine freshwater

Organic-rich sediments belonging to this type of environment were analysed from Ceará, Potiguar, Sergipe/Alagoas and Bahia Sul basins in the equatorial and central areas of the continental margin (Fig. 4). They were deposited during lower Neocomian to Aptian times (Table 1; Fig. 5). Fig. 5 shows two typical geochemical logs (wells BAS-18 and BAS-64) with the stratigraphic position of two important organic rich horizons, chosen as a specific examples, that have been identified in

Table 1: Geological and Geochemical Data For Sediments From Lacustrine Freshwater Environment.

WELLS	BAS-18	BAS-64	BAS-32	CES-14	CES-37D	PTA-1	CS-1	CB-6	RNS-13	RNS-35
Sample Number	1	2	3	4	5	6	7	8	9	10
Sample Nature	Cuttings	Cuttings	Core	Cuttings	Cuttings	Core	Core	Core	Cuttings	Core
Depth (m)	2790	2250	2268	2511	3501	1731	1515	1800	2598	2274
Age	Lower Neocomian	Lower Neocomian	Lower Neocomian	Aptian	Aptian	Lower Neocomian	Lower Neocomian	Lower Neocomian	Aptian	Aptian
Lithology	Dark Grey Shale	Black Shale	Dark Grey Shale	Dark Grey Shale	Dark Grey Shale	Calcareous Grey Shale	Dark Grey Shale	Dark Grey Shale	Dark Grey Shale	Dark Grey Shale
CaCO ₃ (%)	5	7	7	5	7	18	5	7	16	17
Sulphur (%)	0.3	0.3	0.1	0.3	0.35	0.31	0.4	0.3	0.4	0.4
TOC (%)	3.5	1.0	1.4	3.0	2.0	1.8	6.4	1.6	2.4	1.4
S ₂ (KgHC/Ton rock)	16.0	4.3	5.5	4.0	4.3	8.4	37.0	6.0	13.0	9.0
HI (mgHC/gTOC)	451	420	434	433	215	469	576	356	537	666
T-MAX (°C)	440	443	444	430	435	436	433	428	439	444
Ro (%)	0.65	0.50	0.52	0.50	0.58	0.54	0.62	0.56	0.70	0.62
SCI	6.5	5.5	-	5.0	-	5.0	5.5	5.0	6.0	-
EOM (ppm)	1613	60	537	1600	1792	900	2200	921	2300	2545
Pr/Ph	1.7	1.2	1.5	1.5	2.6	1.1	1.5	1.8	1.6	1.5
Pr/nC ₁₇	0.9	0.4	0.3	0.7	0.7	0.4	1.3	0.5	0.4	1.3
Ph/nC ₁₈	0.5	0.4	0.2	0.3	0.4	0.4	0.8	0.3	0.2	0.5
nC ₁₇ /C ₃₁	1.4	0.9	0.5	0.7	0.8	1.3	0.9	1.4	0.7	0.6
δ ¹³ C whole extract	-28.2	-29.0	-29.3	-28.5	-28.2	-31.0	-29.0	-28.5	-28.0	-28.4
Saturates (%)	44	50	51	38	41	66	50	43	47	40
Aromatics (%)	17	17	16	21	24	9	9	19	18	13
NSO (%)	39	33	33	41	35	25	41	38	35	47
Amorphous (%)	40	45	70	70	80	90	80	40	90	40
Herbaceous (%)	50	30	25	10	10	5	10	40	5	40
Woody+Coaly (%)	10	5	5	20	10	5	10	20	5	20

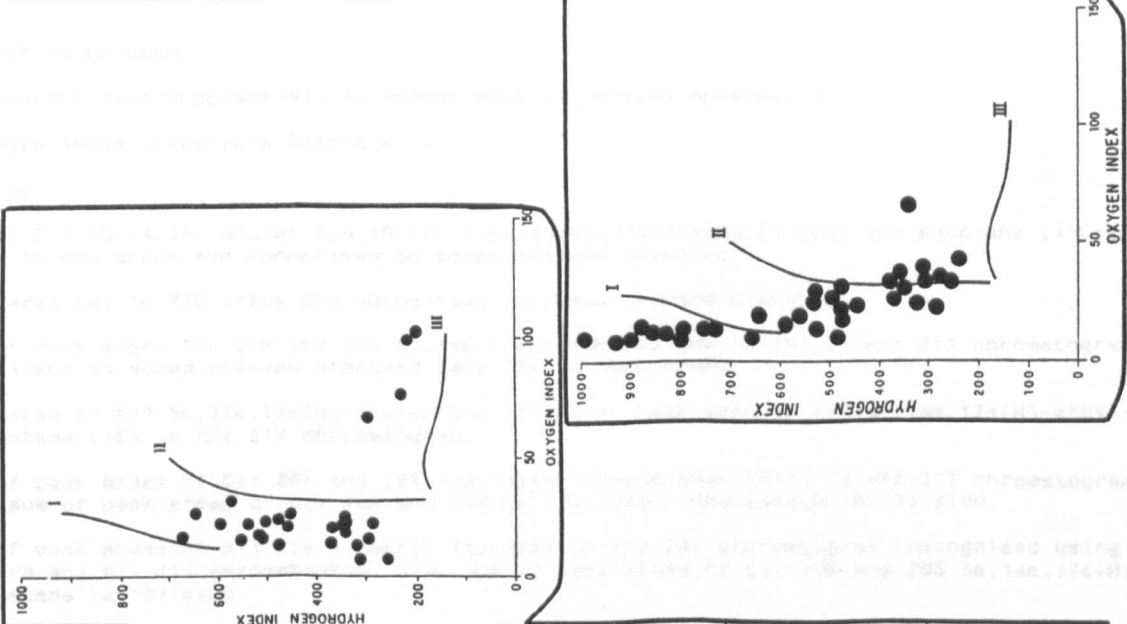
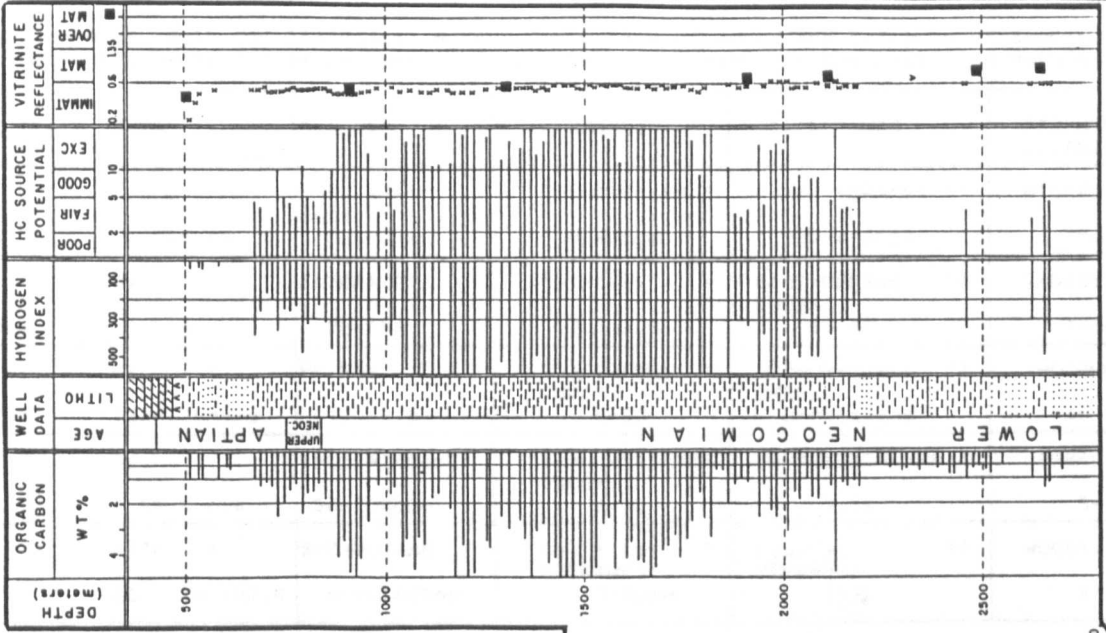
the lower Neocomian sedimentary succession of Bahia Sul basin (1 and 2 in Fig. 4). The organic-rich sediments derived from this type of environment are generally composed of thick beds of black shales and to a minor extent calcareous black shales (CaCO_3 from 5 to 18%), rich in organic matter (TOC up to 6.5%), with low to medium sulphur content (less or equals to 0.4%; Tables 1, 2 and Fig 5). The high hydrocarbon source potential (S_2 from Rock-Eval pyrolysis up to 37 kg Hc/ ton of rock) largely arising from type I kerogen (hydrogen index up to 960 mg Hc/ g organic carbon; Table 1 and Fig. 5), and organic petrology data identify the organic matter as being mainly composed of lipid-rich material (amorphous plus herbaceous organic matter ranging from 50-95%; Tables 1, 2 and Fig. 5).



Figure 4- Location map showing the areas from which samples from lacustrine freshwater depositional environment were investigated.

Figure 5- Geochemical logs of two typical wells from Bahia sul basin, showing the stratigraphic position of the lacustrine freshwater organic-rich sediments and their hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram.

BAS 64



BAS 18

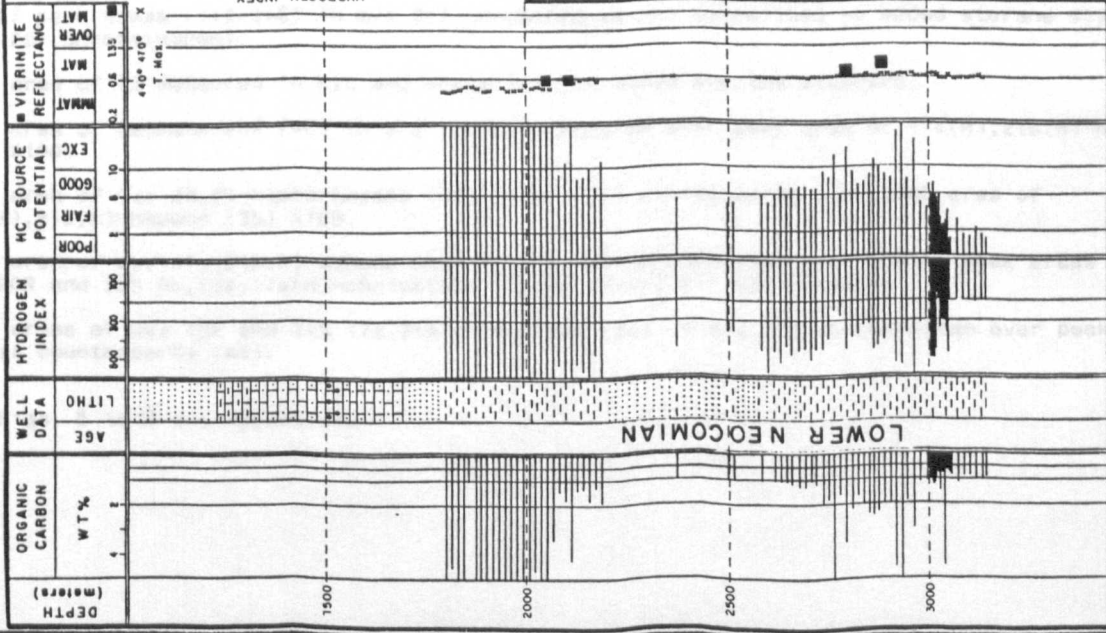


TABLE 2 - Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples From Sediments Derived from Lacustrine Freshwater Environment in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 1.2-4.1%	T.O.C.: 1.0-6.4%	n-ALKANES MAXIMA: C ₂₃ -C ₂₈	C ₂₇ STERANE: ⁶ 0-40ppm	C _{30αβ} HOPANE: ¹¹ 150-470ppm	NICKEL: Trace
HYDROGEN: 0.37-1.02%	S ₂ : ¹ 4.3-37	SATURATES: 38-68%	C ₂₇ /C ₂₈ : ⁷ 0.7-2.0	GAMMACERANE INDEX: ¹² 15-50	VANADYL: Trace
NITROGEN: 0.10-0.20%	HI: ² 133-779mg/g	Pr/Ph: 1.1-2.6	DIASTERANE INDEX: ⁸ 0-50	BISNORHOPANE INDEX: ¹³ undetected	AMORPHOUS: 40-90%
SULPHUR: 0.1-0.4%	R ₀ : 0.50-0.70%	I-C ₂₉ +I-C ₃₀ : ⁴ 50-200ppm	4-Me STERANE ⁹ INDEX: 0-35	HOPANE/STERANE ¹⁴ 5-15	HERBACEOUS: 5-50%
CaCO ₃ : 5-18%	δ ¹³ C: ³ -28 TO -31.0	β-CAROTANE: ⁵ undetected	C ₂₁ + C ₂₂ ¹⁰ STERANES: 0-5ppm	C ₃₄ /C ₃₅ HOPANES: ¹⁵ >1.0	WOODY/COALY: 5-20%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (%)
4. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₉) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (β) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
14. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
15. Peak areas of C₃₄ 22R and 22S 17α,21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 9 to 10 and Appendices.

The excellent hydrocarbon source potential of these sediments, combined with appropriate maturation conditions (see R_o values; Tables 1, 2 and Fig. 5), indicates that they have good source rock characteristics. Tables 1 and 2 and Fig. 6 show for these samples a trend towards high saturate content (up to 66%), a dominance of n-alkanes around C_{23} - C_{25} , pristane > than phytane and odd/even n-alkane dominance.

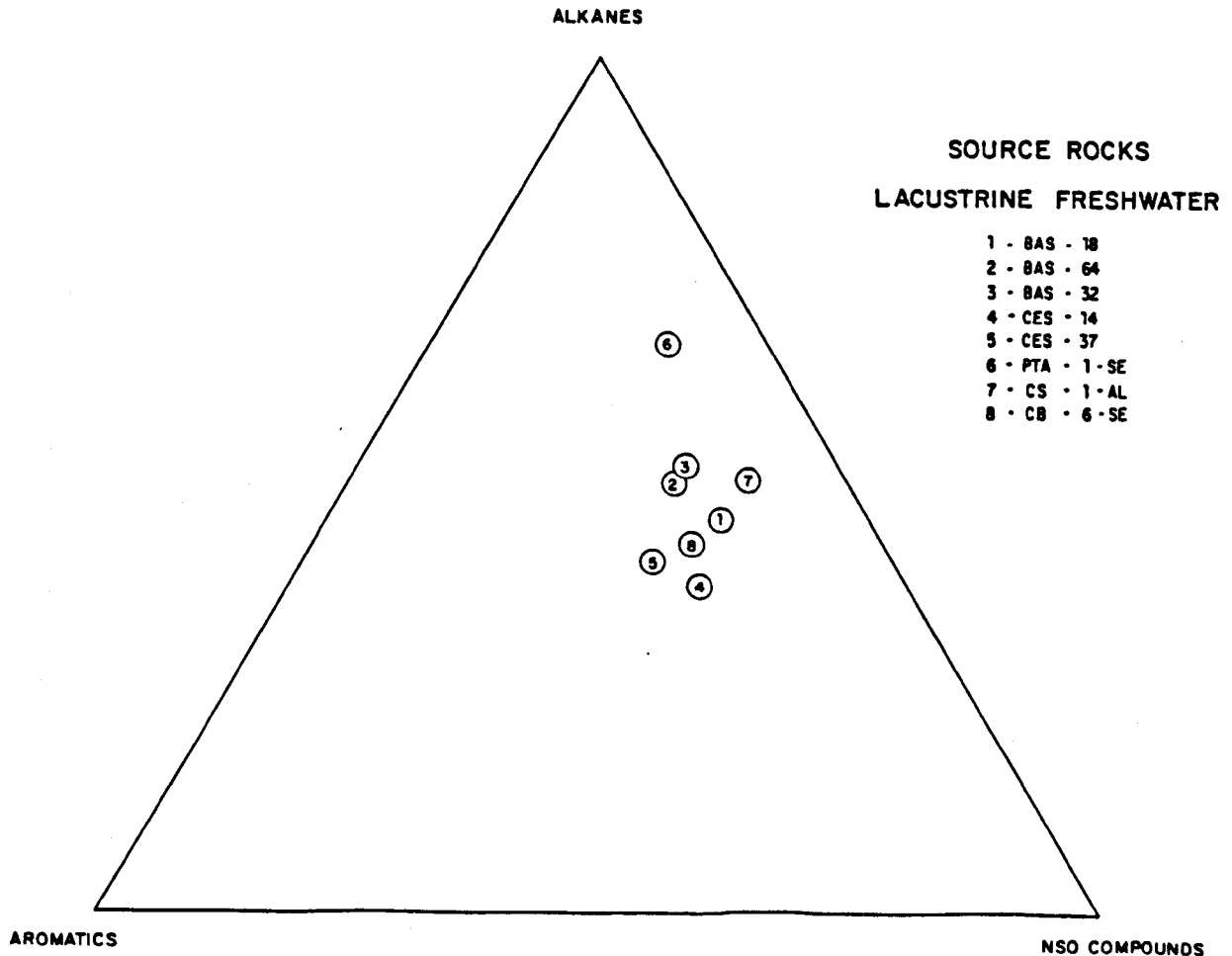


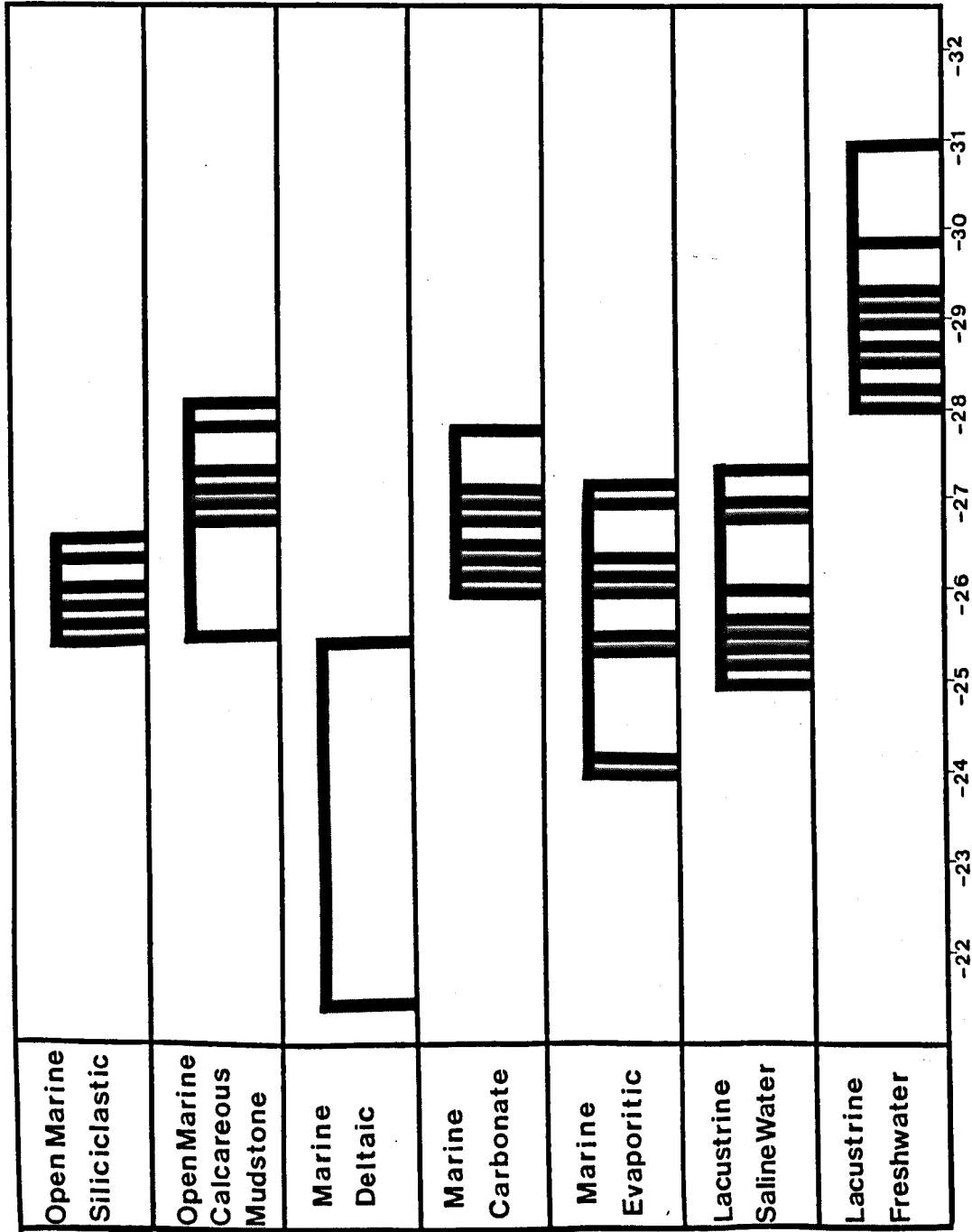
Figure 6- Relative abundance of alkanes, aromatics and NSO compounds in extracts from rock samples derived from lacustrine freshwater environment.

The tendency towards high saturate content and the odd/even n-alkane predominance plus the bias towards high molecular weight n-alkanes(> C_{23}) indicate a major

contribution of long chain lipids from higher plants and freshwater algae (Lijmbach, 1975; Didyk et al., 1978; McKirdy et al., 1986) to the depositional environment (cf. Chapter IV). The isotopically light values of $\delta^{13}\text{C}$ ($< -28\%$; Fig. 7), for the whole extracts are consistent with a freshwater origin, since their principal lipid constituents, originating from terrestrial plants and freshwater algae are generally depleted in ^{13}C relative to those of marine or lacustrine saline plants and organisms (Galimov, 1973; Tissot & Welte, 1984). The high pristane/phytane ratios (Tables 1, 2 and Figs. 8-10), probably reflect the relationship between the contributing organisms and the chemistry of the environment (cf. Chapter IV), e.g. low salinity, rather than simply the anoxic/oxic condition of sedimentation (Didyk et al., 1978). In a freshwater environment, photosynthetic organisms and methanogenic bacteria containing lipids that are considered major sources of pristane would be expected to be abundant (see Chapter IV). With marked increase in salinity (higher Eh), however, the archaeobacterial population (mainly halophiles, which are considered to contain lipids that are a major source of phytane; ten Haven et al., 1987) might be expected to increase in abundance. Thus, the more saline the environment, the greater the potential for an increase in the concentration of phytane precursors. This may help explain the high predominance of pristane in freshwater environments compared with a dominance of phytane in hypersaline environments (Tables 1, 2 and Figs. 8-10, see below; cf. Chapter IV for details).

Moldowan et al. (1985) found carbon isotopes and pristane/phytane ratios to be ineffective for distinguishing non-marine and marine environments on a global basis. Taken together, the carbon isotope values ($\delta^{13}\text{C}$) and pristane/phytane ratios in the present study (Fig. 8) do allow distinction between lacustrine freshwater and marine environments. Some of the lacustrine saline water samples (see below) plot near the samples from the open marine with dominance of siliciclastic lithology environment. In general,

Figure 7- Variation of carbon isotopic data for whole extract from organic-rich sediments from Brazilian marginal basins, with depositional environment. Bars = number of samples.



δ ¹³C ‰ (PDB)

-22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32

however, if the data from the samples other than those shown in Tables 1-14 are also included (not shown) there is a trend towards higher pristane/ phytane ratios in the lacustrine saline samples when compared with the open marine ones. Hence, the type of plot represented by Fig.8 can be a useful geochemical measure in the differentiation of non-marine and marine environments in the Brazilian marginal basins.

Fig. 9 illustrates a typical lithological log showing the stratigraphic position of a source rock horizon (lower Neocomian in the well 1-BAS-64). Also shown are the gas chromatogram and m/z 191 and m/z 217 mass chromatograms of the alkane fraction. As can be observed there are several features in the bulk data and biological marker distribution and concentration that help to characterize this type of environment.

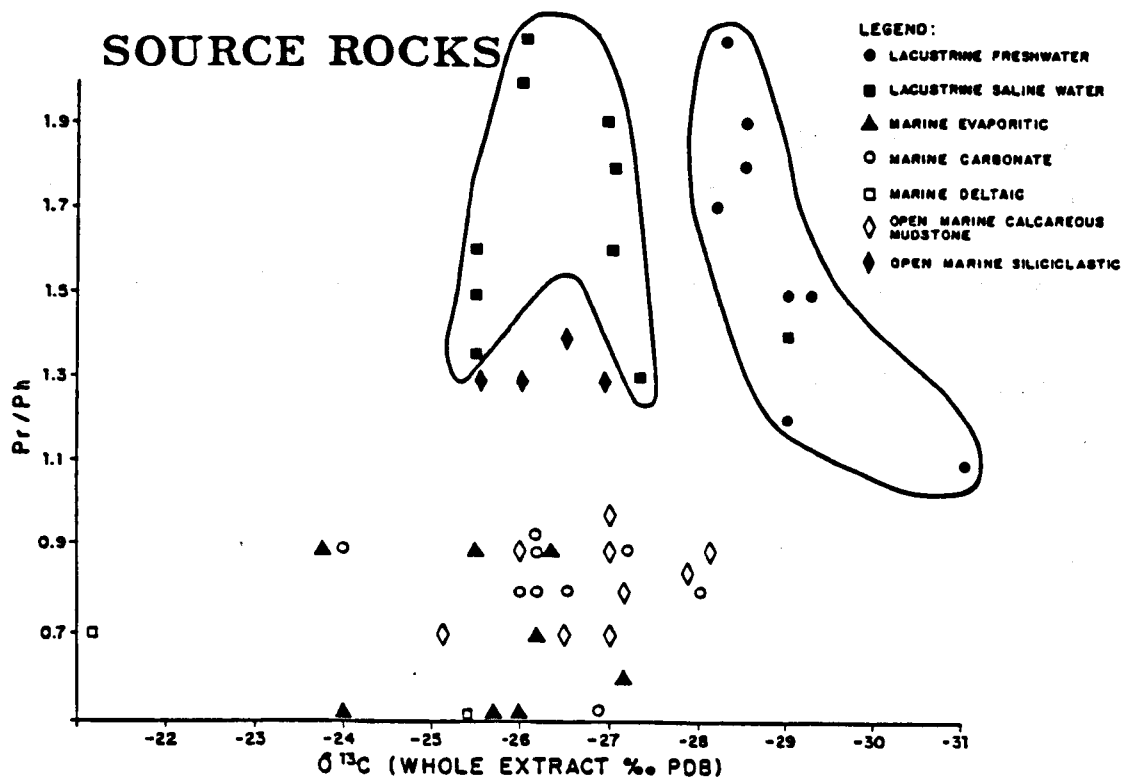
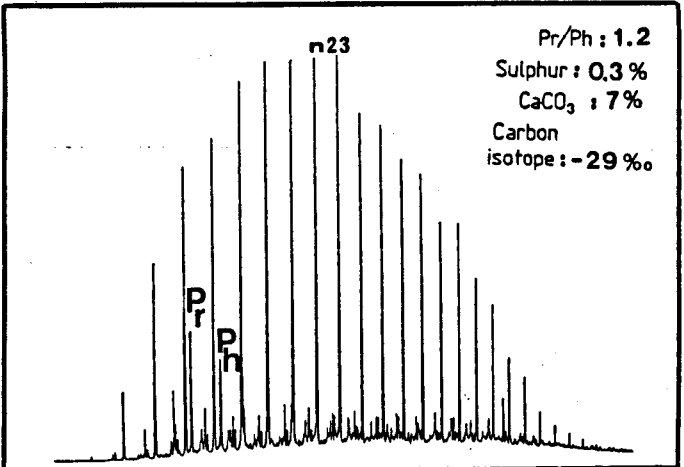
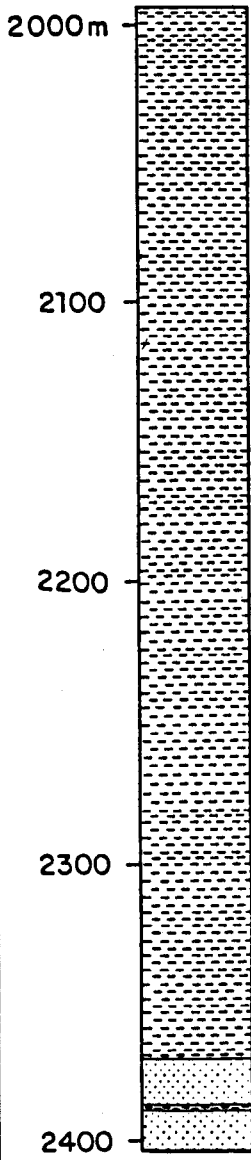


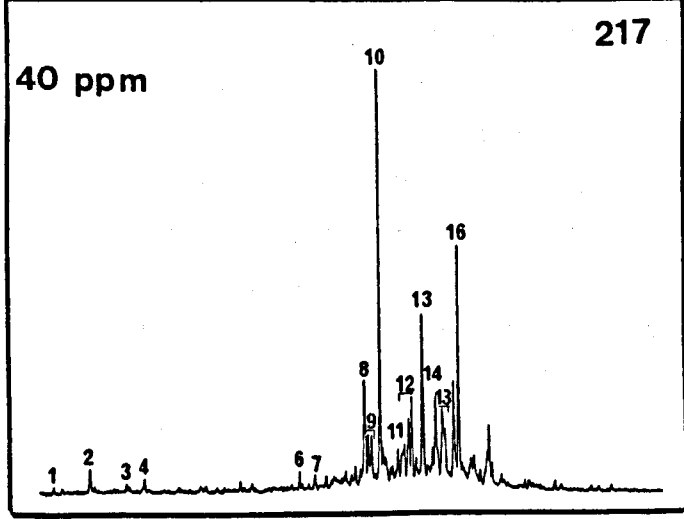
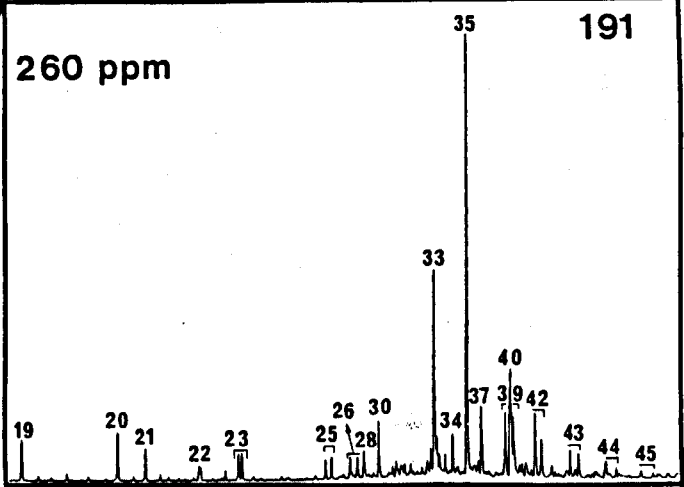
Figure 8- Variance of carbon isotope values with pristane/ phytane ratios of whole extract from organic-rich sediments from Brazilian marginal basins.

Figure 9- Lithological log of a typical well from Bahia sul basin, showing the stratigraphic position of the organic-rich sample BAS-64 for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

**BAS-64
LOWER NEOCOMIAN**



LACUSTRINE FRESH WATER



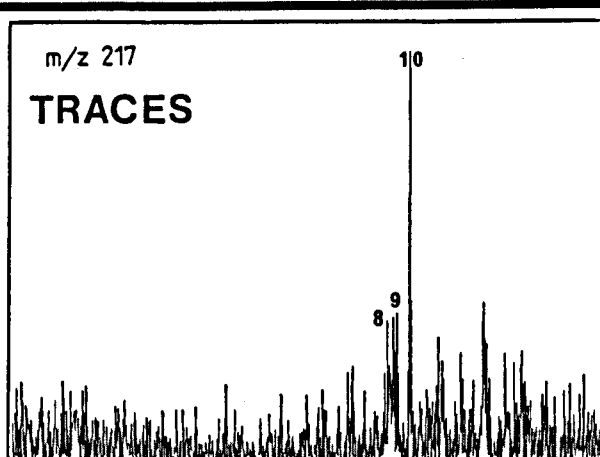
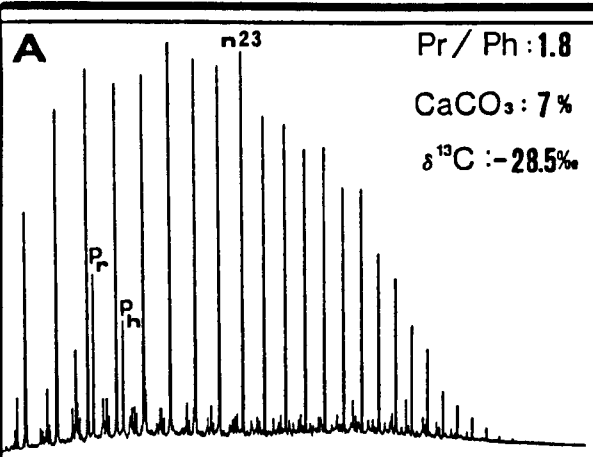
191

217

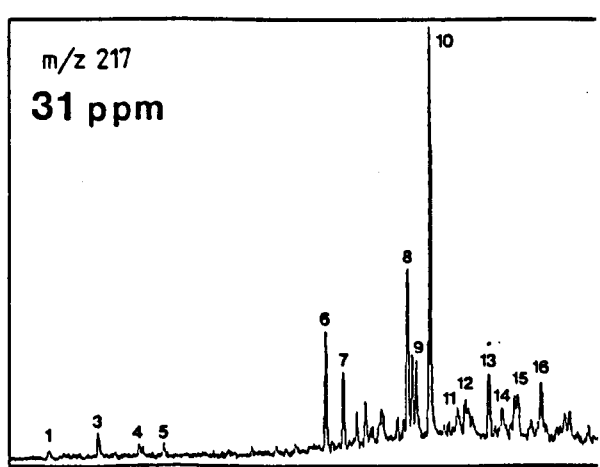
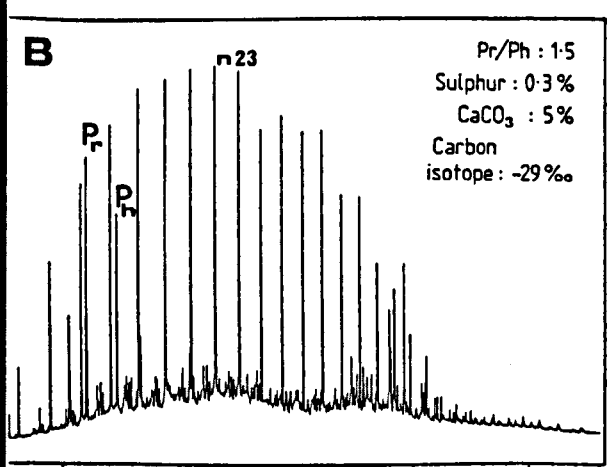
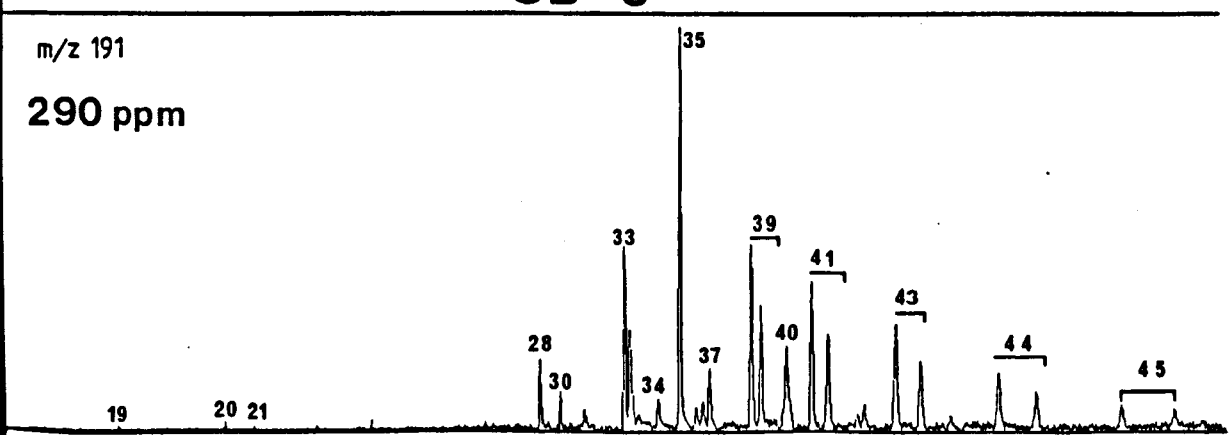
The most marked are the presence of low concentrations (< 40 ppm of extract; Table 2) of C₂₇ $\alpha\alpha\alpha$ steranes (peaks 8 and 10), medium concentration of C₃₀ $\alpha\beta$ hopane (260 ppm of extract, peak 35), low to medium relative abundance of gammacerane (peak 40), high pristane / phytane ratio, low sulphur content, low relative abundances of tricyclic terpanes (peaks 19 to 26), and light $\delta^{13}\text{C}$ value for the whole extract (-29‰). Fig. 10 shows gas chromatograms and m/z 217 and m/z 191 mass chromatograms of the alkane fractions of two samples from a different basin (7 and 8 in Fig. 4). The similarities in the biological markers and bulk data for these samples and 1-BAS-64 are clear. Moldowan et al. (1985) and McKirdy et al. (1986), also reported a paucity of steranes in lacustrine freshwater samples from Brazil, China, Sudan and Australia. This characteristic may be due to the organisms living in such a habitat using lipids other than sterols as rigidifiers and protectors of cell wall materials. A possible explanation for such a phenomenon could be that terrestrial and freshwater plants live under higher oxygen conditions than their saline counterparts and therefore require greater protection for their cells.

The tendency towards a dominance of C₂₇ steranes (Figs. 9-11), contrasts with previous reports (Huang and Meinschein, 1979; Mackenzie et al., 1984; Hoffmann et al., 1984 and Moldowan et al., 1985) of a predominance of C₂₉ steranes in non-marine environments. The interpretation which has been given is that such environments may be expected to receive major contributions of higher plant material, whose precursor sterols are mainly C₂₉. Only one of the samples in Table 1 shows such a feature (PTA-1; 5 in Fig. 11). Hence, interpretation of a predominance of C₂₉ steranes as an indication of higher plant input, or as characteristic of a non-marine environment must be made with caution. A peculiar feature is the presence, in low to medium abundance, of gammacerane (peak 40). The use of a standard and an efficient GC column DB-1701, 60 m; used for analyses presented in Fig. 10), allowed its identification, with complete separation from the hopanes (cf. peak 40 in

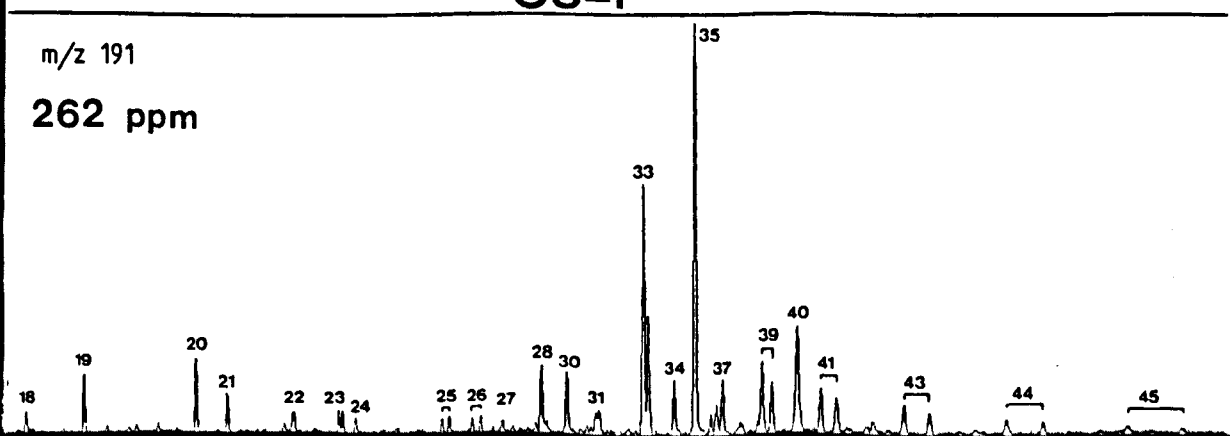
Figure 10 - Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentration of steranes and hopane for two organic-rich rock samples derived from lacustrine freshwater environment from Sergipe/ Alagoas basin (for peak assignments and quantitation see appendices I and II).



CB-6



CS-1



Figs. 9 and 10). Recently, Moldowan *et al.* (1985) have stated that gammacerane cannot be used to distinguish between marine and non-marine samples, since it occurs in several different environments. Such evidence suggests the possibility of a bacterial origin, given its widespread occurrence in time and space. Hence, our results for these samples together the results of this study (see below) suggest that the value of gammacerane as an environmental indicator lies in its relative abundance (and concentration), rather than its mere presence (see 2.5 below). Furthermore, similarities in the above features and other characteristics (Tables 1 and 2), such as high hopane/sterane ratios (5 to 15), an absence of β -carotane and 28,30-bisnorhopane and traces or absence of porphyrins are sufficient to discriminate this environment in the Brazilian marginal basins (Tables 1, 2 and Figs. 7-10).

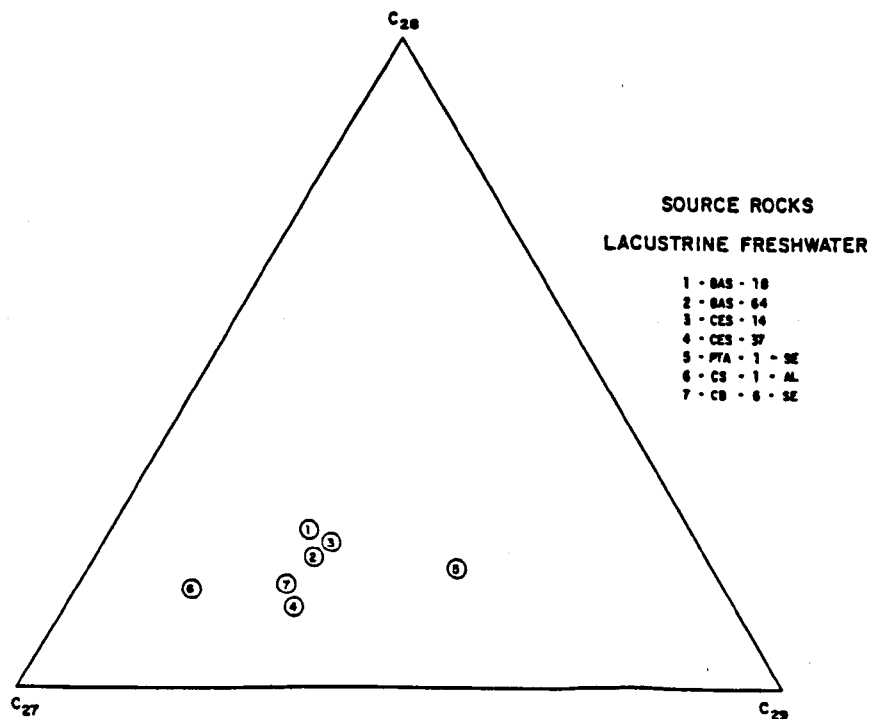


FIG 11- Carbon number (C_{27} , C_{28} , C_{29}) distributions of $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20R steranes for a number of sediment extracts derived from lacustrine freshwater depositional environment.

All these features, together with the absence of C₃₀ steranes and dinosteranes (sample A in Fig. 12, see Chapter IV and Mello *et al.*, 1988 b for details) in the samples derived from this type of environment lend support to the non-marine character of these source rocks (such compounds are considered to be diagnostic features of marine organic matter (sample C in Fig. 12; Moldowan *et al.*, 1985; Summons *et al.*, 1987; Goodwin *et al.*, 1988).

Integration of the data in Tables 1, 2 and Figs. 5-12 show, therefore, a set of bulk, elemental and molecular data for this group that suggest an origin of the organic matter from sediments deposited in a lacustrine freshwater environment.

The most marked are;

- 1) high pristane/phytane ratio, linked with odd n-alkane predominance;
- 2) tendency towards high saturates content, associated with dominance of high molecular weight n-alkanes;
- 3) low to medium sulphur content;
- 4) $\delta^{13}C$ values of whole extract more negative than -28‰;
- 5) very low concentrations of steranes and 4-methyl steranes;
- 6) medium concentration of hopane;
- 7) high hopane/sterane ratio;
- 8) absence of C₃₀ steranes, dinosterane, β -carotane, 28,30-bisnorhopane and nickel and vanadyl porphyrins;
- 9) low relative abundances of gammacerane

Similarities to many of the data above have been reported for samples derived from typical freshwater environments in Shanganning and Songliao Basins in China; Otway and Gippsland Basins in Australia (Powell, 1986; Wang Tieguan *et al.*, 1987; McKirdy *et al.*, 1986; Philp and Gilbert, 1986).

2.2.2 Lacustrine Saline Water.

The organic rich sediments investigated in this group are confined to Campos, Espirito Santo and Potiguar basins in the

M / Z

414 - 217

414 - 231 - 98 - 95

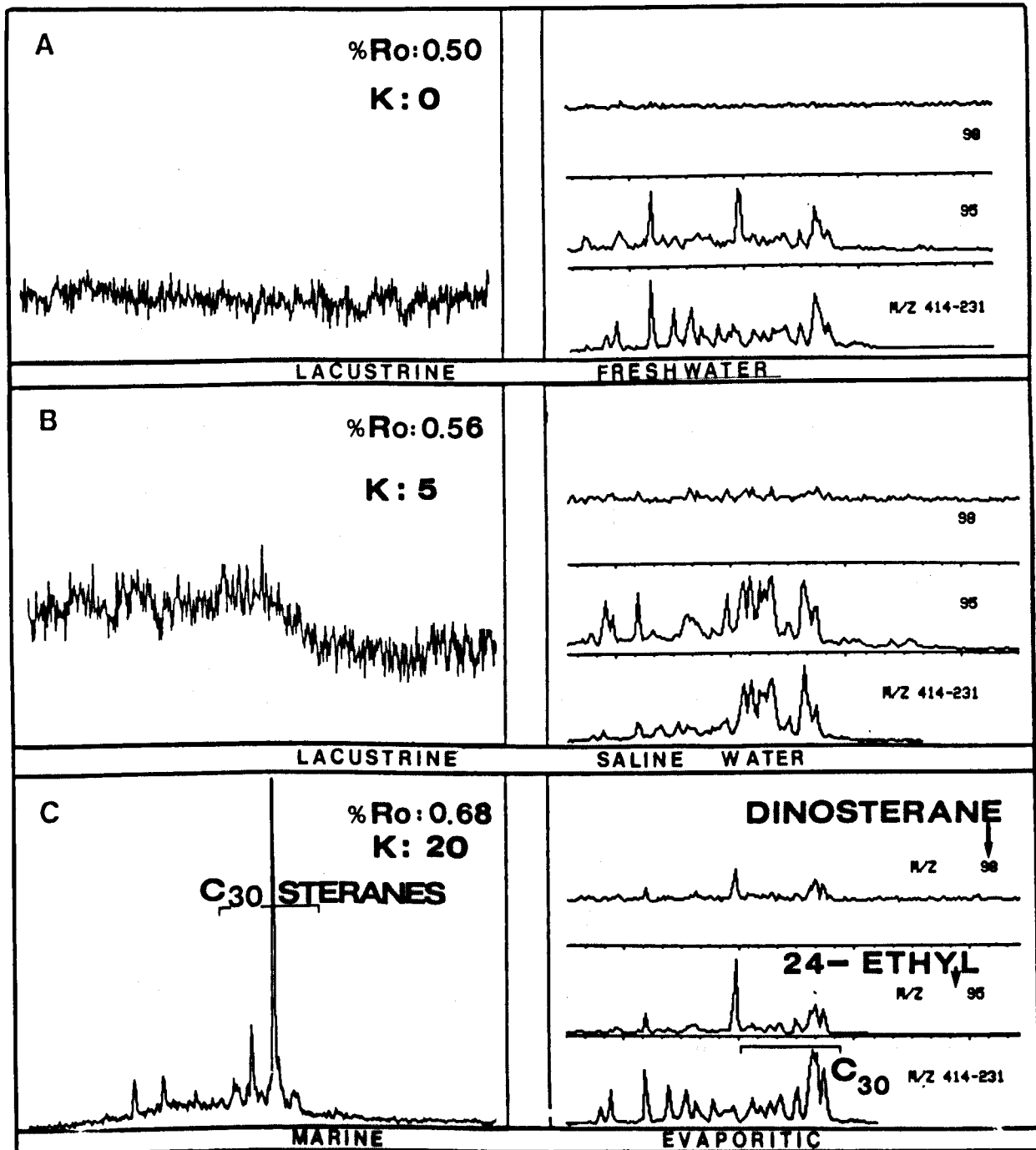


Figure 12- Mass chromatograms from metastable ion monitoring of transition m/z 414-217 (C₃₀ steranes), MS-MS mass chromatogram of transitions m/z 414-231, 414-95 and 414-98 (4-methyl steranes) of alkane fractions, and vitrinite reflectance data from sediment extracts from different depositional environments from Brazilian marginal basins ; A: lacustrine freshwater (CES-14); B: lacustrine saline water (RJS-71); C: marine evaporitic (CES-42). K values indicate concentration relative to constant amounts of added deuteriated sterane standard.

Table 3: Geological and Geochemical Data for Sediments From Lacustrine Saline Environments.

Wells	RD-1	ESS-43	IP-1	ESS-34	RJS-101	RJS-71	RJS-76	RJS-226	RJS-51	RJS-164	UPN-1
Sample Number	11	12	13	14	15	16	17	18	19	20	21
Sample Nature	Cuttings	Core	Core	Cuttings	Core	Core	Cuttings	Core	Core	Core	Core
Depth (m)	2895	2532	3370	2310	4410	3060	4835	3597	3318	4260	1337
Age	Upper Neocomian	Upper Neocomian	Lower Neocomian	Upper Neocomian	Upper Neocomian	Upper Neocomian	Upper Neocomian	Upper Neocomian	Upper Neocomian	Lower Neocomian	Aptian
Lithology	Dark Grey Shale	Dark Grey Shale	Dark Grey Shale	Calcareous Grey Shale	Light Grey Marl	Calcareous Grey Shale	Dark Grey Shale	Calcareous Grey Shale	Dark Grey Shale	Dark Grey Shale	Black Shale
CaCO ₃ (%)	4.5	5.0	2.0	24	45	19	8.3	17	10	14	8
Sulphur (%)	0.60	0.40	0.42	0.40	0.10	0.30	0.60	0.20	0.35	0.30	0.40
TOC (%)	2.9	5.0	3.3	5.0	3.3	3.6	2.0	4.2	2.6	3.5	2.4
S ₂ (KgHC/Ton rock)	12	37	18	36	10	22	14	21	24	38	21
HI (mgHC/gTOC)	584	740	537	730	300	630	360	509	436	980	874
T-MAX (°C)	443	436	442	436	431	425	440	437	438	439	433
Ro (%)	0.66	0.52	0.63	0.45	0.57	0.56	0.66	0.59	0.52	0.65	0.50
SCI	6.5	5.5	6.5	4.0	5.0	-	8.0	5.5	5.5	-	4.0
EOM (ppm)	1350	1600	442	900	1020	3750	5541	3900	810	6973	2200
Pr/Ph	2.0	1.6	1.4	2.2	1.6	1.3	1.3	1.5	1.6	1.8	2.2
Pr/nC ₁₇	2.3	1.2	1.1	3.9	0.5	0.9	1.5	1.5	0.6	5.8	4.8
Ph/nC ₁₈	1.1	0.8	0.8	2.4	0.3	0.6	1.3	1.5	0.3	2.5	2.3
nC ₁₇ /C ₃₁	0.6	1.5	0.8	4.5	1.7	1.6	2.2	2.2	1.9	3.4	2.2
δ ¹³ C whole extract	-26.0	-27.0	-28.8	-26.0	-25.0	-25.5	-	-25.6	-25.5	-26.9	-32.0
Saturates (%)	48	40	49	23	40	49	38	43	43	48	25
Aromatics (%)	13	26	15	15	30	17	18	26	26	16	14
NSO (%)	39	34	36	62	30	34	44	31	31	36	61
Amorphous (%)	80	90	80	90	5	90	90	90	100	90	65
Herbaceous (%)	10	5	15	5	90	5	5	5	Tr	10	30
Woody+Coaly (%)	10	5	5	5	5	5	5	5	Tr	Tr	5

southern, eastern and northern areas of the continental margin, ranging in age from lower Neocomian to Aptian (Fig. 13 and Table 3).

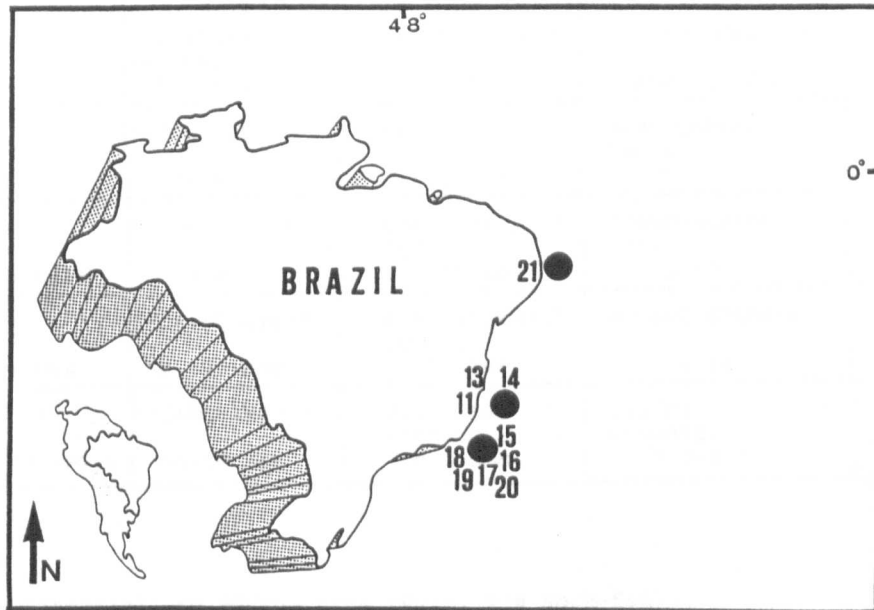


Figure 13- Location map showing the areas from which samples from lacustrine saline water depositional environment were investigated.

Specifically, three source rock systems have been identified: lower Neocomian dark grey shales in the Campos and Espirito Santo basins (samples 13 and 20 in Table 3 and Fig 13), upper Neocomian dark grey shales and calcareous grey shales and marls in the Campos and Espirito Santo basins (samples 11, 12 and 14-19 in Table 3 and Fig 13), and Aptian black shales in the Potiguar basin (sample 21 in Table 3 and Fig 13). Fig. 14 shows two typical geochemical logs with the stratigraphic position of two organic rich horizons (upper Neocomian, Campos and Aptian, Espirito Santo basins), chosen as specific examples (see also Tables 3 and 4). They are composed of thick beds of well laminated calcareous/ dark grey to black shales and marls (CaCO_3 from 2 to 45%), rich in organic matter (TOC up to 5%), with low to medium sulphur

TABLE 4 - Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples From Sediments Derived from Lacustrine Saline Water Environment in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 1.5-11.2%	T.O.C.: 2-5%	n-ALKANES MAXIMA: C ₁₈ -C ₂₁	C ₂₇ STERANE: ⁶ 0-150ppm	C _{30αβ} HOPANE: ¹¹ 200-1520ppm	NICKEL: Tr-2831ppm
HYDROGEN: 0.36-1.0%	S ₂ : ¹ 12-38	SATURATES: 37-49%	C ₂₇ /C ₂₉ : ⁷ 1.4-2.5	GAMMACERANE INDEX: ¹² 13-72	VANADYL: Tr-95ppm
NITROGEN: 0.07-0.20%	HI: ² 300-980mg/g	Pr/Ph: 1.3-2.2	DIASTERANE INDEX: ⁸ 10-45	BISNORHOPANE INDEX: ¹³ 3-10	AMORPHOUS: 80-90%
SULPHUR: 0.3-0.9%	R ₀ : 0.45-0.66%	I-C ₂₅ +I-C ₃₀ : ⁴ 70-1811ppm	4-Me STERANE ⁹ INDEX: 20-165	HOPANE/STERANE ¹⁴ 4-14	HERBACEOUS: 5-15%
CaCO ₃ : 4-49%	δ ¹³ C: ³ -25.5 TO -26.9	β-CAROTANE: ⁵ 10-500ppm	C ₂₁ + C ₂₃ STERANES: ¹⁰ 8-30ppm	C ₃₄ /C ₃₅ HOPANES: ¹⁵ 1.3-2.1	WOODY/COALY: 5-10%

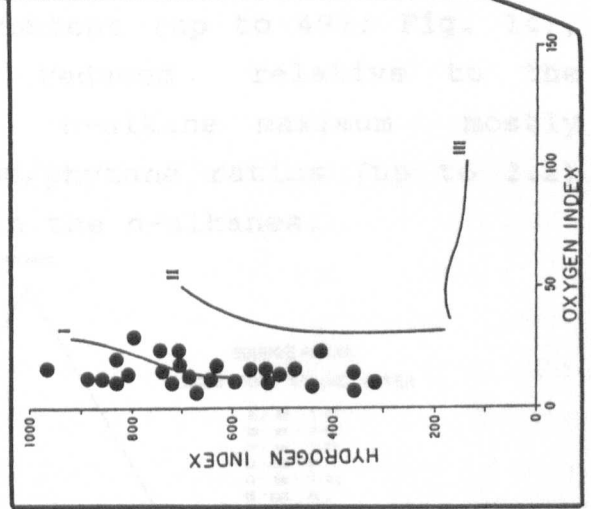
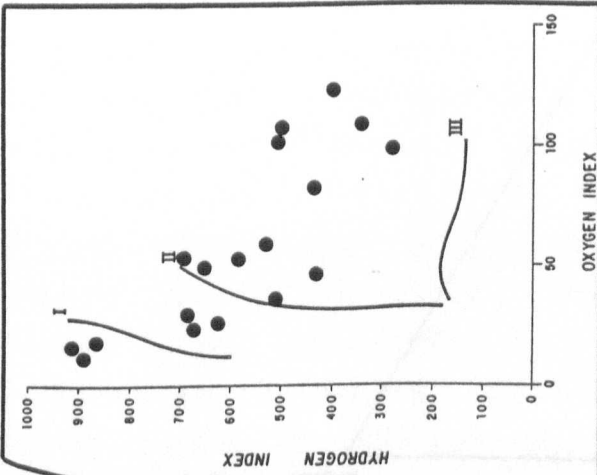
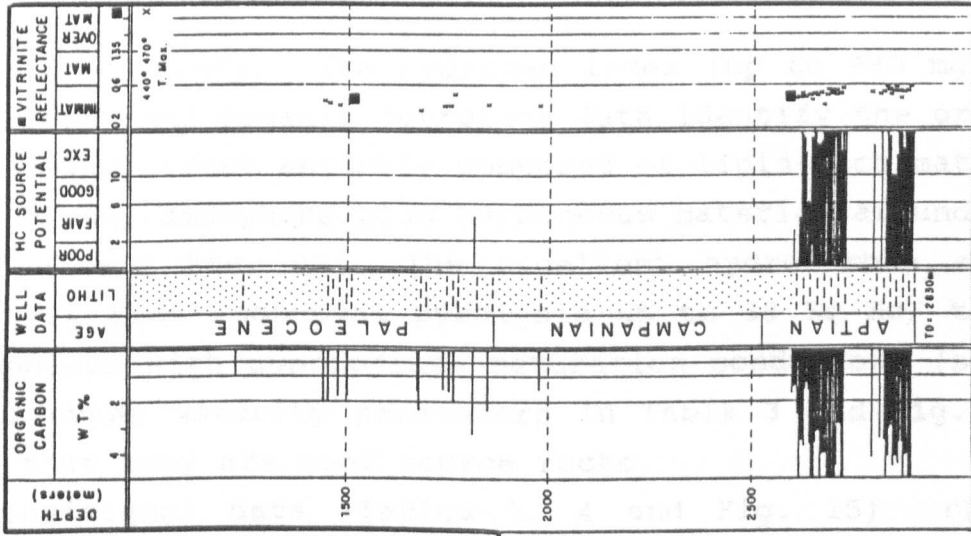
MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (%)
4. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (β) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
14. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
15. Peak areas of C₃₄ 22R and 22S 17α,21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

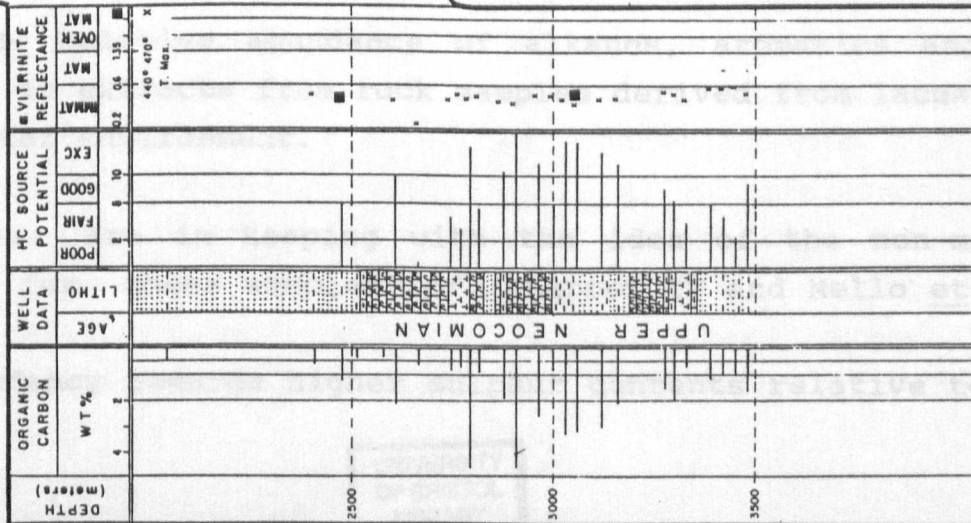
* See Figs. 18 to 21 and Appendices.

Figure 14- Geochemical logs of two wells from Campos (RJS-71 and Espirito Santo (PDI-1) basins, showing the stratigraphic position of two lacustrine saline water organic-rich sedimentary succession and the hydrogen index (S_2 / TOC) vs oxygen index (S_3 / TOC), presented on van Krevelen type diagram, for samples from the upper Neocomian and Aptian.

PDI 1-ES



RJS 71



content (up to 0.6%). The hydrogen index (up to 980 mg HC/g organic carbon) and organic petrology data identify the organic matter as being almost entirely composed of lipid-rich material (type I kerogen, amorphous plus herbaceous material around 95%; Tables 3, 4 and Fig. 14). The excellent hydrocarbon source potential (S_2 from Rock-Eval pyrolysis up to 38 Kg Hc/ ton of rock), combined with appropriate maturation conditions (see Ro values and other maturity parameters in Table 3 and Fig. 14), indicates that they are good source rocks.

The compositional data (Tables 3, 4 and Fig. 15) show a tendency towards high saturates content (up to 49%; Fig. 14), although on the whole slightly reduced relative to the lacustrine freshwater samples, n-alkane maximum mostly around C_{19} to C_{21} , high pristane/phytane ratios (up to 2.2) and an odd over even preference in the n-alkanes.

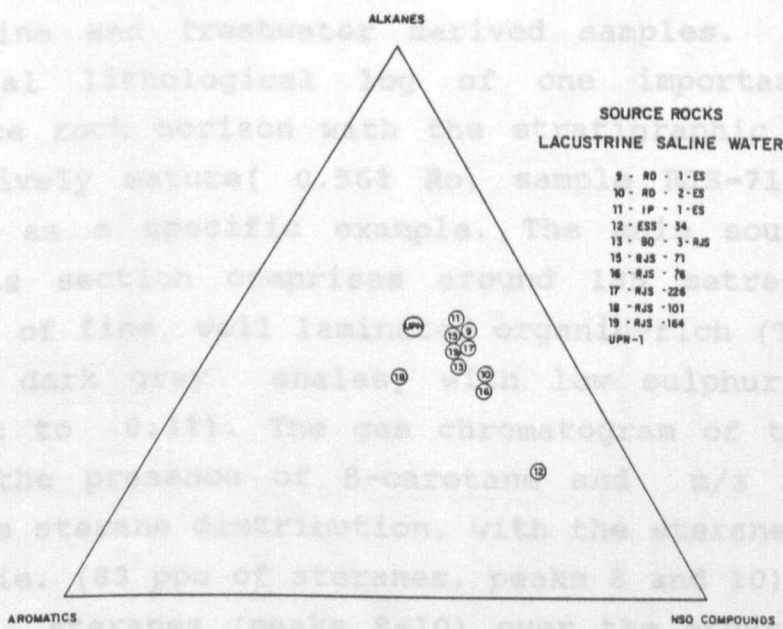


Figure 15- Relative abundance of alkanes, aromatics and NSO compounds in extracts from rock samples derived from lacustrine saline water environment.

These data are in keeping with the idea of the non-marine character for these samples (cf. Chapter IV and Mello *et al.*, 1988b).

The tendency towards higher sulphur contents relative to the

lacustrine freshwater samples (Tables 2 and 4), may reflect the more saline character (high Eh) of the depositional environment of these sediments. Enhanced salinity might also explain the isotopically heavy ($\delta^{13}\text{C}$ values $>$ than -27%). Note that the two samples outside this range (samples 13 and 21) are not included in Fig. 7 because they are considered "anomalous" in the sense that they are not typical when the large number of samples from this type of environment whose $\delta^{13}\text{C}$ ratios have been measured are considered overall (unpublished; Tables 3, 4 and Fig. 7). Plants from saline environments can preferentially utilise carbonate complexes as their carbon source for photosynthesis. These are richer in ^{13}C than atmospheric carbon dioxide, which is enhanced in ^{12}C (Tissot and Welte, 1984). The $\delta^{13}\text{C}$ and pristane /phytane data shown in Figs. 7 and 8 suggest that carbon isotopes might be useful in discriminating between lacustrine saline and freshwater derived samples. Fig. 16 shows a typical lithological log of one important upper Neocomian source rock horizon with the stratigraphic position of the relatively mature (0.56% Ro) sample RJS-71 (Campos basin), chosen as a specific example. The main source rock horizon in this section comprises around 185 metres (2890-3175m; Fig. 14) of fine, well laminated organic-rich (TOC up to 5%) calcareous dark grey shales, with low sulphur content (less or equals to 0.3%). The gas chromatogram of the total alkanes shows the presence of β -carotane and m/z 217 mass chromatogram the sterane distribution, with the steranes in low concentration, ie. (83 ppm of steranes, peaks 8 and 10), with a dominance of C_{27} steranes (peaks 8-10) over the other species (peaks 11-16) and high relative abundances of low molecular weight steranes (peaks 1 to 5). The m/z 191 mass chromatogram shows high concentrations of C_{30} $\alpha\beta$ hopane (320 ppm, peak 35), medium relative abundances (cf. Table 4) of gammacerane (peak 40) and abundant tricyclic terpanes up to C_{35} . All these features, together with the absence of C_{30} steranes and dinosteranes (sample B in Fig. 12; also see Chapter IV and Mello et al., 1988a, b for details), lend support to the idea

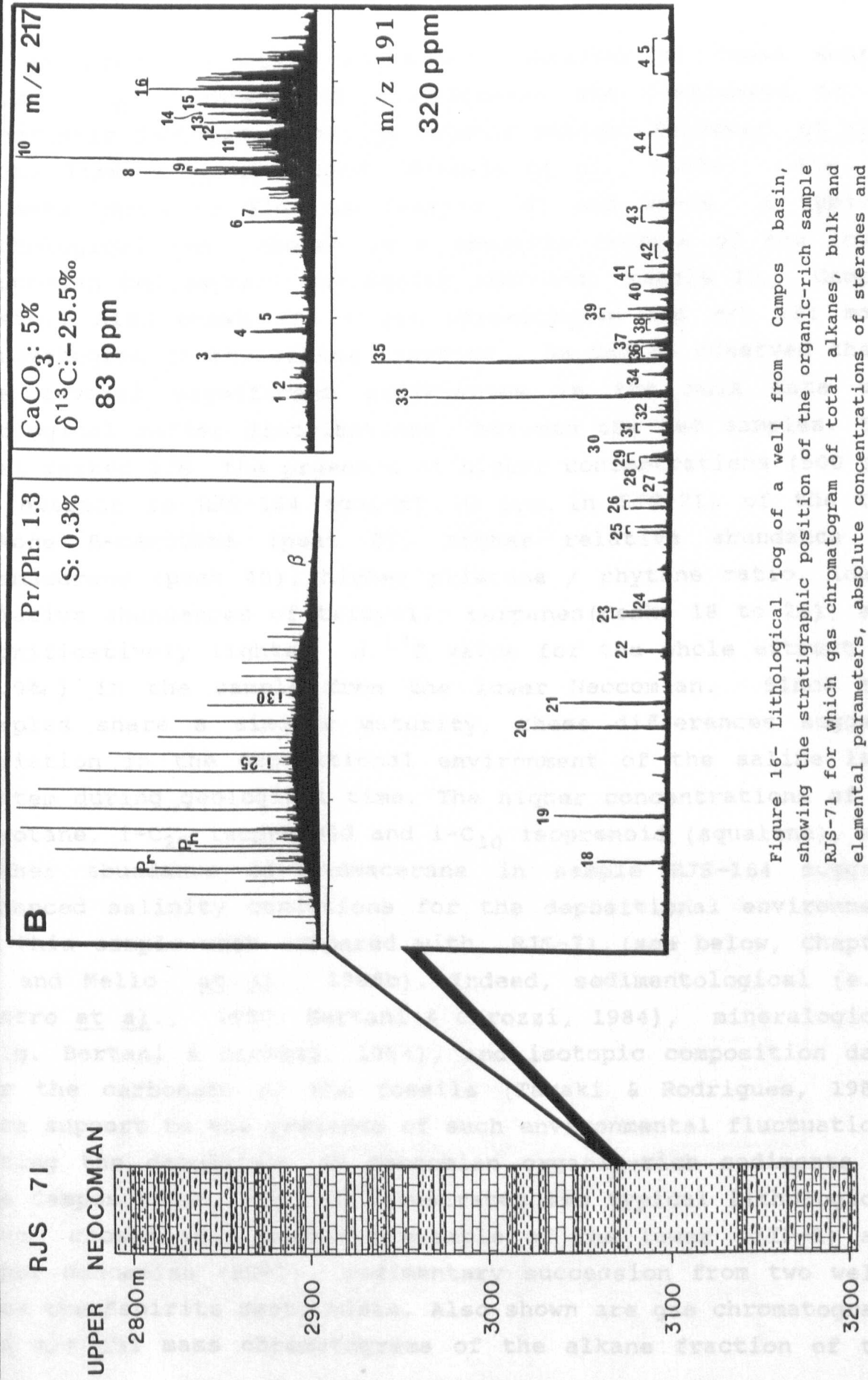


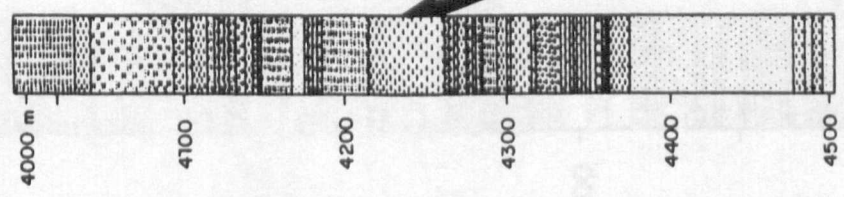
Figure 16- Lithological log of a well from Campos basin, showing the stratigraphic position of the organic-rich sample RJS-71 for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

of enhanced salinity, non-marine character of these source rocks (C_{30} steranes and dinosteranes are considered to be diagnostic features of marine organic matter; Moldowan et al., 1985; Summons et al., 1988; Goodwin et al., 1988). Fig. 17 repeats parts of Fig. 16 (sample 16) and shows a typical lithological log chosen as a specific example of the lower Neocomian sedimentary succession (RJS-164, sample 20, Campos basin). Also shown are a gas chromatogram and m/z 191 mass chromatogram of the alkane fraction. As can be observed there are several significant differences in the bulk data and biological marker distributions between the two samples. The most marked are the presence of higher concentrations (500 ppm of extract in RJS-164 against 30 ppm in RJS-71) of the C_{40} alkane β -carotane (peak β), higher relative abundance of gammacerane (peak 40), higher pristane / phytane ratio, lower relative abundances of tricyclic terpanes (peaks 18 to 26), and significantly lighter $\delta^{13}C$ value for the whole extract (-26.9‰) in the sample from the lower Neocomian. Since the samples share a similar maturity, these differences suggest variation in the depositional environment of the saline lake system during geological time. The higher concentrations of β -carotane, i- C_{25} isoprenoid and i- C_{30} isoprenoid (squalane), and higher abundance of gammacerane in sample RJS-164 suggest enhanced salinity conditions for the depositional environment of this sample when compared with RJS-71 (see below, Chapter IV and Mello et al., 1988b). Indeed, sedimentological (e.g. Castro et al., 1980; Bertani & Carozzi, 1984), mineralogical (e.g. Bertani & Carozzi, 1984), and isotopic composition data for the carbonate of the fossils (Takaki & Rodrigues, 1984) data support to the presence of such environmental fluctuations during the deposition of Neocomian organic-rich sediments in the Campos basin. Fig. 18 illustrates two typical lithological logs chosen as a specific example of the lower (IP-1) and upper Neocomian (RD-1) sedimentary succession from two wells from the Espirito Santo Basin. Also shown are gas chromatograms and m/z 191 mass chromatograms of the alkane fraction of two

Figure 17- Lithological logs of two wells from Campos basin, showing the stratigraphic position of two organic-rich samples from upper (RJS-71) and lower Neocomian (RJS-164) for which gas chromatogram of total alkanes, bulk and elemental parameters, and partial m/z 191 chromatograms are shown (for peak assignments see appendix I).

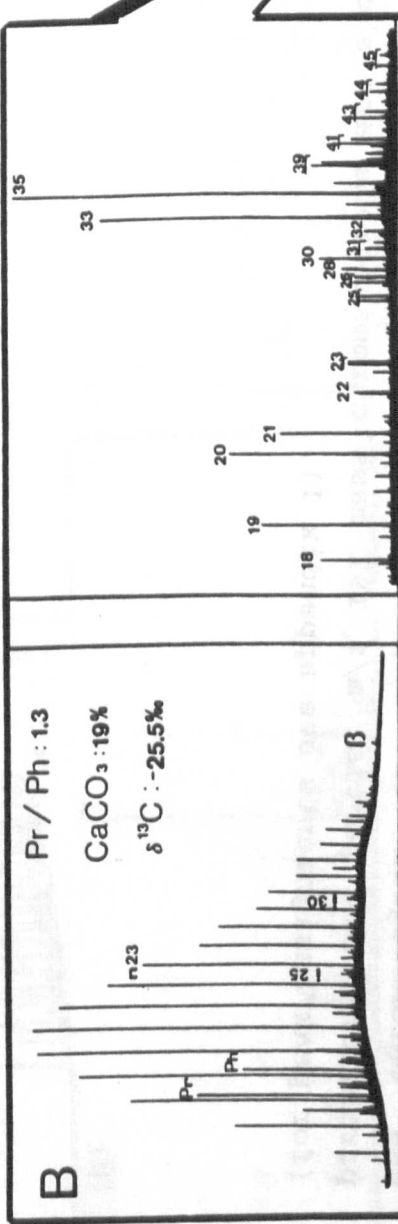
RJS 164

LOWER NEOCOMIAN

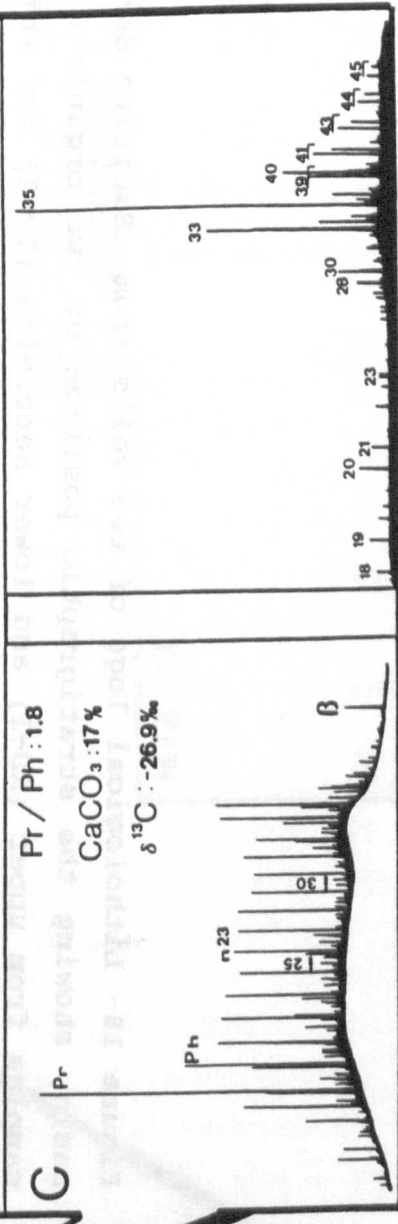


GAS CHROMATOGRAM

B
 Pr / Ph : 1.3
 CaCO₃ : 19%
 δ¹³C : -25.5‰



C
 Pr / Ph : 1.8
 CaCO₃ : 17%
 δ¹³C : -26.9‰



RJS 71

UPPER NEOCOMIAN

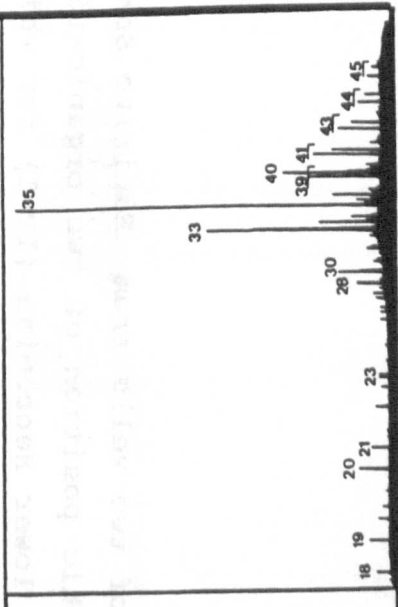
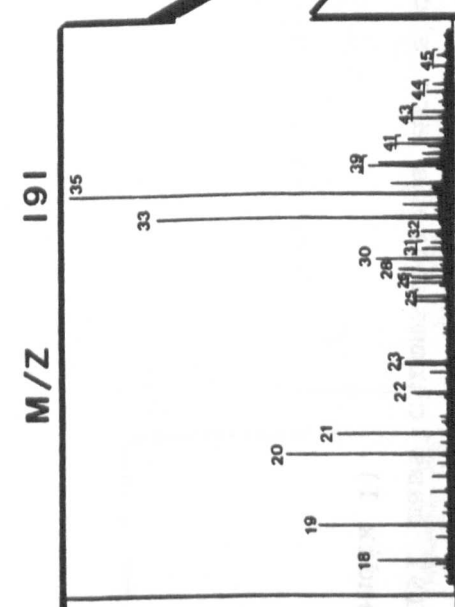
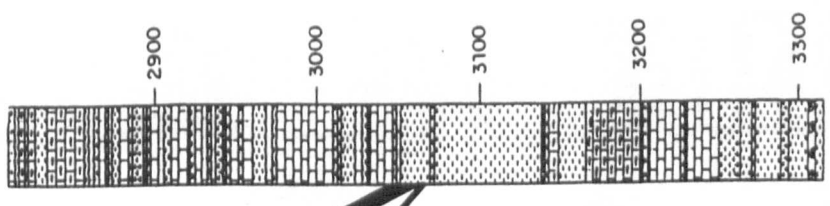
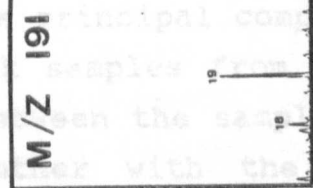
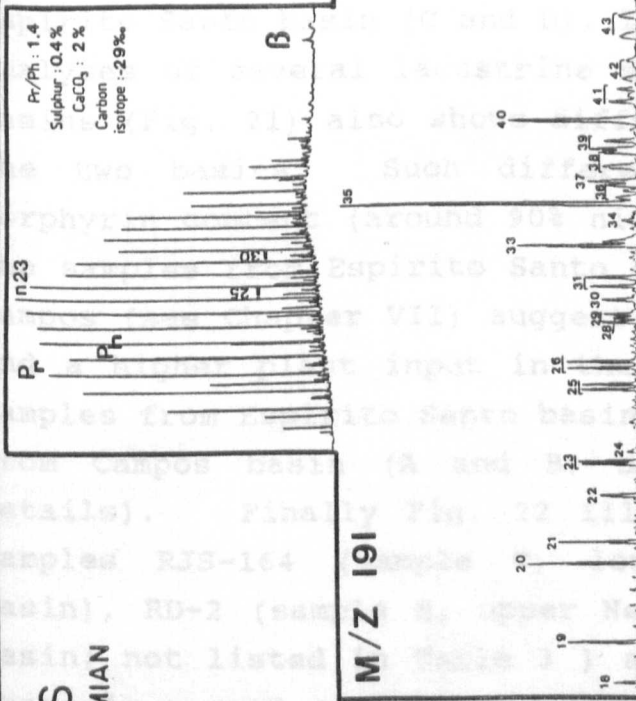
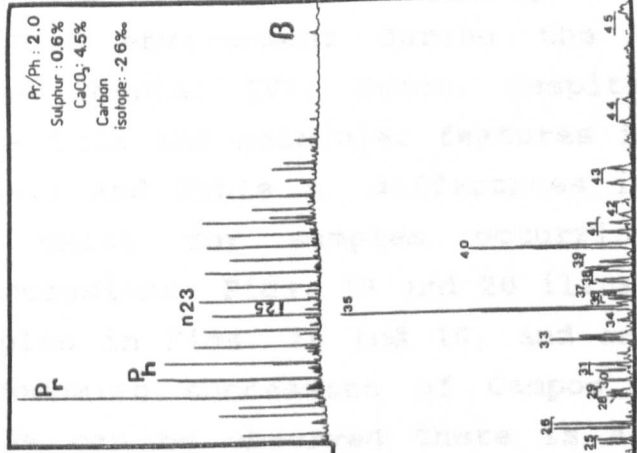
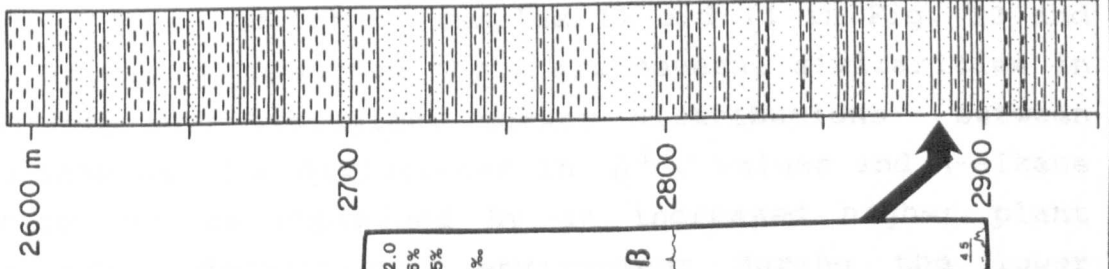
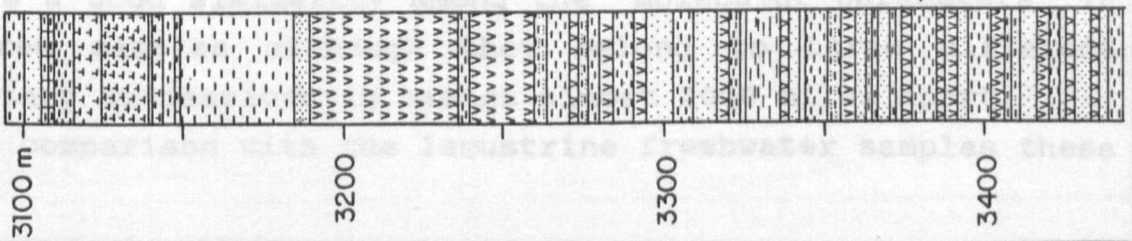


Figure 18- Lithological logs of two wells from Espirito Santo basin, showing the stratigraphic position of two organic-rich samples from upper (RD-1) and lower Neocomian (IP-1) for which gas chromatogram of total alkanes, bulk and elemental parameters, and partial m/z 191 mass chromatograms are shown (for peak assignments see appendix I).

RD-1-ES
UPPER NEOCOMIAN



IP-1-ES
LOWER NEOCOMIAN



samples from these horizons (samples 11 and 13 in Fig. 13 and Table 3). As can be observed there are several similarities in the bulk data and biological marker distributions between these two samples. The differences in $\delta^{13}\text{C}$ values and n-alkane distribution can be explained by an increased higher plant input in the depositional environment during the lower Neocomian (for details see Chapter IV). Hence, despite the overall similarities in the bulk and molecular features in the samples shown in Figs. 16-18 and Table 3, differences in the molecular properties do exist for samples occurring at different stratigraphic successions. Figs. 19 and 20 illustrate a comparison for the samples in Figs. 16 and 18, and another sample from the upper Neocomian succession of Campos basin (sample 18 in Table 3). As can be observed there is a good correlation between the samples, with some differences in the n-alkane distributions, gammacerane abundance (peak 40), C_{30} $\alpha\beta$ hopane concentration, and CaCO_3 content between samples from Campos basin (A and B), compared to the samples from Espirito Santo basin (C and D). Indeed, the principal component analyses of several lacustrine saline rock samples from these basins (Fig. 21) also shows differences between the samples of the two basins. Such differences together with the high porphyrin content (around 90% nickel; Table 4, Chapter VII) in the samples from Espirito Santo basin versus almost absence in Campos (see Chapter VII) suggest the idea of enhanced salinity and a higher plant input in the environment of deposition of samples from Espirito Santo basin (C and D) compared to samples from Campos basin (A and B; see below and Chapter IV for details). Finally Fig. 22 illustrates a comparison between samples RJS-164 (sample C, lower Neocomian of the Campos basin), RD-2 (sample B, upper Neocomian of the Espirito Santo basin; not listed in Table 3) and UPN-1. As can be observed there is a good similarity among the molecular parameters in the three samples although they belong to three different sedimentary successions in basins almost 2000 miles apart.

In comparison with the lacustrine freshwater samples these

Figure 19- Gas chromatograms of total alkanes, bulk and elemental parameters, partial m/z 217 chromatograms and absolute concentration of steranes of four organic-rich rock samples derived from lacustrine saline water environment from Campos (A: RJS-71; B: RJS-226) and Espirito Santo (C: IP-1; D: RD-1), basins (for peak assignments and quantitation see appendices I and II).

GAS CHROMATOGRAM

M / Z 217

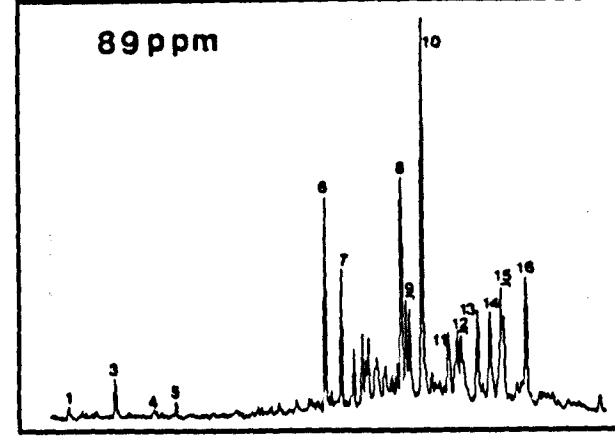
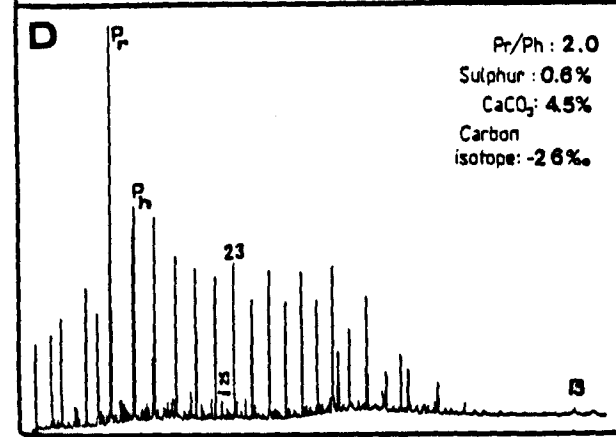
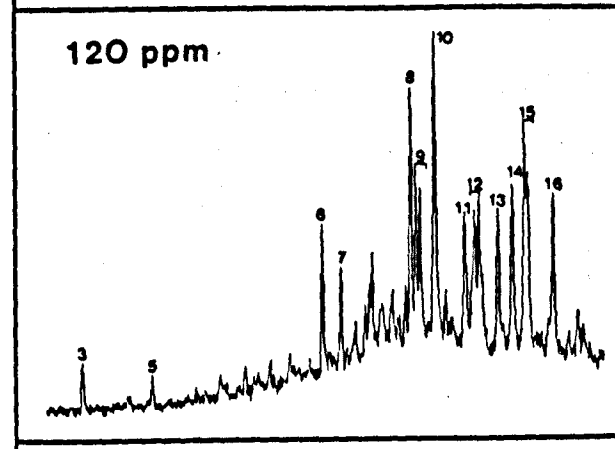
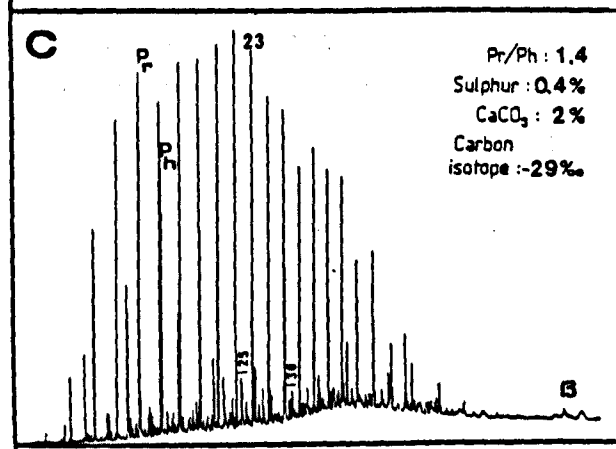
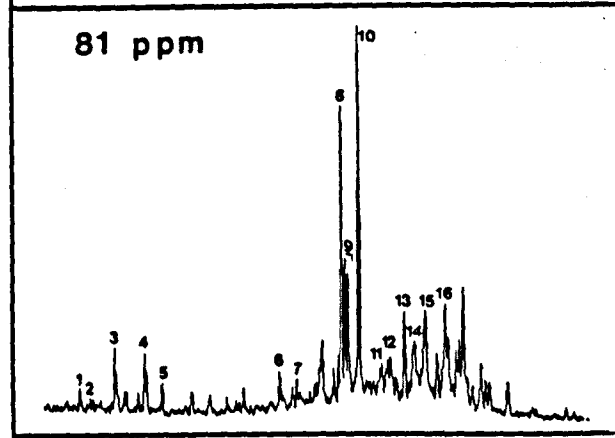
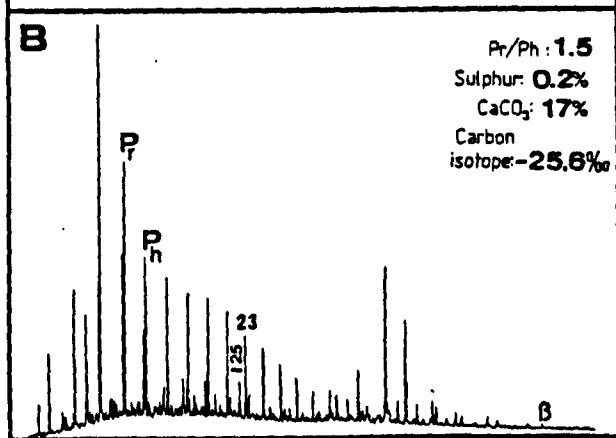
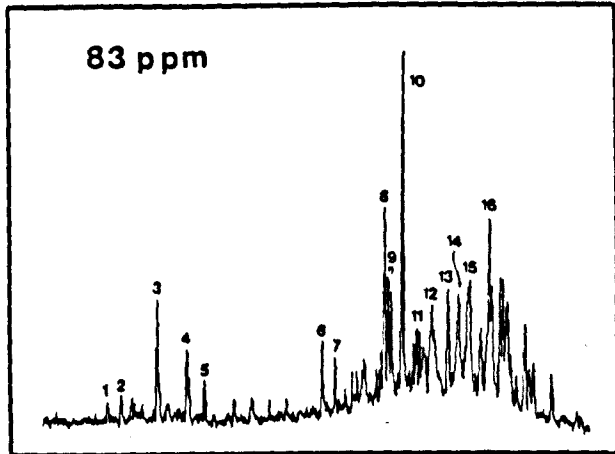
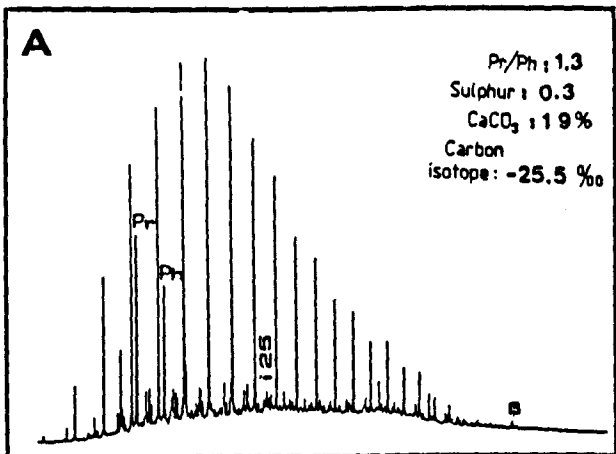


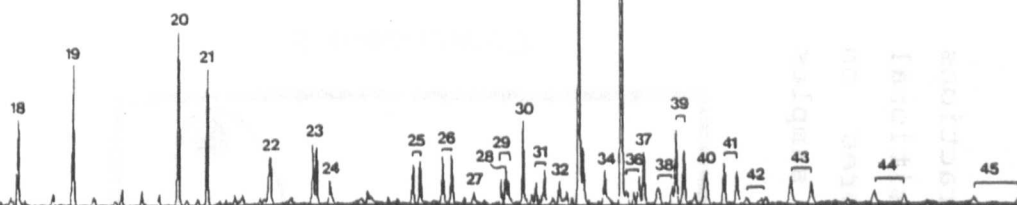
Figure 20- Partial m/z 191 chromatograms of total alkanes, vitrinite reflectance data and absolute concentration of hopane for the same samples as Fig. 19 (for peak assignments and quantitation see appendices I and II).

M/Z 191

A

Ro: 0.56 %

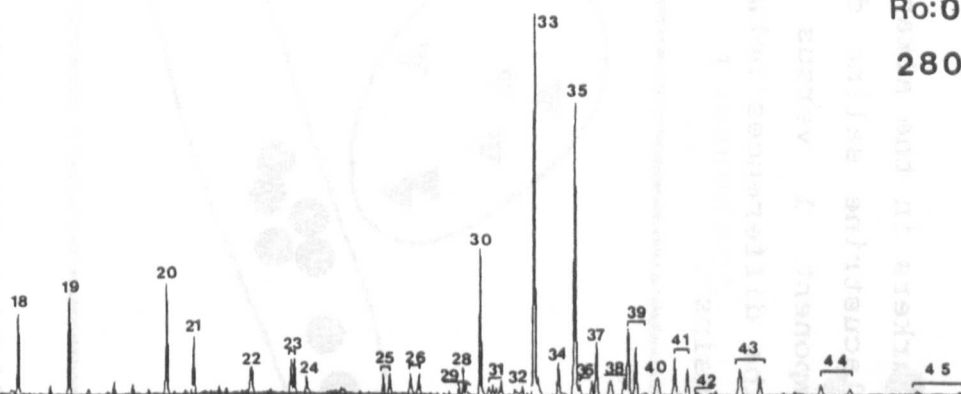
320 ppm



B

Ro: 0.59 %

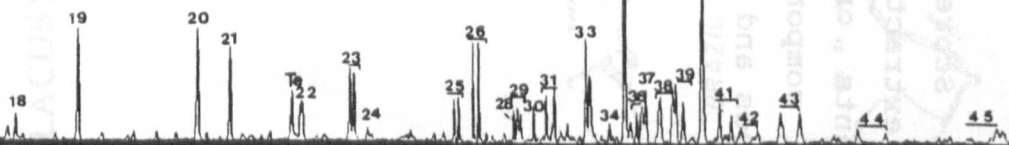
280 ppm



C

Ro: 0.63 %

1445 ppm



D

Ro: 0.66 %

379 ppm

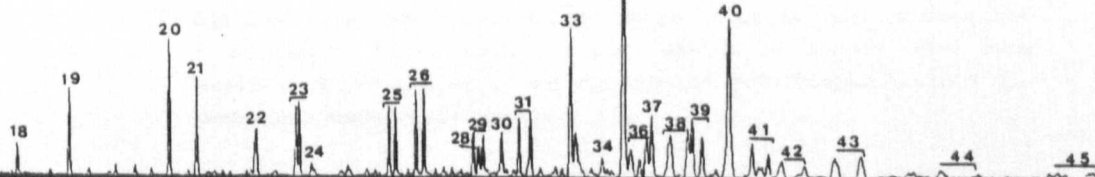
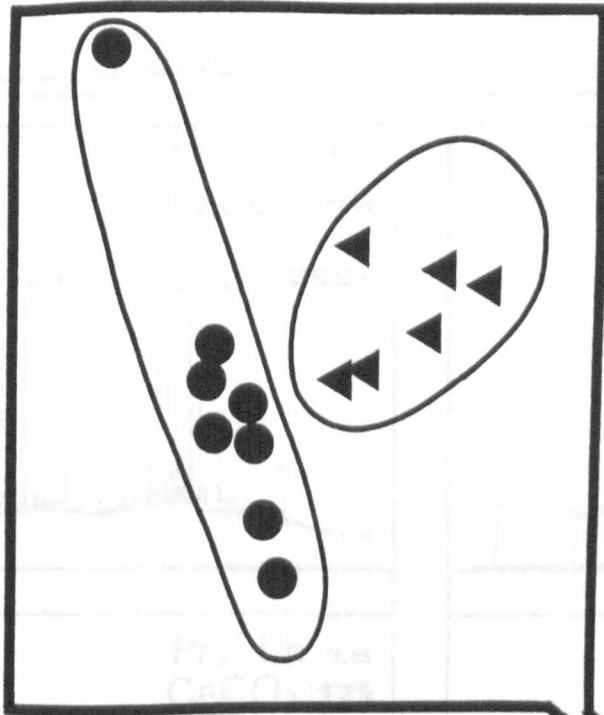


Figure 21- Scores of biological markers in the alkane fractions of rock extracts derived from lacustrine saline depositional environments on principal component 1 versus scores on principal component 2, showing the differences between samples from Campos and Espirito Santo basins .

LACUSTRINE SALINE WATER SOURCE ROCKS



Component 1

INCREASE SALINITY

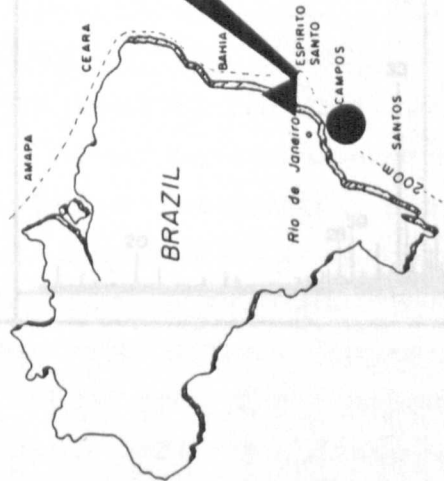


Figure 22- Gas chromatograms of total alkenes, bulk and elemental parameters and partial m/z 191 mass chromatograms and absolute concentrations of hopane from sediment extracts derived from lacustrine saline water depositional environment (A: sample UPB-1 from Potiguar basin; B: sample UD-1 from Espírito Santo basin; C: sample RVD-104 from Campos basin) for peak assignments see appendix 5.

LACUSTRINE

SALINE WATER

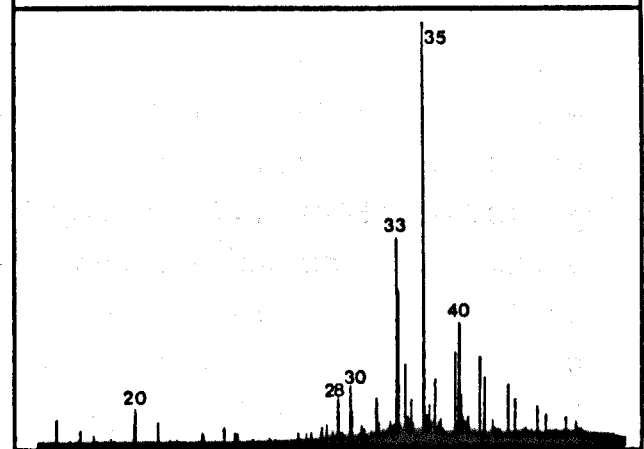
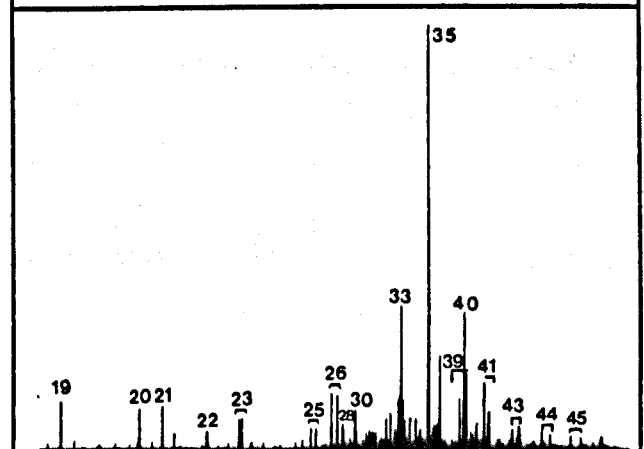
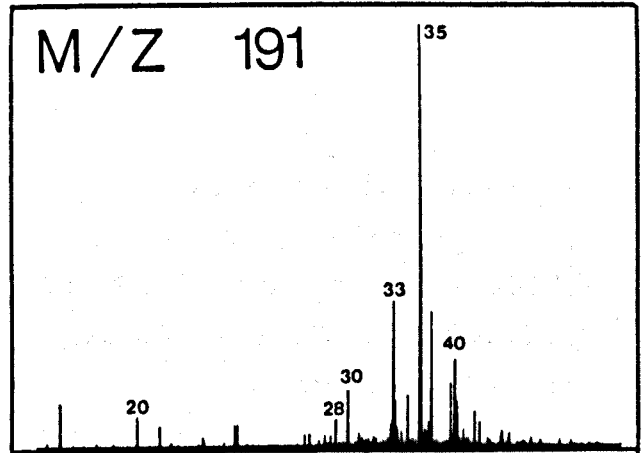
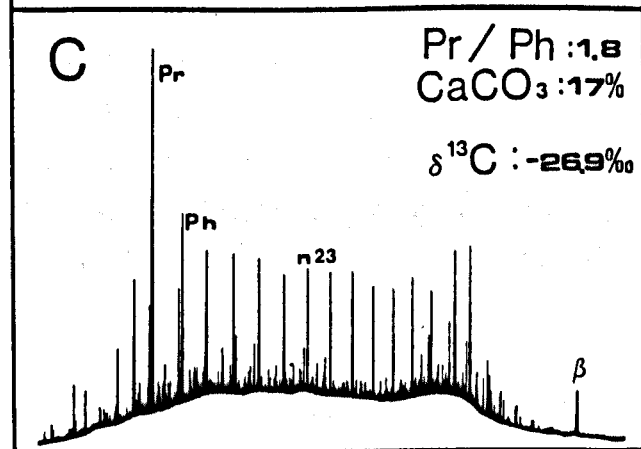
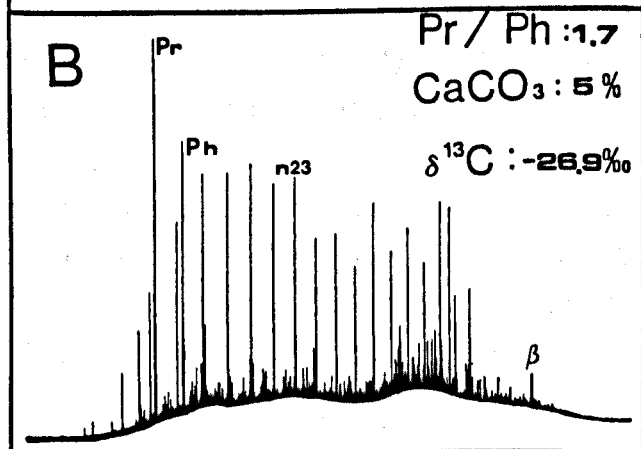
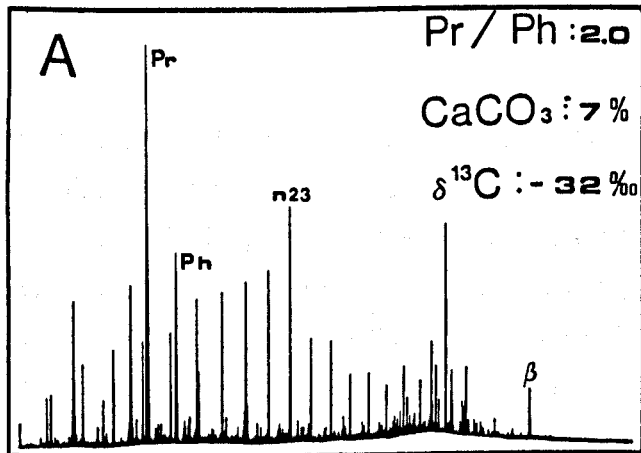


Figure 22- Gas chromatograms of total alkanes, bulk and elemental parameters and partial m/z 191 mass chromatograms and absolute concentrations of hopane from sediment extracts derived from lacustrine saline water depositional environment ; A: sample UPN-1 from Potiguar basin; B: sample RD-2 from Espirito Santo basin; C: sample RJS-164 from Campos basin (for peak assignments see appendix I).

saline water samples show higher concentrations and greater relative abundances of the C₂₅ isoprenoid and i-C₃₀ (squalane; Table 4 and Fig. 16-20 and 22), may reflect an increase in the salinity of the depositional environment (Waples et al., 1983; ten Haven et al., 1985, 1987; Fu Jiamo et al., 1986; Mello et al., 1988a, b; see below and Chapter IV). A further characteristic of the saline nature of the samples of this group is the occurrence, ranging from small to high concentrations, of β -carotane (10-500 ppm of extract; Table 4, Figs. 16-20 and 22). Hall and Douglas, (1983) suggested that its presence might be related to a lacustrine saline environment. Moldowan et al. (1985) regarded β -carotane as a terrestrial marker because it had not been reported from sources of marine origin. Its abundance in samples from lacustrine saline and hypersaline environments (Shi Ji-Yang et al., 1982; Jiang and Fowler, 1986) supported by the evidence from this study suggests that salinity is one of the main controlling factors of β -carotane concentrations (see below and also Chapter IV). The low concentrations of steranes, like in the lacustrine freshwater samples, (Table 2 and 4, and Figs. 16-20 and 22) have been considered a characteristic of non-marine samples from Australia, Sudan, Chad, China, Brazil and U.S.A (Moldowan et al., 1985; McKirdy et al., 1986; Mello et al., 1988a, b). Another significant feature in the lacustrine saline samples is the presence of low to medium concentrations (up to 30 ppm; Table 4; cf. lacustrine freshwater samples in Table 2) of low molecular weight C₂₁ and C₂₂ steranes, and high relative abundances of 4-methylhomopregnanes (peak 4 in Fig. 16, and 19, 20). These compounds often appear to be associated with enhanced salinity in the depositional environment (ten Haven et al., 1985, 1988; Fu Jiamo et al., 1986). The predominance of C₂₇ steranes over C₂₉ steranes (Figs. 16, 19, 20 and 21, Table 4) in all the samples again demonstrates that a C₂₉ sterane predominance is not always diagnostic of non-marine environments. The concentrations of the bacterially-derived hopanes in the samples are high (Table

4; Figs. 16 and 20), perhaps reflecting the importance of bacterial lipids in saline lakes (hopane/sterane ratios ranging from 4-14; Table. 4). In addition, the prominence of tricyclic components ranging from C₂₀ to C₃₅ (tricyclic index ranging from 100-200; Figs.16-20 and 22) may be a result of the saline conditions of such lakes. Since they appear to arise from bacterial precursors, perhaps specific membrane lipids (Ourisson et al., 1982), their abundance might be expected in saline lakes where bacteria thrived (see Chapter IV for details). The low Ts/Tm ratios, typically < 1 (peaks 28 and 30; Figs. 16-20 and 22; cf. Seifert et al., 1980; Mello et al., 1988a, b) may reflect a specific source input or mineral matrix (cf. Chapter IV).

The triterpanes 17 α (H),21 β (H) 28,30-bisnorhopane (Table 4; and peak 32 in Figs. 16-18) and 25,28,30-trisnorhopane (not present in m/z 191) have been recognised in most of the samples of this environment. Their presence may indicate that salinity at the time of deposition (and consequent increase in anoxicity) might play a role in determining the occurrence of these compounds. In summary the samples investigated in this group show a set of data (Tables 3 and 4) diagnostic of a non-marine environment, characterized by some elemental, isotopic and biological marker features that can be ascribed as arising from deposition under lacustrine saline conditions (see Chapter IV and Mello et al., 1988 b). These are (cf. Table 4 and Figs. 16-20 and 22):

- 1) high pristane/phytane ratio, linked with odd n-alkane predominance;
- 2) tendency towards high saturates content, associated with dominance of medium molecular weight n-alkanes;
- 3) medium to low sulphur content;
- 4) low to high concentrations of β -carotane;
- 5) high to very high concentrations of C₃₀ $\alpha\beta$ hopane ;
- 6) medium to high concentration of C₂₅ and C₃₀ isoprenoids;
- 7) medium to low relative abundances of gammacerane

- 8) heavy $\delta^{13}\text{C}$ values of whole extract;
- 9) high relative abundances of low molecular weight steranes (C_{21-22});
- 10) $T_s/T_m < 1$;
- 11) high hopane/sterane ratio;
- 12) presence of low abundances of 28,30-bisnorhopane and 25,28,30-trisnorhopane;
- 13) abundant tricyclic terpanes up to C_{35} ;
- 14) absence of C_{30} steranes and dinosteranes.
- 15) high concentration of nickel porphyrins in the samples from Espirito Santo basin

Overall, the bulk, elemental and molecular features for these source rocks are in agreement with palaeontological and mineralogical data (see Chapter 1), and extend previous evidence for oils and source rocks from lacustrine saline environments in China and the Green River Formation (Reed, 1977; Tissot *et al.*, 1978; Wang Tieguan *et al.*, 1987; Powell, 1986). Few analogous examples of ancient shallow saline lake systems have been reported in the literature. The best comparisons to the Brazilian example appear to be the well-studied Eocene Green River Formation in Uinta Basin, USA (Tissot *et al.*, 1978; Demaison & Moore, 1980; Dean & Fouch, 1983), Chaidamu and Jiangnan Basins in China (Changming *et al.*, 1984; Powell, 1986; Fu Jiamo *et al.*, 1986), and Officer Basin in Australia (McKirdy *et al.*, 1986).

2.2.3 Marine Evaporitic

Organic-rich sediments in this group occur in the Ceará (samples 23, 26 and 31), Potiguar (sample 25), Sergipe/Alagoas (samples 24, 28 and 29), and Bahia Sul (samples 37 and 30) basins in the equatorial, central and eastern areas of the continental margin (Fig. 23 and Table 5). They are characterised by a particular set of bulk, elemental and molecular features (Tables 5 and 6) that provide in some respects the most straightforward of the classifications into

Table 5: Geological and Geochemical Data For Sediments From Marine Evaporitic (Hypersaline) Environment.

Wells	CES-7	CES-41	FGT-1	RNS-15	CES-42	BAS-35	CAU-2	FGT-1	BAS-37	CES-42
Sample Number	22	23	24	25	26	27	28	29	30	31
Sample Nature	Core	Core	Cuttings	Cuttings	Core	Core	Core	Cuttings	Core	Core
Depth (m)	2094	2685	1557	2190	3006	2400	1510	1938	1653	3420
Age	Aptian	Aptian	Aptian	Aptian	Aptian	Aptian	Aptian	Aptian	Aptian	Aptian
Lithology	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale	Calcareous Blk Shale
CaCO ₃ (%)	15	19	26	14	7	23	28	24	45	25
Sulphur (%)	0.90	0.70	0.50	0.50	2.50	0.80	0.30	0.55	0.70	0.70
TOC (%)	3.1	1.8	2.7	10.0	14.0	1.5	2.0	3.7	2.5	6.2
S ₂ (KgHC/Ton rock)	23	17	15	36	97	5	8	19	11	24
HI (mgHC/gTOC)	750	980	543	365	692	333	400	500	414	390
T-MAX (°C)	436	435	430	433	447	433	430	434	424	445
Ro (%)	0.50	0.60	0.56	0.60	0.68	0.60	0.54	0.60	0.60	0.75
SCI	5.0	6.0	4.5	6.0	6.0	-	-	5.0	6.5	6.5
EOM (ppm)	4868	4900	2524	4080	4540	2911	850	2555	700	3200
Pr/Ph	0.4	0.5	0.9	0.6	0.4	0.9	0.9	0.9	0.9	0.4
Pr/nC ₁₇	1.4	0.9	2.6	0.8	0.6	1.0	1.1	2.5	0.8	0.9
Ph/nC ₁₈	4.3	1.5	4.0	1.4	1.6	1.9	4.2	2.6	1.2	7.5
nC ₁₇ /C ₃₁	1.4	1.1	2.5	1.3	1.1	1.4	5.6	1.0	1.3	8.3
δ ¹³ C whole extract	-25.7	-26.0	-23.8	-27.3	-26.0	-26.0	-27.0	-23.6	-25.5	-24.0
Saturates (%)	28	50	32	43	55	35	36	35	27	38
Aromatics (%)	11	19	16	24	18	15	24	16	12	19
NSO (%)	61	31	52	33	27	50	40	49	61	49
Amorphous (%)	60	75	60	40	60	40	50	40	65	65
Herbaceous (%)	20	5	5	40	30	30	30	15	5	15
Woody+Coaly (%)	20	20	35	20	10	30	20	45	30	20

TABLE 6 - Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples from Sediments Derived from Marine Evaporitic (Hypersaline) Environment in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 3.5-8.6%	T.O.C.: 1.5-14%	n-ALKANES MAXIMA: C ₁₈ -C ₂₆	C ₂₇ STERANE: ⁶ 230-1600ppm	C _{30αβ} HOPANE: ¹¹ 300-1400ppm	NICKEL: 310-1870ppm
HYDROGEN: 0.37-1.5%	S ₂ : ¹ 5-97	SATURATES: 27-55%	C ₂₇ /C ₂₈ : ⁷ 1.2-3.1	GAMMACERANE INDEX: ¹² 70-120	VANADYL: 60-630ppm
NITROGEN: 0.08-0.25%	HI: ² 125-980mg/g	Pr/Ph: 0.4-0.9	DIASTERANE INDEX: ⁸ 6-5	BISNORHOPANE INDEX: ¹³ 2-35	AMORPHOUS: 30-75%
SULPHUR: 0.3-2.5%	R ₀ : 0.55-0.68%	I-C ₂₅ +I-C ₃₀ : ⁴ 300-800ppm	4-Me STERANE ⁹ INDEX: 33-225	HOPANE/STERANE ¹⁴ 0.4-4.3	HERBACEOUS: 5-40%
CaCO ₃ : 7-45%	δ ¹³ C: ³ -23.6 TO -27.3	β-CAROTANE: ⁵ 100-350ppm	C ₂₁ + C ₂₂ STERANES: ¹⁰ 10-25ppm	C ₃₄ /C ₃₅ HOPANES: ¹⁵ 0.8-2.5	WOODY/COALY: 10-30%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (%)
4. Sum of 2,6,10,14,18-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (β) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (8+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Sum of peak areas (3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
14. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
15. Peak areas of C₃₄ 22R and 22S 17α,21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 25 to 27 and Appendices.

groups. This feature presumably arises from the fact that the biota in such an environment are expected to be largely restricted to a few species of salinity-tolerant aquatic organisms. These organisms can bloom due to a lack of competition for the available nutrients. Clearly, the effect of these phenomena on the biological marker distributions would be expected to be dramatic, leading to the occurrence of high concentrations and dominance of specific compounds (Table 6; cf. Brassell et al., 1988), for example, those derived from precursors biosynthesised by microorganisms such as archaebacteria (including halophiles), certain green algae, cyanobacteria and sulphur-bacteria (Boon et al., 1983; Goossens et al., 1984; Connan et al., 1986).

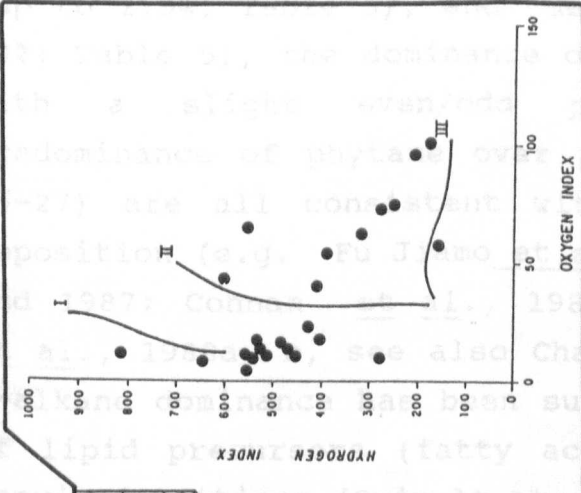
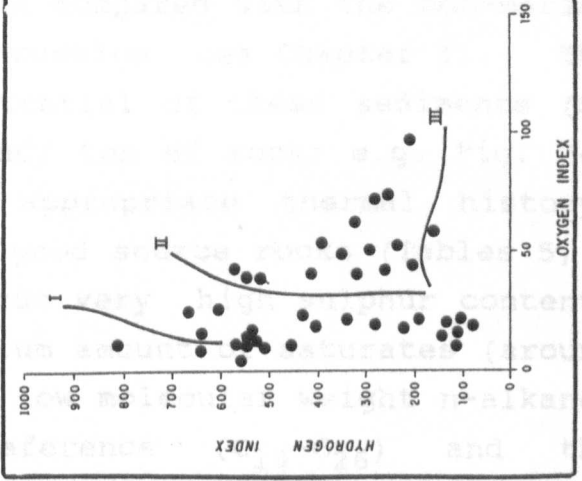
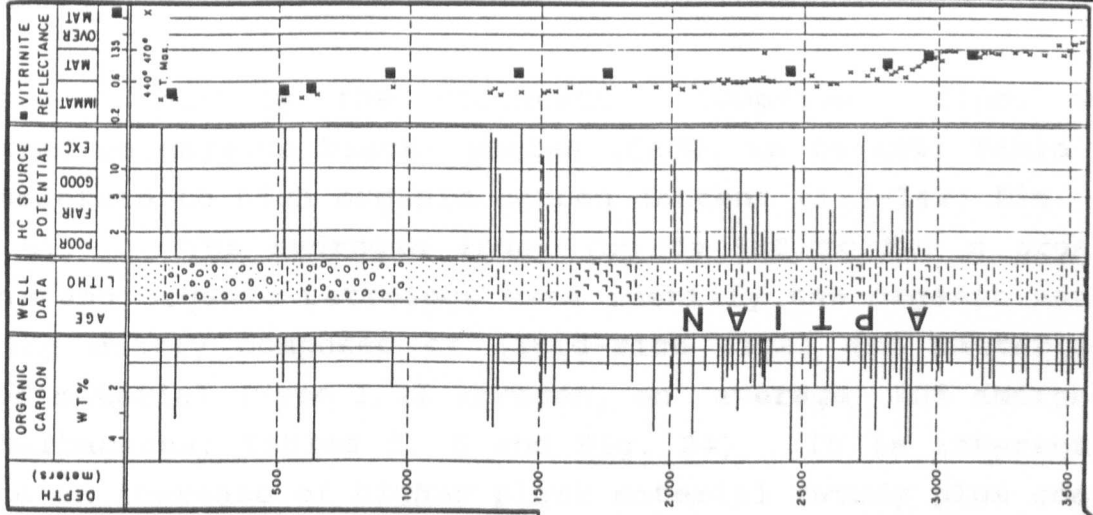


Figure 23- Location map showing the areas from which samples from marine evaporitic depositional environment were investigated.

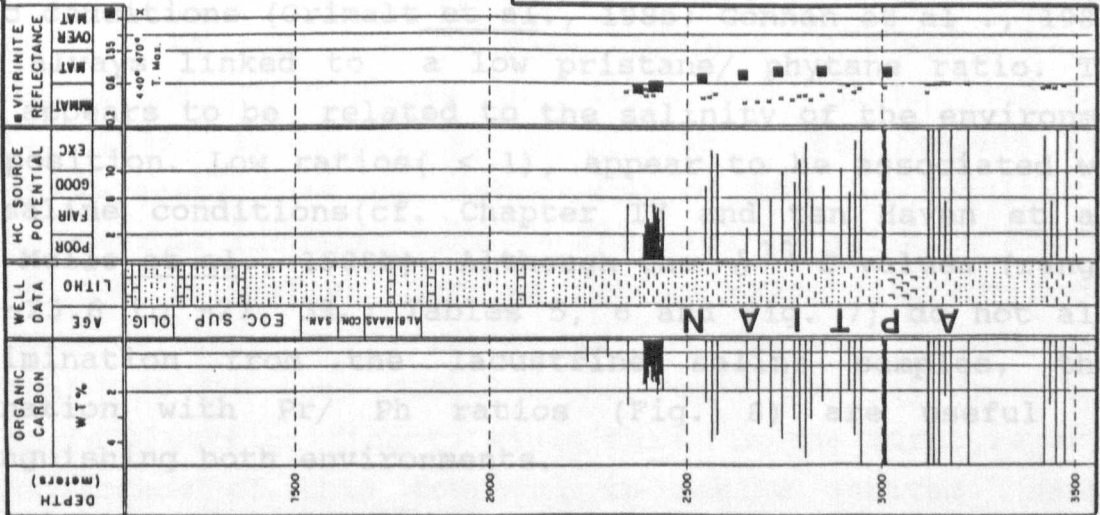
The sediments were deposited during the Aptian (Table 5, Fig. 24). Fig 24 shows two well logs from two typical successions (CES-42, Ceará basin and FGT-1, Sergipe/ Alagoas

Figure 24- Geochemical logs for two wells from Ceará (CES-42) and Sergipe/Alagoas (FGT-1) basins, showing the stratigraphic position of the marine evaporitic organic-rich sedimentary succession and the hydrogen index (S_2/ TOC) vs oxygen index (S_3/ TOC), presented on van Krevelen type diagram, for samples from the Aptian.

FGT 1



CES 42



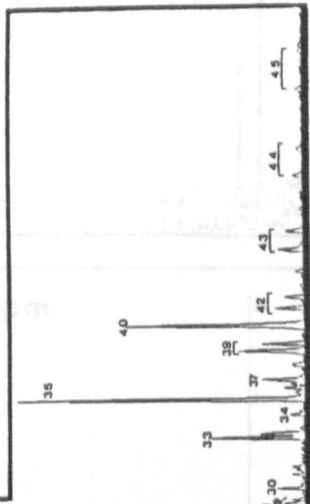
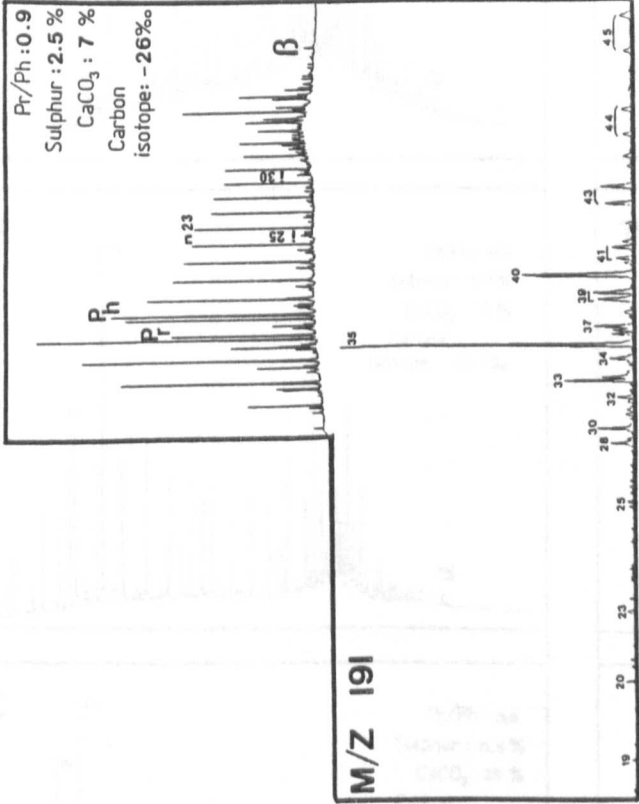
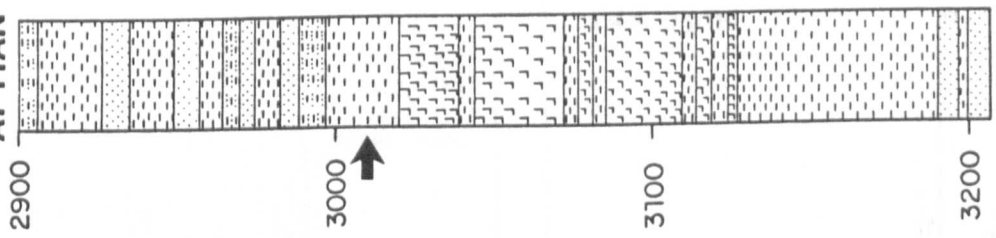
basin). Generally the sediments comprise fine, well laminated calcareous black shales (CaCO_3 up to 45%; Table 5), with moderate to high organic carbon content (1.5-14%; Fig. 24; Table 5). The hydrogen index (up to 980 mg Hc/ g organic carbon) and organic petrology data identify the organic matter as being mostly composed of lipid-rich algal and bacterially derived material (Type I/II kerogen, on average 80% amorphous plus herbaceous; Tables 5, 6 and Fig. 24). It is interesting to note an increase of higher plant material (woody plus coaly) in this environment of deposition compared with the non-marine ones (Tables 2, 4 and 6; for discussion see Chapter I). The excellent hydrocarbon source potential of these sediments (S_2 from Rock-Eval up to 97 Kg of HC/ ton of rock; e.g. Fig. 24; Table 5), combined with the appropriate thermal history, characterise these sediments as good source rocks (Tables 5, 6 and Fig. 24). The tendency towards very high sulphur contents (up to 2.5%; Table 5), and medium amount of saturates (around 40%; Table 5), the dominance of low molecular weight n-alkanes with a slight even/odd preference (C_{19} - C_{26}) and the predominance of phytane over pristane (Tables 5, 6 and Figs. 25-27) are all consistent with a hypersaline environment of deposition (e.g. Fu Jiamo et al., 1986; Ten Haven et al., 1985 and 1987; Connan et al., 1986; Albaiges et al., 1986; Mello et al., 1988a, b, see also Chapter IV). The origin of an even n-alkane dominance has been suggested to result from reduction of lipid precursors (fatty acids and alcohols), under highly anoxic conditions (Grimalt et al., 1985; Connan et al., 1986), being always linked to a low pristane/ phytane ratio. This ratio appears to be related to the salinity of the environment of deposition. Low ratios (< 1), appear to be associated with hypersaline conditions (cf. Chapter IV and ten Haven et al., 1987; Mello et al., 1988b). Although the $\delta^{13}\text{C}$ values (ranging from -23.6 to -27, 3‰; Tables 5, 6 and Fig. 7) do not allow discrimination from the lacustrine saline samples, their combination with Pr/ Ph ratios (Fig. 8) are useful in distinguishing both environments.

Fig. 25 shows two typical lithological logs of Aptian horizons with the stratigraphic position of the relatively mature (around 0.60% Ro; Table 5) samples FGT-1, Sergipe/Alagoas basin (sample 29 in Table 5 and Fig. 23) and CES-42, Ceará basin (sample 26 in Table 5 and Fig. 23), chosen as specific examples. Also, shown are some bulk and elemental properties and the gas chromatograms and m/z 191 mass chromatograms for the alkane fractions. Figs. 26 and 27 compare three other samples from Ceará and Sergipe/Alagoas basin (samples 22-24 in Table 5 and Fig. 23), using bulk, elemental, and biological marker distributions and concentrations. Overall, the similarity in the bulk and elemental data, and biological marker distributions and concentrations for these samples, taken with the data in Tables 5 and 6 shows that these samples are indeed derived from a marine evaporitic environment (see below, Chapter IV, and Mello *et al.*, 1988a, b).

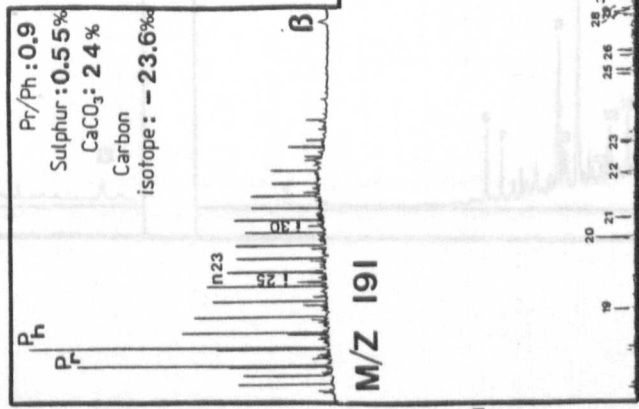
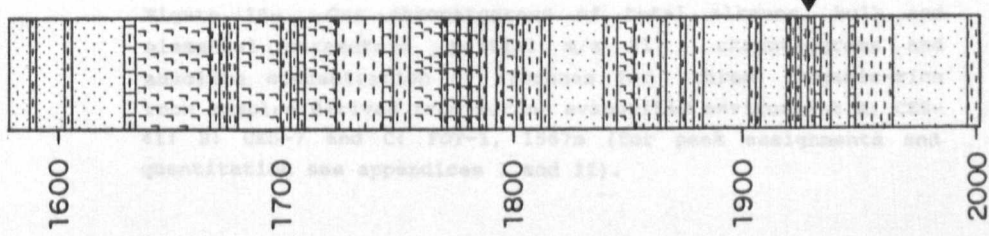
The high concentrations of long chain $i\text{-C}_{25}$ (confirmed in some samples as mainly the 2,6,10,14,18-pentamethyleicosane component by coinjection with a standard), and $i\text{-C}_{30}$ (squalane) isoprenoids (300-800 ppm) are a consistent feature of these samples (Table 6 and Figs 25-27). Although there is some overlaps with the lacustrine saline samples (Table 4), the values of the marine evaporitic are generally higher. Waples *et al.* (1974) suggested that the regular $i\text{-C}_{25}$ isoprenoid is a biological marker for hypersaline environments. Its high abundance, with squalane, is also apparent in samples related to hypersaline environments in Italy and China (ten Haven *et al.*, 1985; Fu Jiamo *et al.*, 1986). The present study further suggests that the abundances of the C_{25} (regular) and C_{30} isoprenoids increase with an increase in salinity and show high values in samples derived from an evaporitic environment (see Chapter IV). The presence of high concentrations of β -carotane (100-350 ppm; Table 4 and Figs. 25, 26) in all the samples is also significant, since this is the first report of the occurrence of this compound in marine derived samples

Figure 25- Lithological logs of the two wells from Fig. 24 showing the stratigraphic position of two organic-rich samples (FGT-1, 1938m and CES-42, 3006m) typical of the hypersaline Aptian sedimentary succession, for which gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 chromatograms are shown (for peak assignments see appendix I).

CES-42 A
APTIAN



FGT-1-AL
APTIAN



GAS CHROMATOGRAM

M / Z 217

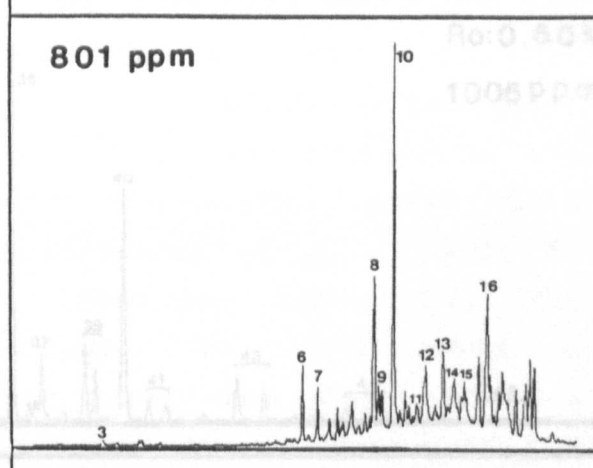
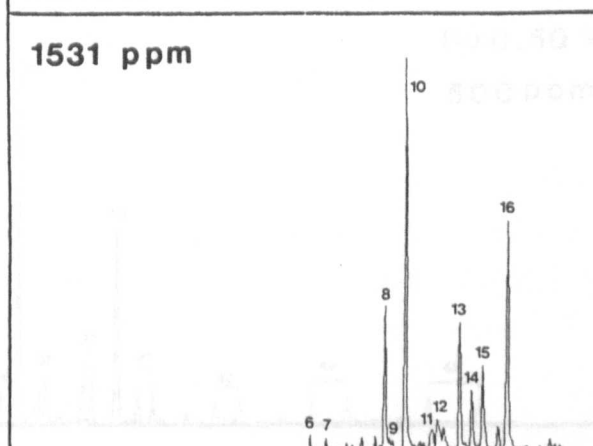
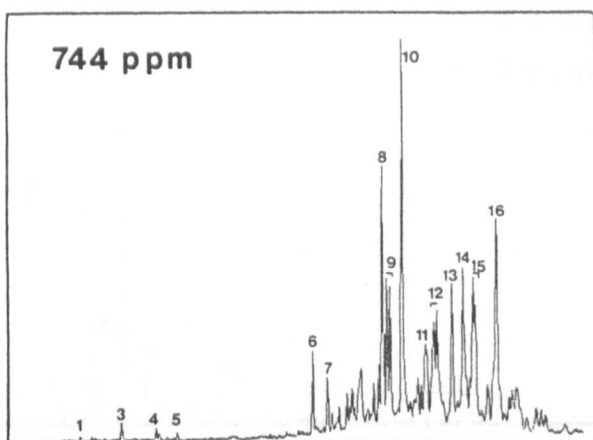
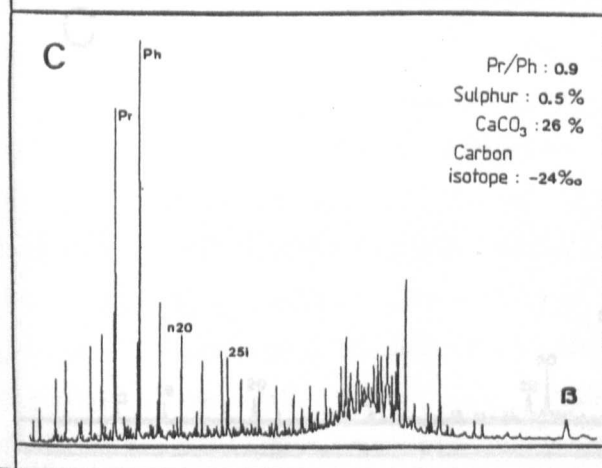
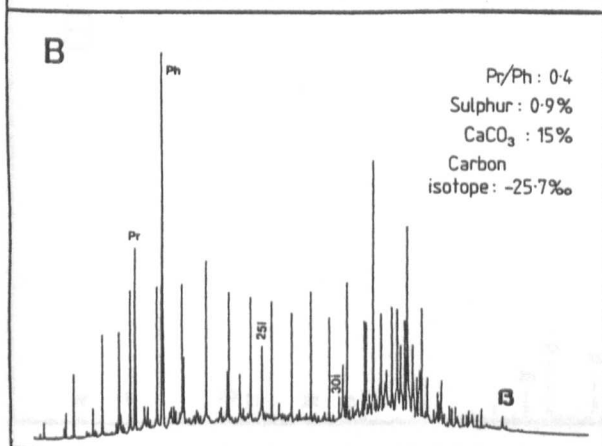
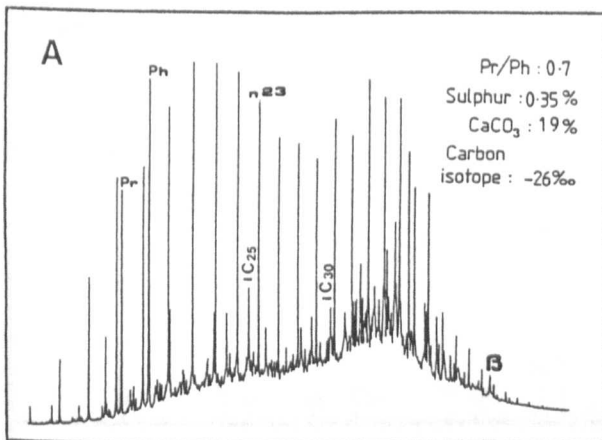


Figure 26- Gas chromatograms of total alkanes, bulk and elemental parameters, partial m/z 217 chromatograms and absolute concentration of steranes for three organic-rich rock samples derived from marine evaporitic environment A: CES-41; B: CES-7 and C: FGT-1, 1557m (for peak assignments and quantitation see appendices I and II).

M/Z 191

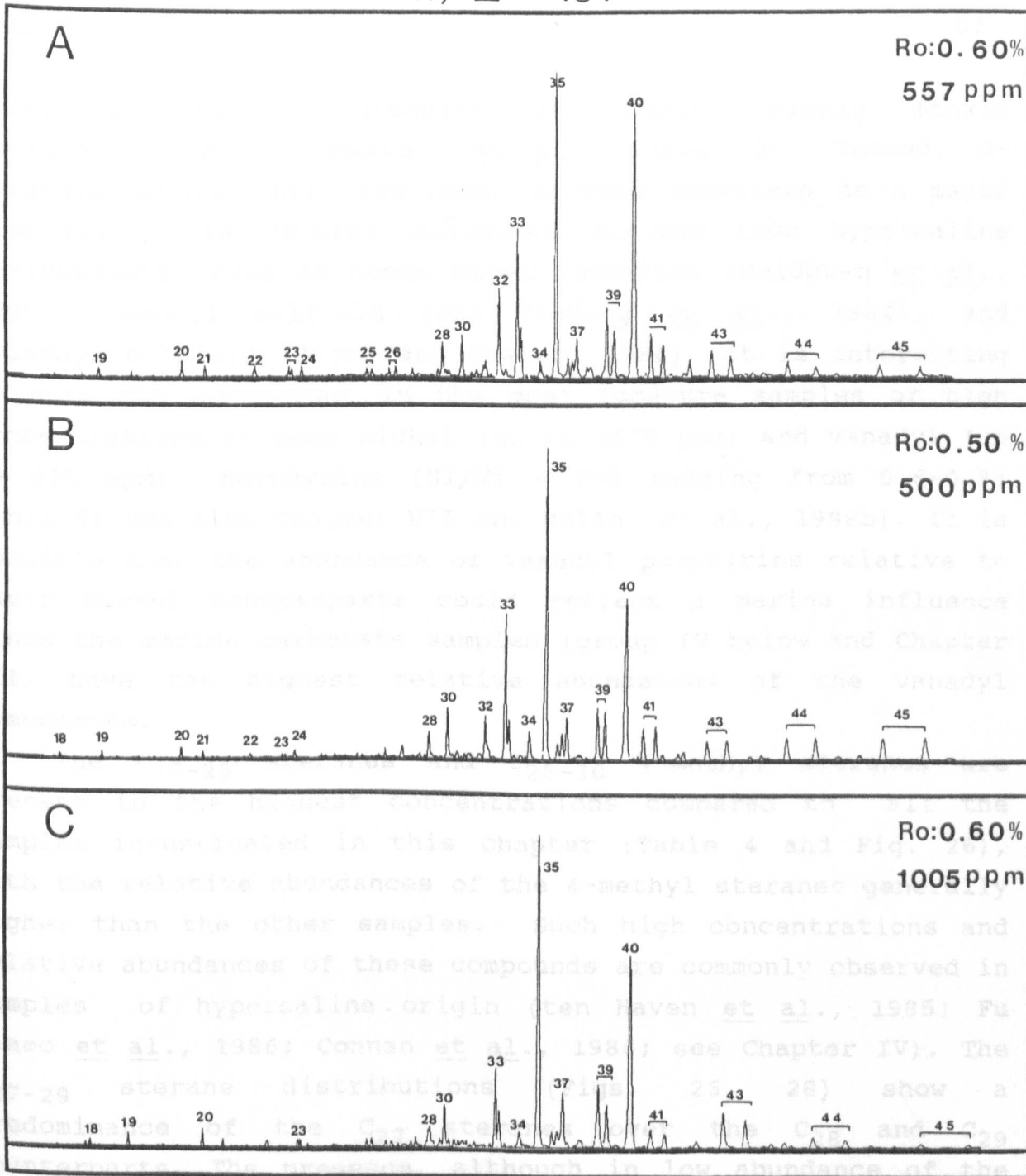


Figure 27- Partial m/z 191 chromatograms of total alkanes, vitrinite reflectance data and absolute concentration of hopane for the same samples as Fig. 26 (for peak assignments and quantitation see appendices I and II).

C₃₀ steranes and dinosteranes (Fig. 12) in the samples of this group might be considered a definitive indicator of a contribution from marine-derived organic matter (see also Chapter IV). The presence of medium to high concentration of C₂₁ and C₂₂ steranes (Fig. 26) is in keeping with a hypersaline environment (cf. Chapter IV). The low relative abundance of diasteranes (Table 6 and Fig. 26) can be explained in terms of a low availability of acidic clay

(also see marine carbonate and marine highly anoxic environments below; Mello et al., 1988a, b). Indeed, β -carotane occurs, and has been reported sometimes as a major component, in several sediments derived from hypersaline environments, such as Green River formation (Moldowan et al., 1985), Shengli oilfield (Shi Ji-Yang et al., 1982), and Kelamayi oilfield (Jiang and Fowler, 1986). It is interesting to note the occurrence in the most immature samples of high concentrations of both nickel (up to 1870 ppm) and vanadyl (up to 630 ppm) porphyrins (Ni/Ni + V=0 ranging from 0.6-0.9; Table 6; see also Chapter VII and Mello et al., 1988b). It is possible that the abundance of vanadyl porphyrins relative to their nickel counterparts could reflect a marine influence since the marine carbonate samples (group IV below and Chapter VII) have the highest relative abundances of the vanadyl components.

The C₂₇₋₂₉ steranes and C₂₈₋₃₀ 4-methyl steranes are present in the highest concentrations compared to all the samples investigated in this chapter (Table 4 and Fig. 26), with the relative abundances of the 4-methyl steranes generally higher than the other samples. Such high concentrations and relative abundances of these compounds are commonly observed in samples of hypersaline origin (ten Haven et al., 1985; Fu Jiamo et al., 1986; Connan et al., 1986; see Chapter IV). The C₂₇₋₂₉ sterane distributions (Figs. 26, 28) show a predominance of the C₂₇ steranes over the C₂₈ and C₂₉ counterparts. The presence, although in low abundance of the C₃₀ steranes and dinosteranes (Fig. 12) in the samples of this group might be considered a definitive indicator of a contribution from marine-derived organic matter (see also Chapter IV). The presence of medium to high concentration of C₂₁ and C₂₂ steranes and 4-methylsteranes (not seen in Fig. 26 B and C as a result of their low relative abundance; Table 6), is in keeping with a hypersaline environment (cf. Chapter IV). The low relative abundance of diasteranes (Table 6 and Fig. 26) can be explained in terms of a low availability of acidic clay

minerals in hypersaline environments to catalyse the sterene rearrangement process (Rubinstein et al., 1975; see also Chapter IV). Similar features have been observed in sediments from both evaporitic and carbonate environments (McKirdy et al., 1984; Fu Jiamo et al., 1986).

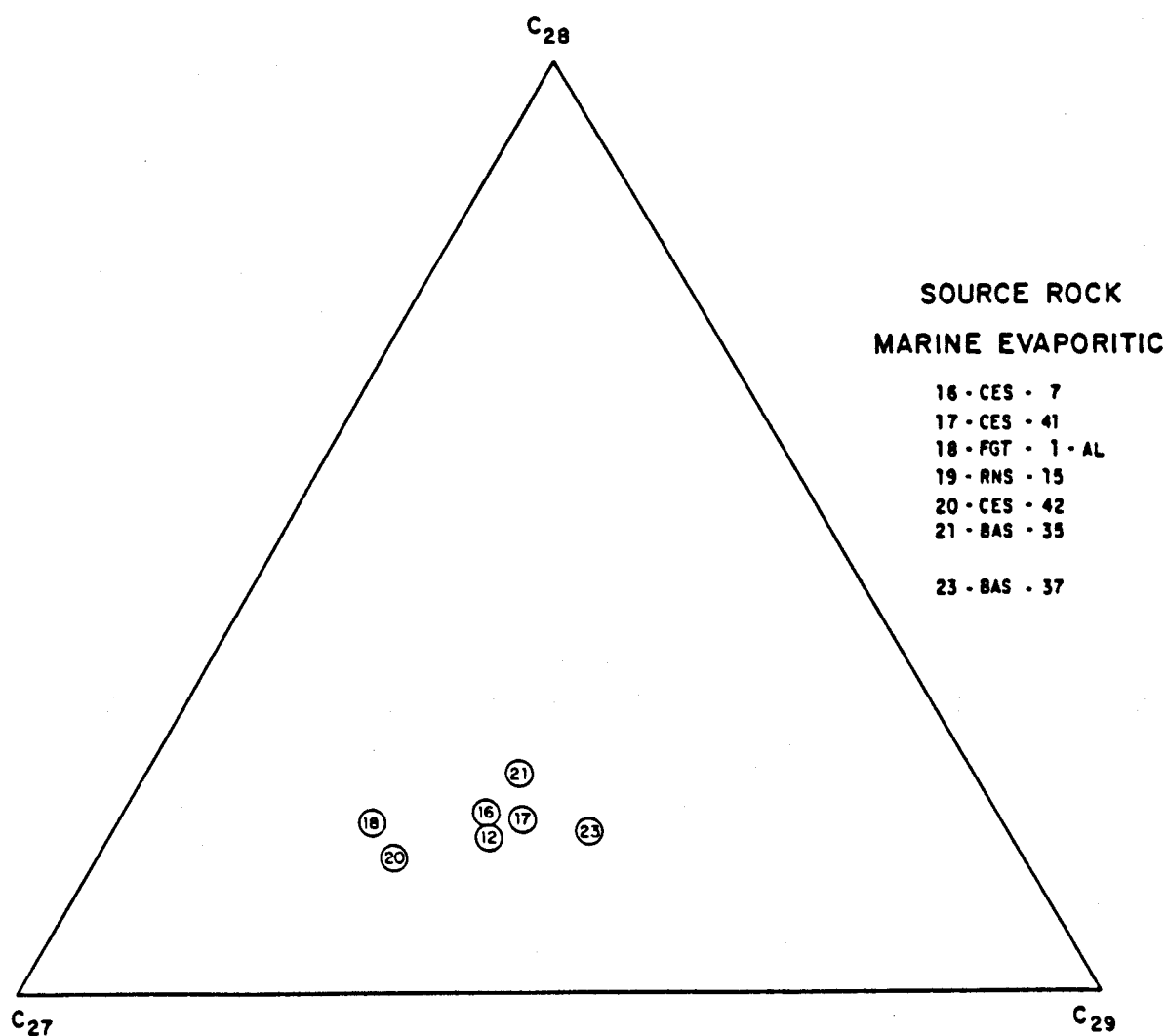


Figure 28- Carbon number (C₂₇, C₂₈, C₂₉) distributions of 5α(H), 14α(H), 17α(H) 20R steranes for a number of sediment extracts from marine evaporitic depositional environment.

The features of the terpanes (m/z 191) in this group are quite distinctive, since hypersaline conditions appear to increase bacterial contributions to the sediments. Thus, the hopanes are present in high concentrations (300-1400 ppm; Table 6 and Figs. 25-27; see also lacustrine saline samples and Chapter IV). The difference in the distribution pattern of tricyclic terpanes (tricyclic index ranging from 10-60) compared to those in the lacustrine saline samples (100-200; cf. Figs. 16-20 and 25-27 respectively) could, perhaps, reflect a response of the bacteria producing the tricyclic precursors to hypersalinity. Connan et al (1986), also report low abundances of tricyclics in rock samples from Guatemalan hypersaline environments.

The high relative abundance of gammacerane (sometimes the major triterpane) in all the samples (gammacerane index ranging from 70-120; Figs. 25, 27 and Table 6), demonstrates that this compound may be an indicator of the hypersalinity conditions of a depositional environment. Indeed, the more saline the environment, the higher appears to be the abundance of gammacerane. Extremely high gammacerane abundances have been reported for samples from hypersaline environments; for example, Jiangnan basin, China (Fu Jiamo et al., 1986), Green River, USA and Prinos, Greece (Moldowan et al., 1985). Like the lacustrine saline samples, most of the evaporitic samples, typically show T_s/T_m ratios < 1 (Figs. 25, 27), suggesting again a source input/or mineral matrix dependence for this ratio. Another important feature is the presence of low to high relative abundances of $17\alpha(H), 21\beta(H)-28, 30$ -bisnorhopane (bisnorhopane index from 2-35; peak 32 in Figs 25-27) and $25, 28, 30$ -trisnorhopane (not shown in the m/z 191 mass chromatogram). These occurrences are keeping with the idea of highly anoxic conditions in such a hypersaline depositional environment (cf. below; Chapter IV; Rullkötter & Wendisch, 1982; Katz and Elrod, 1983; Mello et al., 1988c). A further unusual feature is the occurrence in some samples of $C_{35} \alpha\beta$ hopanes in higher relative abundances than the C_{34} homologues

(Table 6 and Fig. 25, 27). Such a feature has been reported as a characteristic of many samples from marine carbonate and hypersaline environments (ten Haven et al., 1985 and 1988; Brassell et al., 1988; Fu Jiamo et al., 1986; Albaiges et al., 1986; see also Chapter IV). In summary, the bulk, elemental and molecular features (Tables 5, 6 and Figs. 25-27) presented by the samples of this group are diagnostic of sediments deposited in a marine evaporitic environment. Useful features diagnostic of this type of environment are;

- 1) high concentrations of gammacerane, C₃₀ $\alpha\beta$ hopane and steranes;
- 2) high concentrations of β -carotane and the C₂₅ regular isoprenoid and squalane;
- 3) phytane > pristane linked in most samples with a slight even/odd n-alkane dominance and high sulphur contents ;
- 4) medium to high relative abundances of 28,30-bisnorhopane and 25,28,30- trisnorhopane and of 4-methyl steranes;
- 5) low relative abundances of diasteranes and tricyclic terpanes;
- 6) high concentrations of nickel and vanadyl porphyrins (Ni/Ni+V=0 from 0.6-0.9;
- 7) low hopane/ sterane ratios and tricyclic index;
- 8) low concentration of C₃₀ steranes.

It is interesting to note that similarities to these data, have been reported for several Palaeogene lacustrine hypersaline source rocks and oils (e.g. the Jiangnan Basin, Eastern China; Fu Jiamo et al., 1986); marine hypersaline (evaporitic) environments in the Tarragona basin, Spain; Paradox basin (Utah), USA; Prinos basin, Greece, and Messinian basin (northern Apennines), Italy and Camargue basin, Southern France (Albaiges et al., 1986; Peterson and Hite, 1969; ten Haven et al., 1987; Moldowan et al., 1985; Connan and Dessort, 1987)

2.2.4 Marine Carbonate

Marine carbonate organic-rich sediments of Albian age are found widely in the Brazilian continental margin from Campos basin in the south to Cassiporé basin in the north (Fig. 29).

Fig. 30 shows two typical geochemical well logs with the stratigraphic position of an organic-rich Albian sedimentary succession, chosen as specific examples of the marine carbonate system that have been identified in the Sergipe/ Alagoas basin (e.g. 34 in Fig. 29 and Table 7).

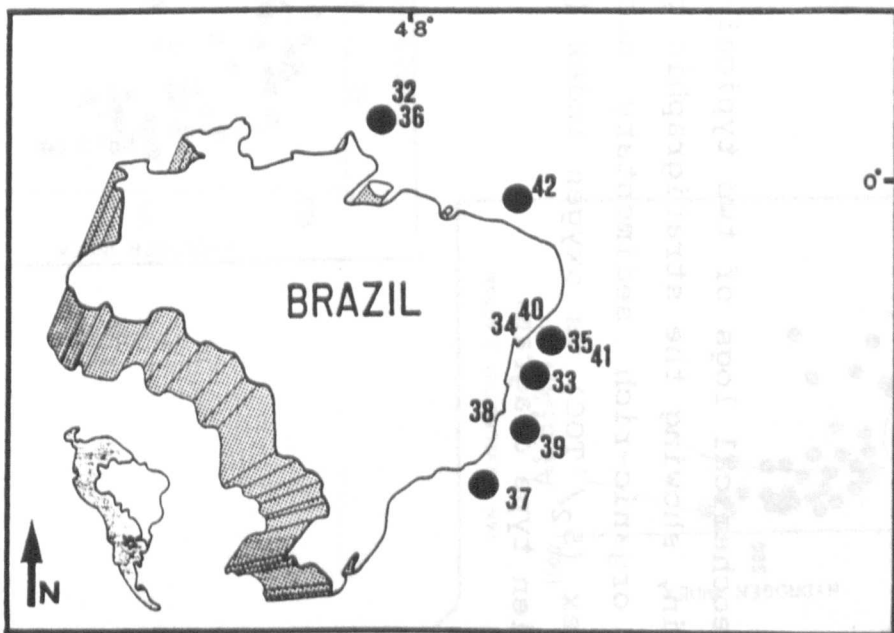
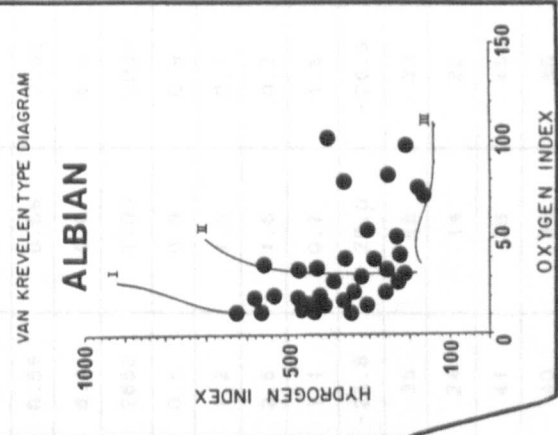
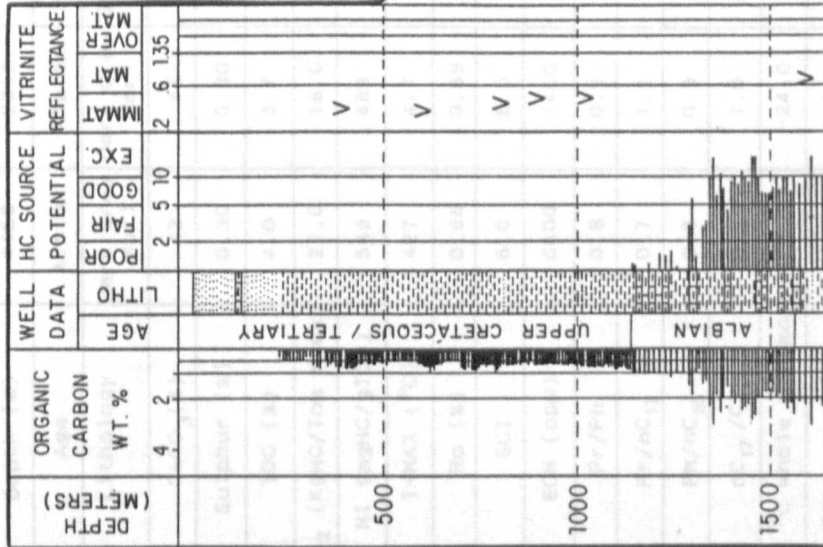


Figure 29- Location map showing the areas from which samples from marine carbonate depositional environment were investigated.

Together with the data of Tables 7 and 8, Fig. 30 shows that the Albian organic-rich succession comprises mainly well laminated dark grey marls (CaCO_3 from 22-65%) and calcareous grey shales (CaCO_3 from 16-30%), rich in organic matter (TOC up to 4.1%), with medium sulphur content (up to 0.6%). Generally,

Figure 30- Geochemical logs of two typical wells from Sergipe/Alagoas basin, showing the stratigraphic position of a marine carbonate organic-rich sedimentary succession and the hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram.

1-CR-2-SE



1-CAU-3-SE

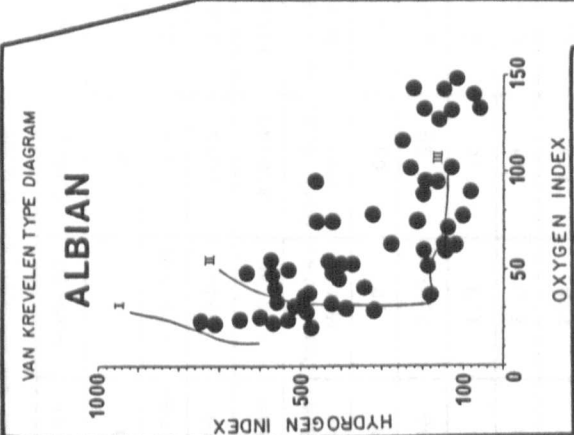
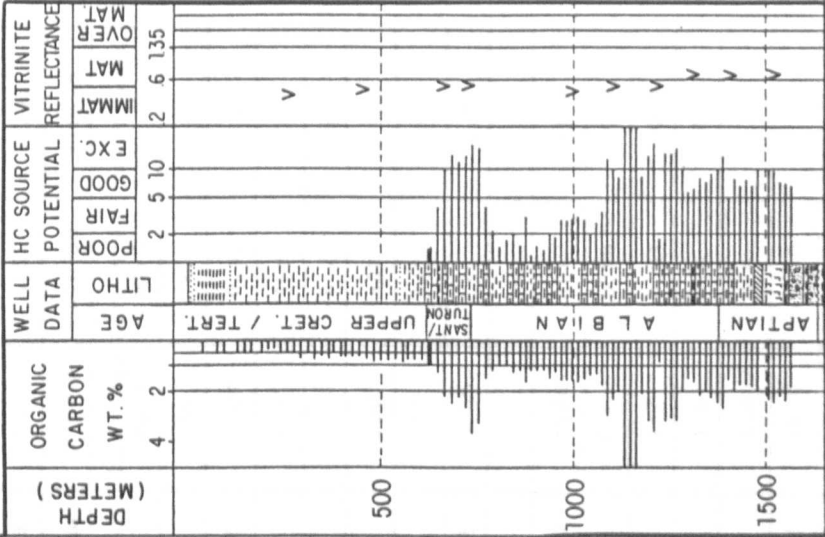


Table 7 : Geological and Geochemical Data For Sediments From Marine Carbonate Environment.

Wells	APS-29	BAS-35	CAU-3	SES-14	APS-31	RJS-30	FRG-1	ESS-23	ANG-1	ALS-11	CES-56
Sample Number	32	33	34	35	36	37	38	39	40	41	42
Sample Nature	Core	Core	Cuttings	Cuttings	Cuttings	Cuttings	Core	Core	Core	Cuttings	Cuttings
Depth (m)	4459	2313	1386	1623	4775	3348	1615	2169	1320	1239	1995
Age	Albian	Albian	Albian	Albian	Albian	Albian	Albian	Albian	Albian	Albian	Albian
Lithology	Dark Grey Marl	Dark Grey Marl	Dark Grey Marl	Calcareous Grey Shale	Dark Grey Shale	Dark Grey Marl	Dark Grey Marl	Dark Grey Marl	Dark Grey Marl	Dark Grey Marl	Calcareous Grey Shale
CaCO ₃ (%)	43	45	36	16	18	22	65	42	39	40	30
Sulphur (%)	0.30	0.30	0.35	0.24	0.60	0.25	0.60	0.45	0.30	0.32	0.60
TOC (%)	4.0	3.7	2.6	2.4	2.4	1.0	1.0	3.2	4.1	1.4	2.4
S ₂ (KgHC/Ton rock)	22.0	18.0	14.0	5.4	9.0	2.0	2.1	9.0	16.0	6.2	9.0
HI (mgHC/gTOC)	549	489	557	216	361	238	211	272	390	432	356
T-MAX (°C)	427	427	431	426	429	431	431	431	425	442	430
Ro (%)	0.66	0.59	0.59	0.56	0.62	0.63	0.65	0.55	0.55	--	0.57
SCI	6.0	6.5	6.5	5.0	6.0	--	--	5.0	--	--	--
EOM (ppm)	6600	1460	2650	1700	9000	1010	371	1390	1060	1540	1100
Pr/Ph	0.8	0.9	0.5	0.8	0.9	0.9	0.8	0.9	0.8	0.96	0.9
Pr/nC ₁₇	0.7	1.1	1.2	1.5	0.7	1.1	0.6	1.1	1.7	0.91	0.6
Ph/nC ₁₈	0.6	0.9	2.5	1.6	0.7	0.9	1.7	0.7	1.8	0.6	0.7
nC ₁₇ /C ₃₁	0.7	1.0	1.1	0.7	1.5	0.7	4.0	0.9	1.0	0.8	1.25
δ ¹³ C whole extract	-27.5	-24.0	-26.8	-26.0	-26.9	-26.4	-26.6	-26.2	-26.0	-27.0	--
Saturates (%)	45	20	35	48	33	46	37	44	30	62	39
Aromatics (%)	15	16	24	14	22	14	17	16	11	9	15
NSO (%)	40	64	41	38	45	40	46	40	59	29	46
Amorphous (%)	85	60	40	60	80	50	35	10	60	90	75
Herbaceous (%)	10	10	20	30	5	20	15	30	10	5	15
Woody+Coaly (%)	5	30	40	10	15	30	50	60	30	5	10

TABLE 8 - Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples Derived from Marine Carbonate Environment in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 3-9%	T.O.C.: 1-5%	n-ALKANES MAXIMA: C ₂₀ -C ₂₂	C ₂₇ STERANE: ⁶ 50-350ppm	C _{30αβ} HOPANE: ¹¹ 150-350ppm	NICKEL: Tr-411ppm
HYDROGEN: 0.4-0.6%	S ₂ : ¹ 2-22	SATURATES: 20-48%	C ₂₇ /C ₂₈ : ⁷ 0.4-1.7	GAMMACERANE INDEX: ¹² 15-25	VANADYL: 75-2926ppm
NITROGEN: 0.05-0.10%	HI: ² 200-550mg/g	Pr/Ph: 0.5-0.96	DIASTERANE INDEX: ⁸ 7-30	BISNORHOPANE INDEX: ¹³ 10-35	AMORPHOUS: 35-65%
SULPHUR: 0.3-0.6%	Ro: 0.50-0.66%	I-C ₂₅ +I-C ₃₀ : ⁴ 100-450ppm	4-Me STERANE ⁹ INDEX: 30-70	HOPANE/STERANE ¹⁴ 1-3	HERBACEOUS: 10-30%
CaCO ₃ : 13-65%	δ ¹³ C: ³ -24 TO -27.8	β-CAROTANE: ⁵ Tr-95ppm	C ₂₁ + C ₂₂ STERANES: ¹⁰ 10-50ppm	C ₃₄ /C ₃₅ HOPANES: ¹⁵ 0.7-1.3	WOODY/COALY: 20-50%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (‰)
4. Sum of 2,6,10,14,18-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (8) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Sum of peak areas (3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
14. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
15. Peak areas of C₃₄ 22R and 22S 17α,21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 32 to 35 and Appendices.

they show fair to good hydrocarbon source potential (S_2 from Rock-Eval pyrolysis ranging from 2 to 22 Kg Hc/ ton of rock). The hydrogen index (ranging from 211-557 mg HC/g organic carbon) and organic petrology data identify the organic matter as being composed of mixed lipid-rich and hydrogen-lean land plant material (type II kerogen; Tables 7, 8 and Fig. 30). Nevertheless, the lack of sufficient thermal maturity in most of the Brazilian marginal basins (except in the northern part) indicates that they generally have not good source rock characteristics (see maturity data in Tables 7, 8 and Fig. 30).

In many respects the marine carbonate samples show geochemical features which are similar to those of the marine evaporitic samples. In general, they possess similar compositional and elemental data including medium to low content of saturates (Fig. 31), medium to high values for sulphur, a dominance of phytane over pristane and n-alkane maxima ranging from C_{20} to C_{22} linked in some samples with a slight even/odd predominance in the n-alkanes (Tables 7, 8 and Figs. 32-34).

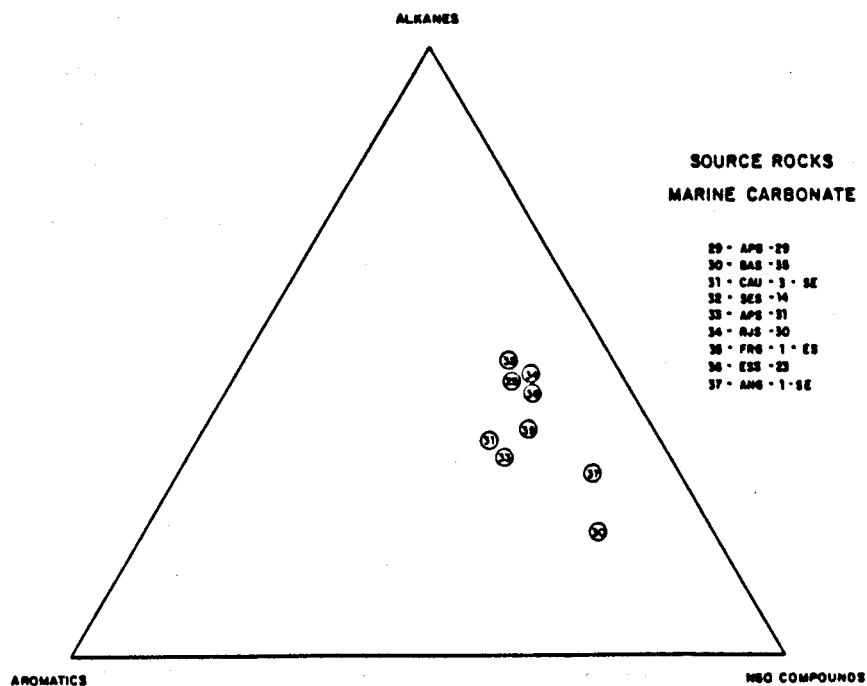


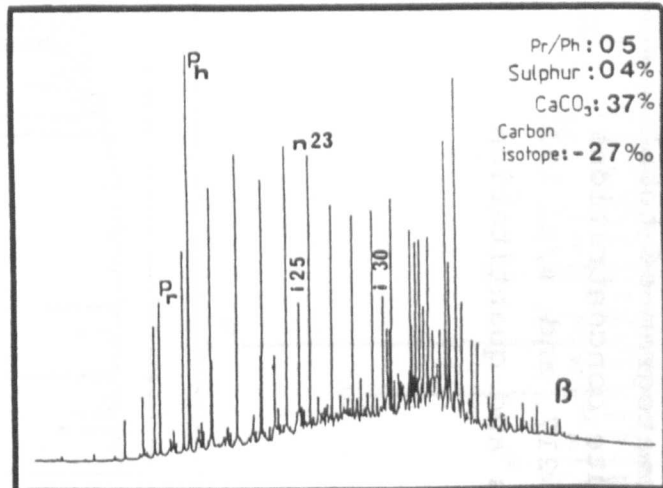
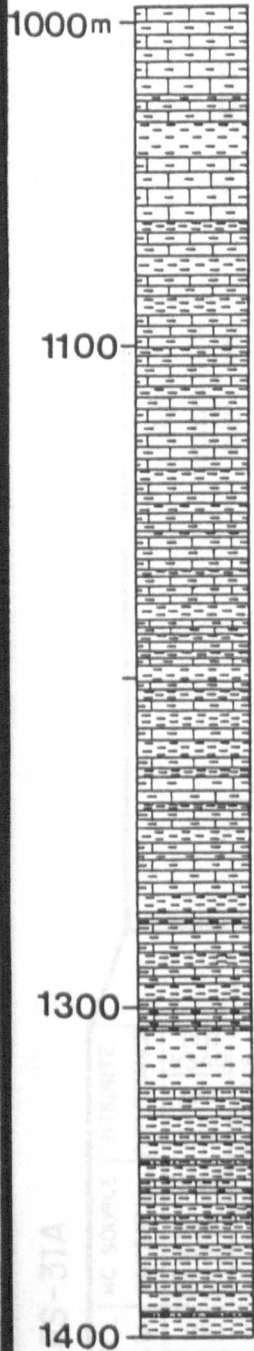
Figure 31- Relative abundance of alkanes, aromatics and NSO compounds in extracts from rock samples derived from marine carbonate environment.

The $\delta^{13}\text{C}$ values for the whole extracts (Fig. 7 and Tables 7, 8) are typical of samples associated with a marine carbonate environment, tending to be more negative than the values of the lacustrine saline and marine evaporitic samples, but heavier than the lacustrine freshwater ones (Fig. 7; Sofer, 1984; Tissot and Welte, 1984; Palacas et al., 1984). Similar features are typically associated with samples derived from marine carbonate environments, for example, the La Luna and Querencual formations, Venezuela; Sunniland formation, South Florida; Aquitaine basin, France; the Magdalena Valley, Colombia, and Officer basin, South Australia (McKirdy et al., 1984; Palacas et al., 1984; Moldowan et al., 1985; Cassani, 1986; Talukdar et al., 1986; Connan et al., 1983).

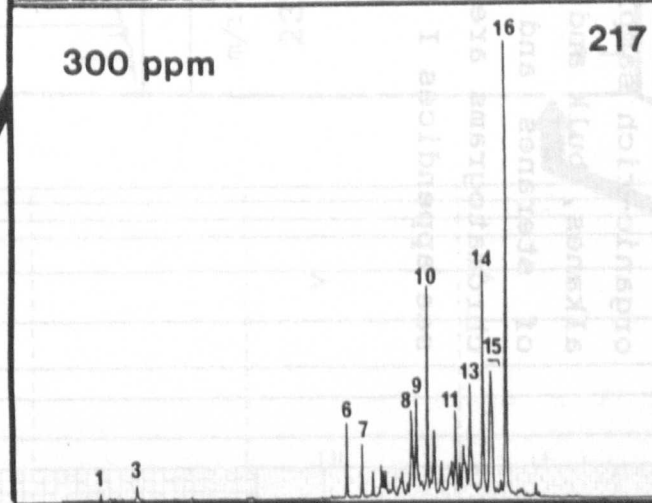
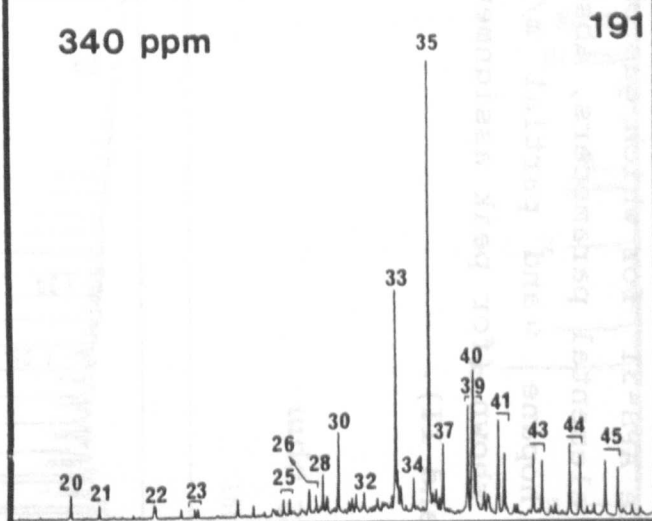
Figs. 32 and 33 illustrate two typical lithological logs chosen as specific examples, showing the stratigraphic position of two Albian organic-rich horizons (sample 34, Sergipe/ Alagoas basin and sample 36, Cassiporé basin respectively in Table 7 and Fig. 29). Also shown are gas chromatograms and m/z 191 and m/z 217 mass chromatograms of the alkane fraction of two samples from these horizons. Figs. 34 and 35 also show gas chromatograms and m/z 217 and m/z 191 mass chromatograms of the alkane fraction from three other samples from different basins along the continental margin (samples 33, 35 and 39 in Fig. 29 and Tables 7 and 8). The similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and the others in Tables 7 and 8 (cf. Chapter IV and Mello et al., 1988a and b for details) are clear. However, despite the overall similarities, differences in the molecular properties do exist for samples occurring at different stratigraphic horizons (different CaCO_3 content) in the marine carbonate succession. As an example the sterane distributions shown in Figs. 32-34 and 36 reveal an alternation in predominance between C_{27} and C_{29} components. Such a feature, in the case of the C_{29} predominance, appears to be linked with an increase of land plant input to the samples CAU-3, SES-14 and BAS-35

Figure 32- Lithological log of a well from Sergipe/ Alagoas basin, showing the stratigraphic position of a marine carbonate organic-rich sample (CAU-3) for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

CAU-3 - SE
ALBIAN



MARINE CARBONATE



1-A3-31A

ORGANIC
CARBON
WT %

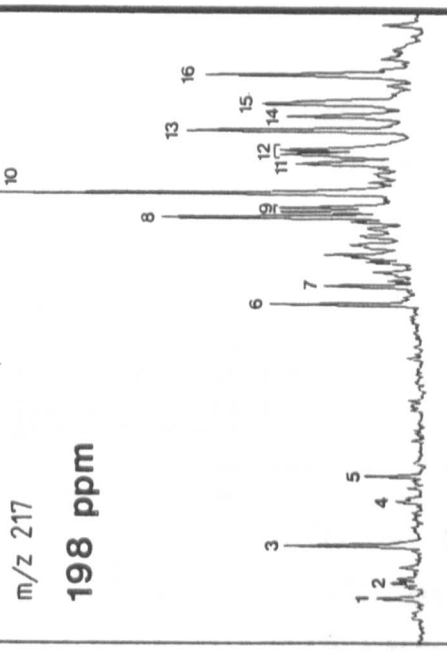
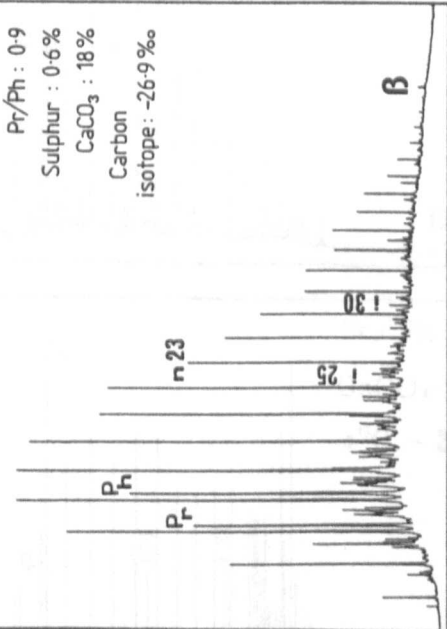
(SHELL)

Figure 33- Lithological log of a well from Cassiporé basin, showing the stratigraphic position of a marine carbonate organic-rich sample APS-31 for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

1-APS-31A

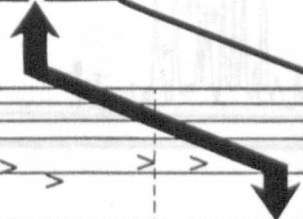
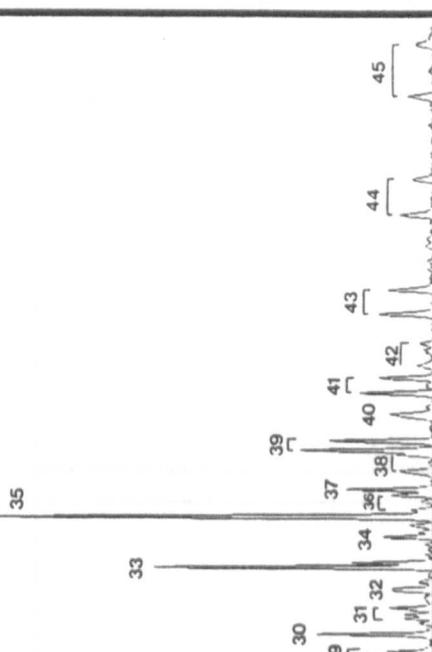
DEPTH (METERS)	ORGANIC CARBON WT. %	WELL DATA		HC SOURCE POTENTIAL			VITRINITE REFLECTANCE			
		AGE	LITHO	POOR	FAIR	GOOD	EXC.	IMMAT	MAT	OVER MAT
4	2						2	6		
							5	10		
							2	135		

DEPTH (METERS)	MAASTRICHTIAN	CENOM./CAMP	MED. ALB.
3000			
3500			
4000			
4500			



Pr/Ph : 0.9
 Sulphur : 0.6%
 CaCO₃ : 18%
 Carbon isotope : -26.9‰

β



GAS CHROMATOGRAM

M / Z 217

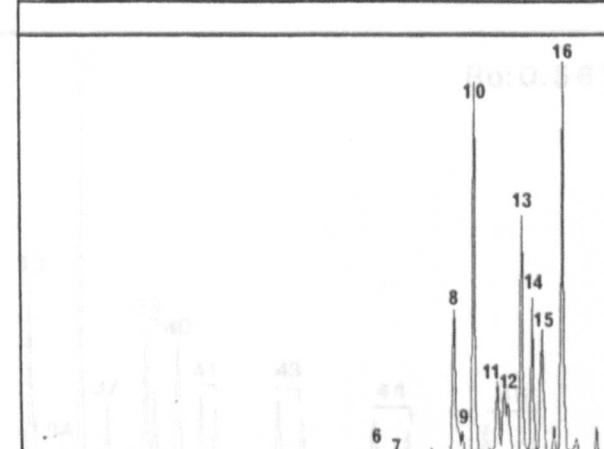
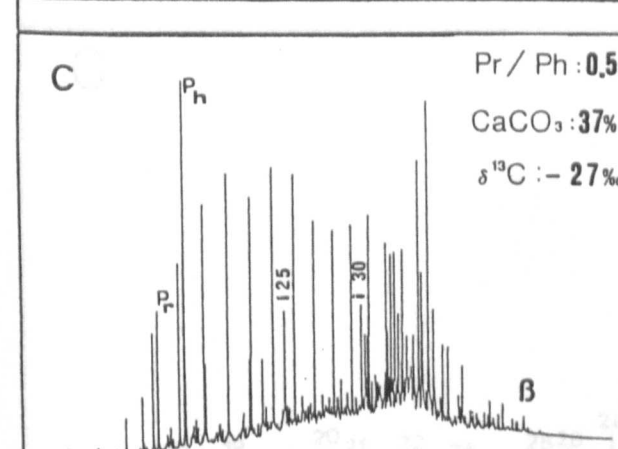
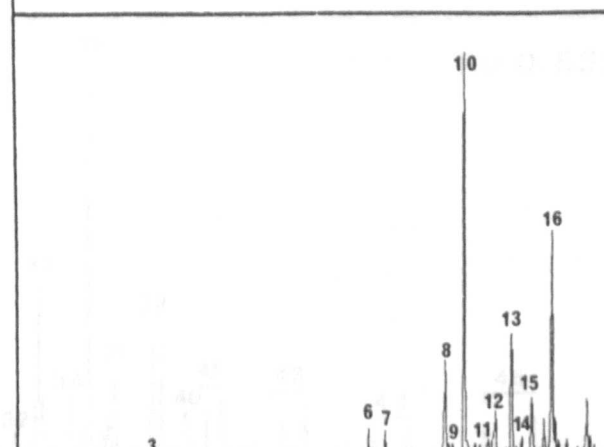
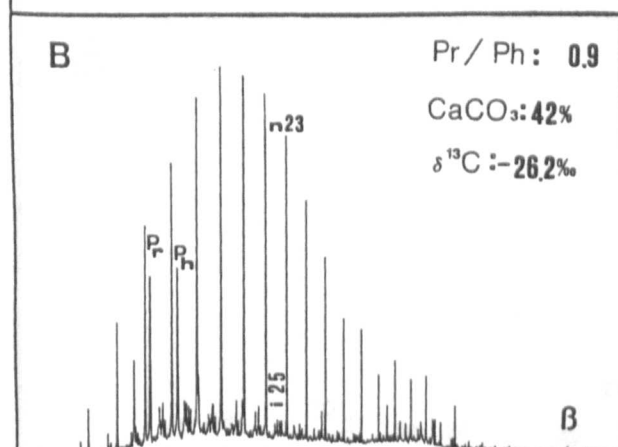
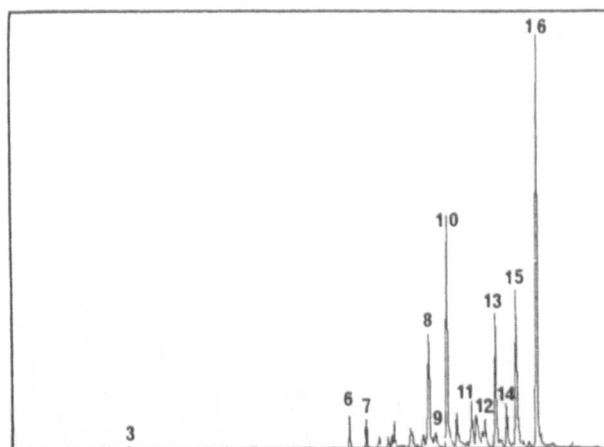
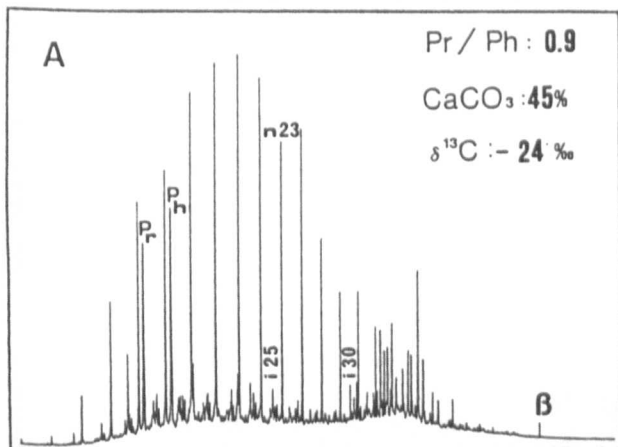


Figure 34- Gas chromatograms of total alkanes, bulk and elemental parameters, partial m/z 217 chromatograms of three organic-rich rock samples derived from marine carbonate environment from Bahia Sul (A: BAS-35), Espirito Santo (B: ESS-23) and Sergipe/ Alagoas (C: SES-14) basins (for peak assignments see appendix I).

M/Z 191

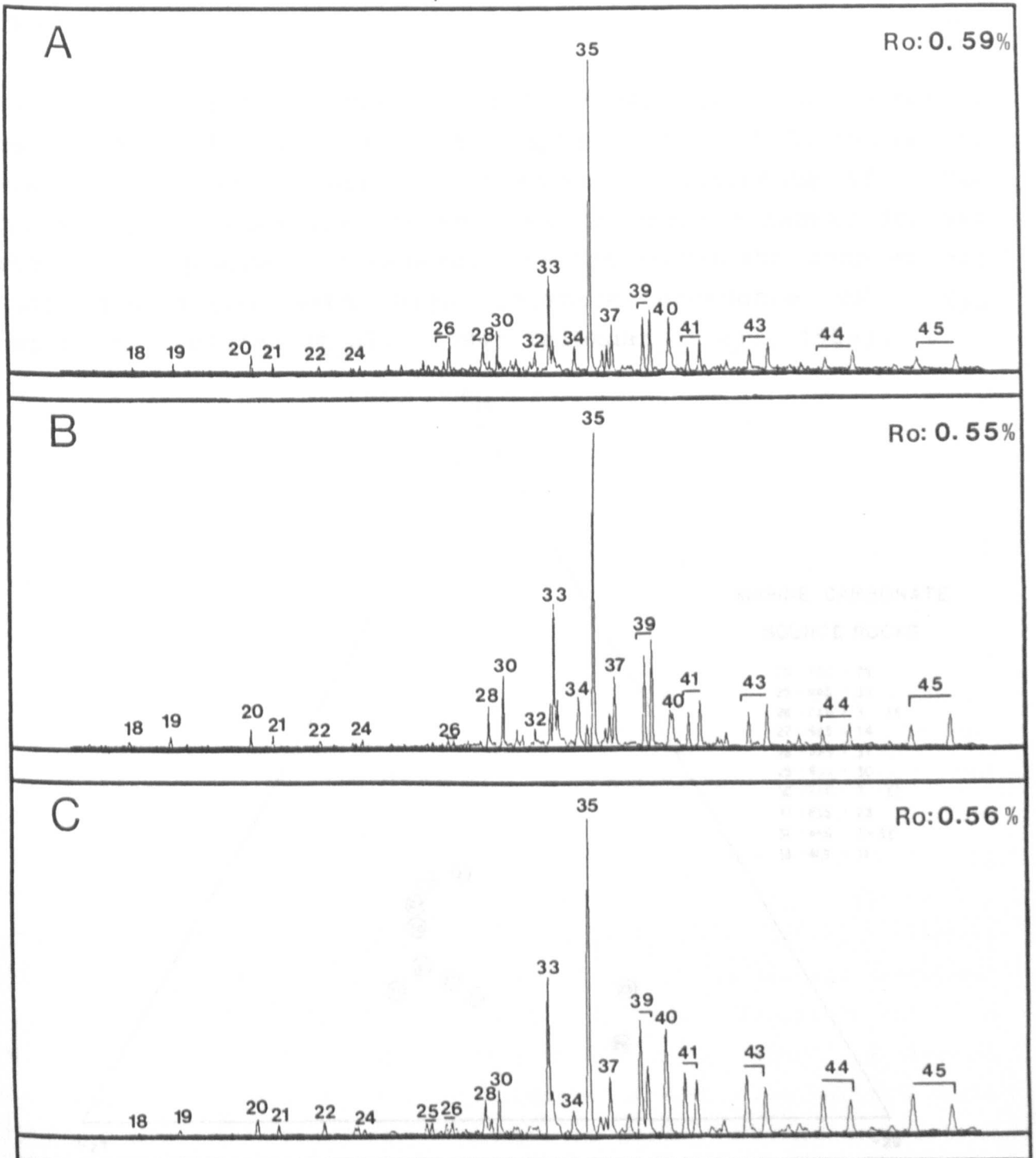


Figure 36- Carbon number (C_{27} , C_{29} , C_{29}) distributions of 50(H), 142(H), 172(H), 202-steranes for a number of sediment extracts from marine carbonate depositional environment.

Figure 35- Partial m/z 191 chromatograms for total alkanes and vitrinite reflectance data for the same samples as Fig. 34 (for peak assignments see appendix I).

On a whole, the chromatograms show a similar pattern of peaks, with the intensity of the peaks generally decreasing as the carbon number increases. The reflectance data (Ro) for each sample is provided in the top right corner of each chromatogram: A (0.59%), B (0.55%), and C (0.56%). The dominance of phytane over pristane (Pr/Ph ratios from 0.5 to 0.96), medium

(60%, 40% and 40% herbaceous and woody plus coaly material respectively; Table 7) against samples APS-31 (20%; Table 7). However, although sample ESS-23 shows a dominance of C_{27} components, it contains around 90% of organic matter derived from higher plants. In general, marine carbonate samples are often associated with high relative abundance of C_{29} components (Palacas et al., 1984; Talukdar et al., 1986).

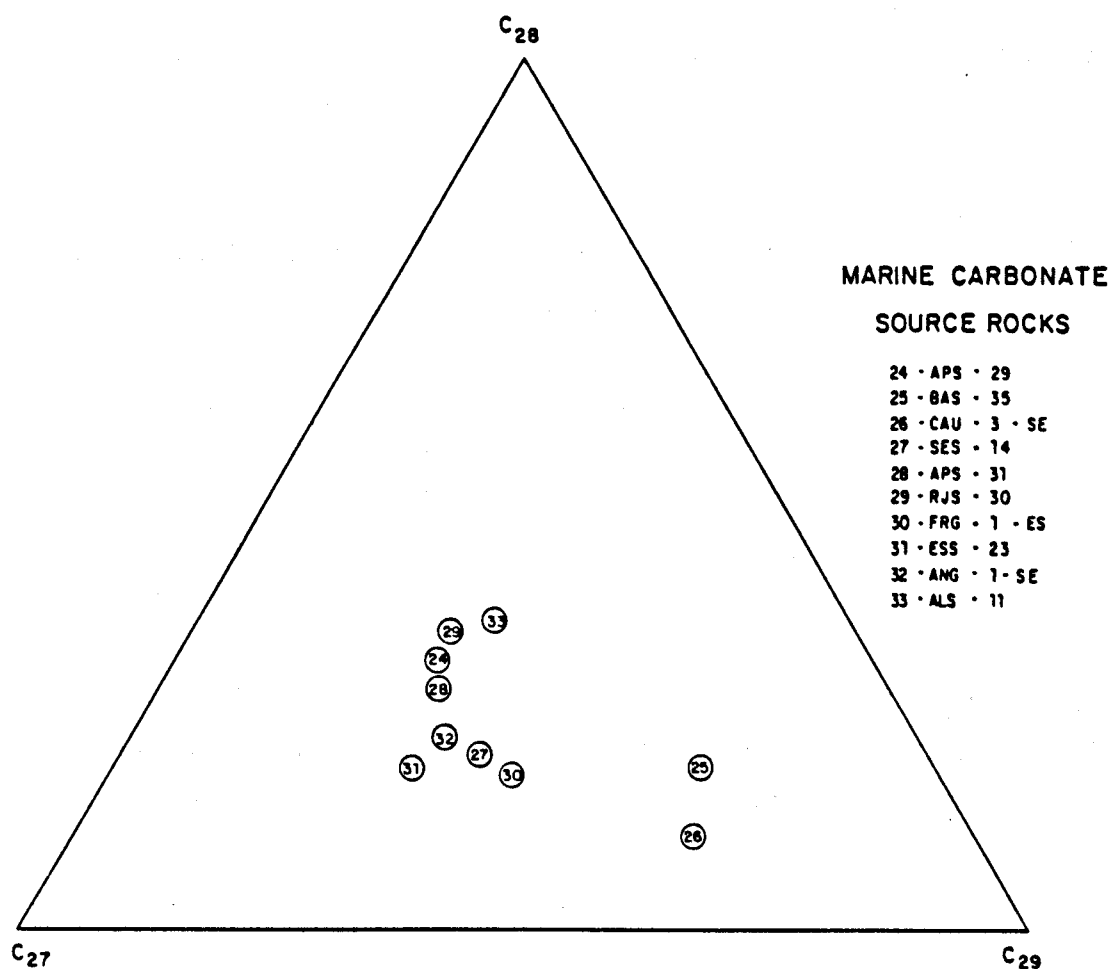


Figure 36- Carbon number (C_{27} , C_{28} , C_{29}) distributions of $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20R steranes for a number of sediment extracts from marine carbonate depositional environment.

On a whole, there are several features in the bulk data and biological marker distributions and concentrations that are diagnostic of a marine carbonate depositional environment with enhanced salinity (cf. Chapter IV). The dominance of phytane over pristane (Pr/ Ph ratios from 0.5 to 0.96), medium

to high concentrations of the C₂₅ and C₃₀ isoprenoid components (ranging from 100-450 ppm), the presence of β -carotane (up to 95 ppm) in these samples (Table 4 and Fig. 32-35), are consistent with enhanced salinities in the environment during carbonate deposition (cf. lacustrine saline and marine evaporitic samples and also Chapter IV). The significant abundances of β -carotane are further evidence of its value as a diagnostic indicator of enhanced salinity in both marine (this work) and lacustrine (Hall and Douglas, 1984) environments, rather than as a terrestrial marker (cf. Moldowan et al., 1985).

The sterane concentrations tend to be high (up to 350 ppm; Table 8 and Figs. 32, 33), only lower than those of the evaporitic samples, suggesting that salinity may also influence the biological marker concentrations in marine carbonate sediments. Similarly, high concentrations of low molecular weight steranes occur (up to 50 ppm; Table 8 and Fig. 33; ten Haven et al., 1985; Talukdar et al., 1986). As for the evaporitic samples, diasteranes are present in low abundance (diasterane index < 30; Table 8) a feature commonly observed for samples from carbonate environments in Australia, Venezuela, Tunisia and France (McKirdy et al., 1984; Cassani, 1986); Connan et al., 1983). As for the other marine samples, C₃₀ steranes are present, and in the higher abundance than in the samples from the marine evaporitic environment (K around 438, sample C in Fig. 37; cf. Tables 4 and 8). Perhaps this increase reflects the establishment of wholly marine conditions when compared with the evaporitic environment (transitional; cf. geology in Chapter 1). In contrast to the steranes, the relative abundances and distributions of the tricyclic terpanes differ from the evaporitic samples and show a similar pattern to those of the lacustrine saline samples (tricyclic index ranging from 60-200; Figs. 33 and 35), suggesting indirectly that their precursors are suppressed by hypersalinity (cf. Chapter IV). Examples of well-documented carbonate samples with comparable tricyclic features occur in Venezuela (Cassani,

M / Z

414 - 217

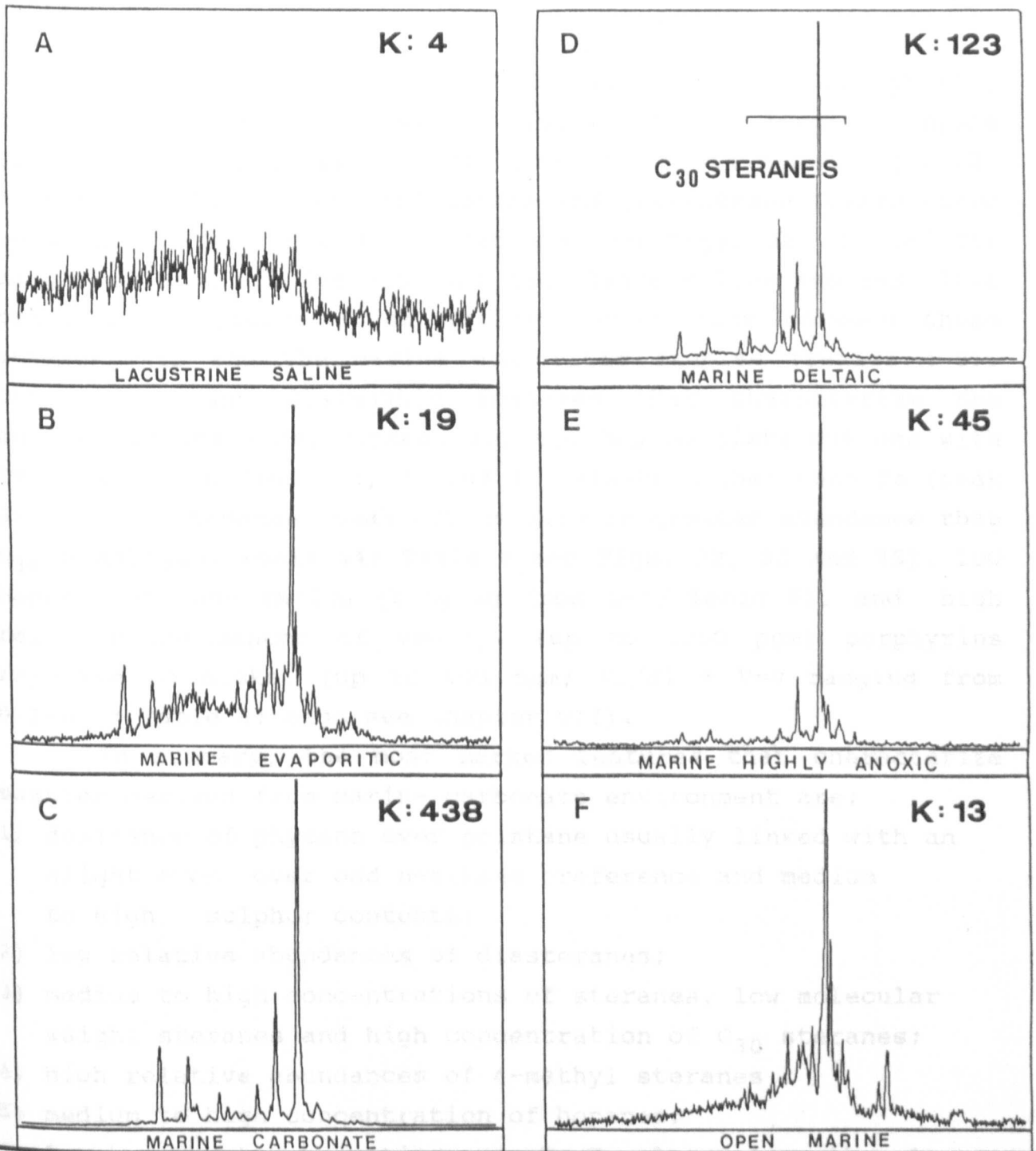


Figure 37- Mass chromatograms from metastable ion monitoring for transition m/z 414-217 (C_{30} steranes) of alkane fractions from sediment extracts from different depositional environments; A: lacustrine saline water (RJS-101); B: marine evaporitic (BAS-35); C: marine carbonate (SES-14); D: marine deltaic (APS-36); E: open marine highly anoxic with dominance of calcareous lithology (CES-28); and F: open marine anoxic with dominance of siliciclastic lithology (RNS-15). "K" values indicate concentration relative to constant amounts of added deuteriated sterane standard

1986; Talukdar et al., 1986), South Florida (Palacas et al., 1984), and Colombia (Zumberge, 1984). The 28,30-bisnorhopane (bisnorhopane index from 10-35; peak 32; Table 8 and Figs. 32, 33 and 35), 25,28,30-trisnorhopane and gammacerane (gammacerane index up to 25; peak 40 in Table 8 and Figs. 32, 33 and 35) also show similarities with the lacustrine saline samples. This presumably reflects lower salinity conditions between these environments and the marine evaporitic samples (Tables 4-8). Other important diagnostic features that characterize the marine carbonate environment are the hopane distributions with T_m (peak 30 in Figs. 32, 33 and 35) always higher than T_s (peak 28), C_{35} $\alpha\beta$ hopanes (peak 45) usually in greater abundance than C_{34} homologues (peak 44; Table 8 and Figs. 32, 33 and 35), low hopane/sterane ratios (ranging from 1-3; Table 8), and high relative abundances of vanadyl (up to 3000 ppm) porphyrins relative to nickel (up to 400 ppm; $Ni/Ni + V=0$ ranging from 0.1-0.3; Table 8; also see chapter VII).

In summary, the most marked features that characterize samples derived from marine carbonate environment are;

- 1) dominance of phytane over pristane usually linked with an slight even over odd n-alkane preference and medium to high sulphur contents;
- 2) low relative abundances of diasteranes;
- 3) medium to high concentrations of steranes, low molecular weight steranes and high concentration of C_{30} steranes;
- 4) high relative abundances of 4-methyl steranes ;
- 5) medium to high concentration of hopanes;
- 6) low hopane/sterane ratios and T_s/T_m always less than 1;
- 7) medium relative abundances of 28,30-bisnorhopane ;
- 8) tendency towards a dominance of C_{35} over C_{34} hopanes;
- 9) medium concentration β -carotane, regular C_{25} and C_{30} (squalane)isoprenoids;
- 10) low to medium relative abundance of gammacerane;
- 11) high concentrations and relative abundances of vanadyl porphyrins relative to nickel;

Many of these features have been reported to be

diagnostic of marine carbonate samples (cf. Chapter IV) and are similar to those found in marine carbonate samples from La Luna and Querencual Formations, Venezuela and Colombia; Eastern Officer Basin, Australia and South Florida Basin, USA (Talukdar *et al.*, 1986; Zumberge, 1984; McKirdy *et al.*, 1984; Palacas *et al.*, 1984).

2.2.5 Marine Deltaic With Carbonate Influence

The organic-rich sediments of this group are confined to Tertiary sequences, being localized in the Cassiporé and Maranhão basins in the northern part of the continental margin (43 and 44 respectively in Fig. 38 and Table 9).



Figure 38- Location map showing the areas from which samples from marine deltaic environment with carbonate influence were investigated.

Fig. 39 shows a geochemical well log (1-APS-36) with the Van Krevelen-type diagram, showing the stratigraphic position

Table 9: Geological and Geochemical Data For Sediments From Marine Deltaic Environment with Marine Carbonate Influence.

WELLS	APS-36	MAS-10
Sample Number	43	44
Sample Nature	Cuttings	Cuttings
Depth (m)	4230	3018
Age	Eocene	Eocene
Lithology	Grey Marl	Grey Marl
CaCO (%)	77	53
Sulphur (%)	0.4	0.35
TOC (%)	7.2	0.92
S ₂ (KgHC/Ton rock)	28	4.27
HI (mgHC/gTOC)	370	464
T-MAX (°C)	428	420
Ro (%)	0.55	0.50
SCI	4.5	4.5
EOM (ppm)	3400	420
Pr/Ph	0.7	0.4
Pr/nC ₁₇	0.86	-
Ph/nC ₁₈	0.87	-
nC ₁₇ /C ₃₁	0.75	-
δ ¹³ C whole extract	-21.3 ‰	-25.4 ‰
Saturates (%)	42	20
Aromatics (%)	17	19
NSO (%)	41	61
Amorphous (%)	85	90
Herbaceous (%)	10	10
Woody+Coaly (%)	5	-

DEPTH (METERS)	ORGANIC CARBON WT. %		WELL DATA		HC SOURCE POTENTIAL				VITRINITE REFLECTANCE			
			AGE	LITHO	POOR	FAIR	GOOD	EXC.	MMAT	MAT	OVER MAT.	
	4	2			2	5	10		2	6	135	
2500			UPPER MIOCENE									
3000			MED MIOCENE									
3500			OLIGOCENE									
4000			EOCENE									

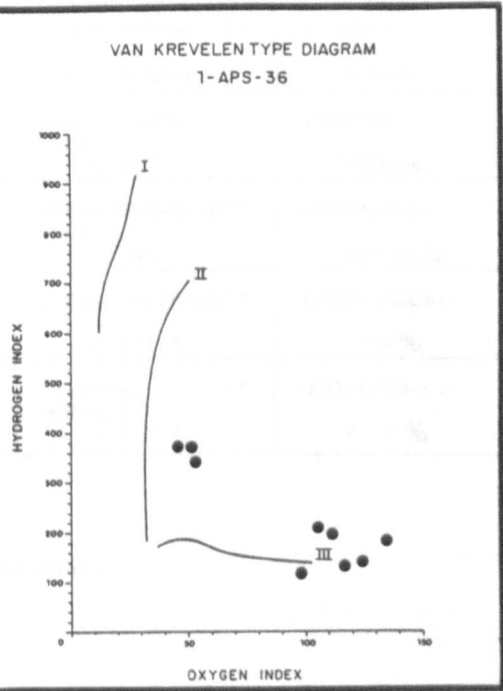


Figure 39- Geochemical log of a well from Cassiporé basin, showing the stratigraphic position of the marine deltaic with carbonate influence organic-rich sediments and the hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram, of samples for the Eocene/ Oligocene sedimentary succession.

TABLE 10- Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples from Sediments Derived from Marine Deltaic Environment with Marine Carbonate Influence in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 1.4-10.36%	T.O.C.: 1-7.2%	n-ALKANES MAXIMA: C ₂₀ -C ₂₂	C ₂₇ STERANE: ⁶ 250-333ppm	C _{30αβ} HOPANE: ¹¹ 270-383ppm	NICKEL: ≈48ppm
HYDROGEN: 0.21-0.34%	S ₂ : ¹ 4-26	SATURATES: 22-42%	C ₂₇ /C ₂₉ : ⁷ 1.1-1.6	GAMMACERANE ¹² INDEX: 5-15	VANADYL: ≈12ppm
NITROGEN: 0.07%	HI: ² 370-464	Pr/Ph: 0.7-0.9	DIASTERANE ⁸ INDEX: 20-30	18α(H)OLEANANE ¹³ INDEX: 48-60	AMORPHOUS: 85-90%
SULPHUR: 0.35-0.40%	Ro: 0.50-0.55%	I-C ₂₉ +I-C ₃₀ : ⁴ 200-308ppm	4-Me STERANE ⁹ INDEX: 10-20	HOPANE/STERANE ¹⁴ 0.4-1.5	HERBACEOUS: 10%
CaCO ₃ : 45-77%	δ ¹³ C: ³ -21.9 to -25.4	β-CAROTANE: ⁵ trace-10ppm	C ₂₁ + C ₂₂ ¹⁰ STERANES: 30-45	C ₃₄ /C ₃₅ ¹⁵ HOPANES: 0.1-0.7	WOODY/COALY: 0-5%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index mgHC/gTOC (Pyrolysis Rock-Eval).
3. PDB (%)
 - i. Sum of 2,6,10,14,18-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
 - ii. Peak area (β) in RIC trace and normalised to added sterane standard.
 - iii. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
 - iv. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
 - v. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
 - vi. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
 - vii. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
 - viii. Peak area of 35 measured in RIC and normalised to added sterane standard.
 - ix. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
 - x. Peak area of 18α(H) oleanane (X) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
 - xi. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
 - xii. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

of an organic-rich Tertiary sedimentary succession in the Cassiporé basin (43 in Fig. 38 and Table 9). Together with the data of Tables 9 and 10, it is seen that the Tertiary organic-rich succession comprises mainly, well laminated grey marls/ calcilutites (CaCO_3 from 53 to 77%), rich in organic matter (TOC up to 7.2%), with medium sulphur content (up to 0.4%). They have fair to good hydrocarbon source potential (S_2 from Rock-Eval pyrolysis ranging from 4.2 to 26 Kg Hc/ ton of rock). The hydrogen index (up to 464 mg HC/g organic carbon) and organic petrology data identify the organic matter as being almost entirely composed of lipid-rich material (type II/III kerogen; amorphous plus herbaceous organic matter around 95%; Fig. 39 and Tables 9 and 10). A detailed examination through visual kerogen analysis, suggests that much of the amorphous organic matter detected appears to be derived from microbial degradation of land plant material. Nevertheless, the lack of sufficient thermal maturity in the samples available indicates that they are not source rocks (see maturity data in Tables 9 and 10 and Fig. 39).

In many respects the samples show geochemical features which are similar to those of the marine carbonate samples, but with properties that can be ascribed as characteristic of deltaic depositional environments where a large input of higher plants occurs. They possess medium content of saturates (up to 42%), medium values for sulphur (around 0.4%) and very high CaCO_3 content (Tables 9 and 10), and n-alkane maxima around C_{22} (Tables 7, 8). The $\delta^{13}\text{C}$ values for the whole extracts (Fig. 7 and Tables 9, 10) are a little heavier than typical marine samples, being significantly heavier than the values of the marine evaporitic and marine carbonate samples (Fig. 7; Sofer, 1984; Tissot and Welte, 1984; Palacas *et al.*, 1984). Fig. 40 illustrates the lithological log of a organic-rich horizon from well 1-APS-36 (Cassiporé basin), showing the stratigraphic position of sample APS-36 (43 in Fig. 38 and Table 9). Also shown are gas chromatograms, m/z 191 and m/z 217 mass chromatograms of the alkane fraction and concentrations of

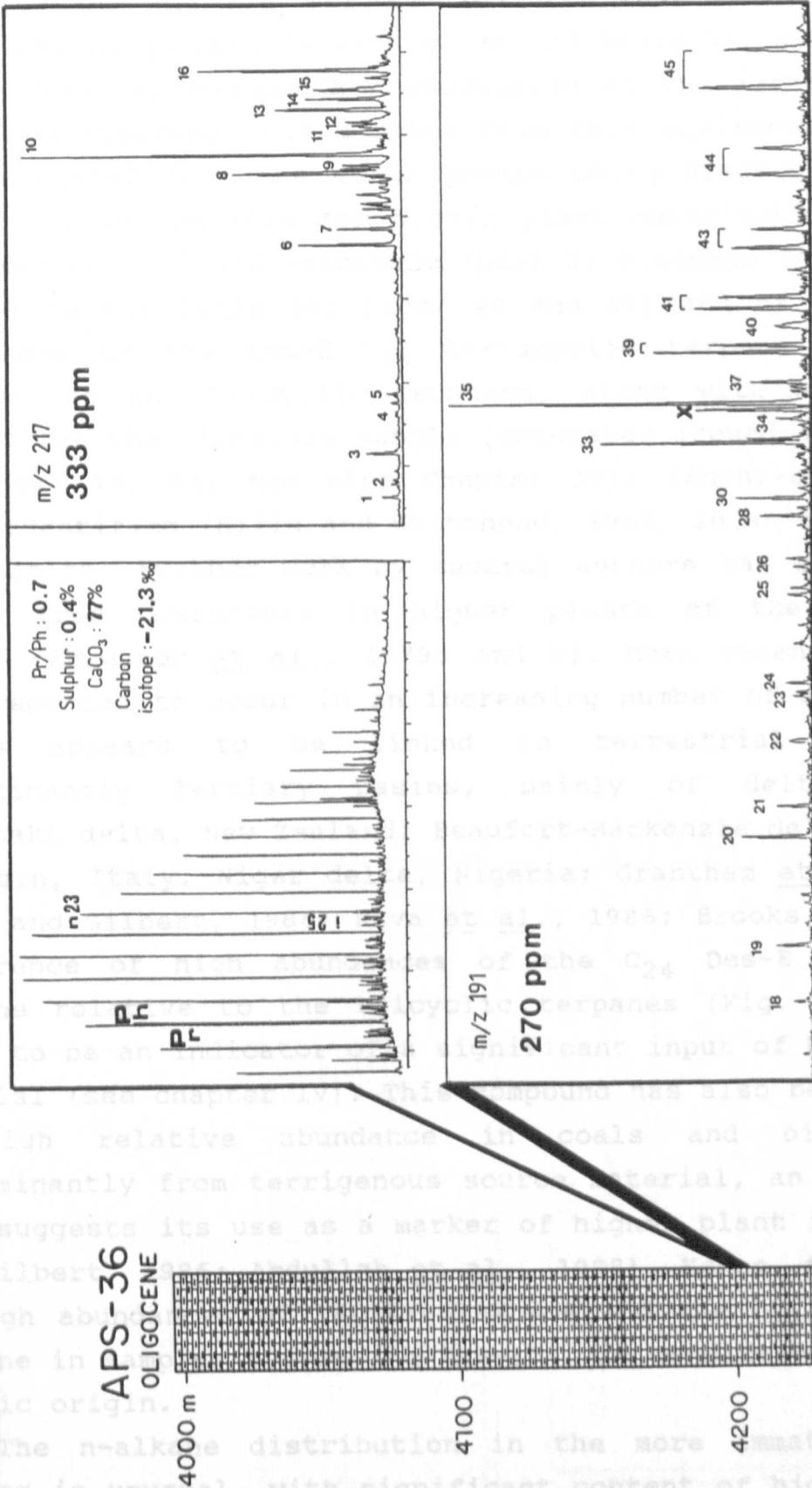
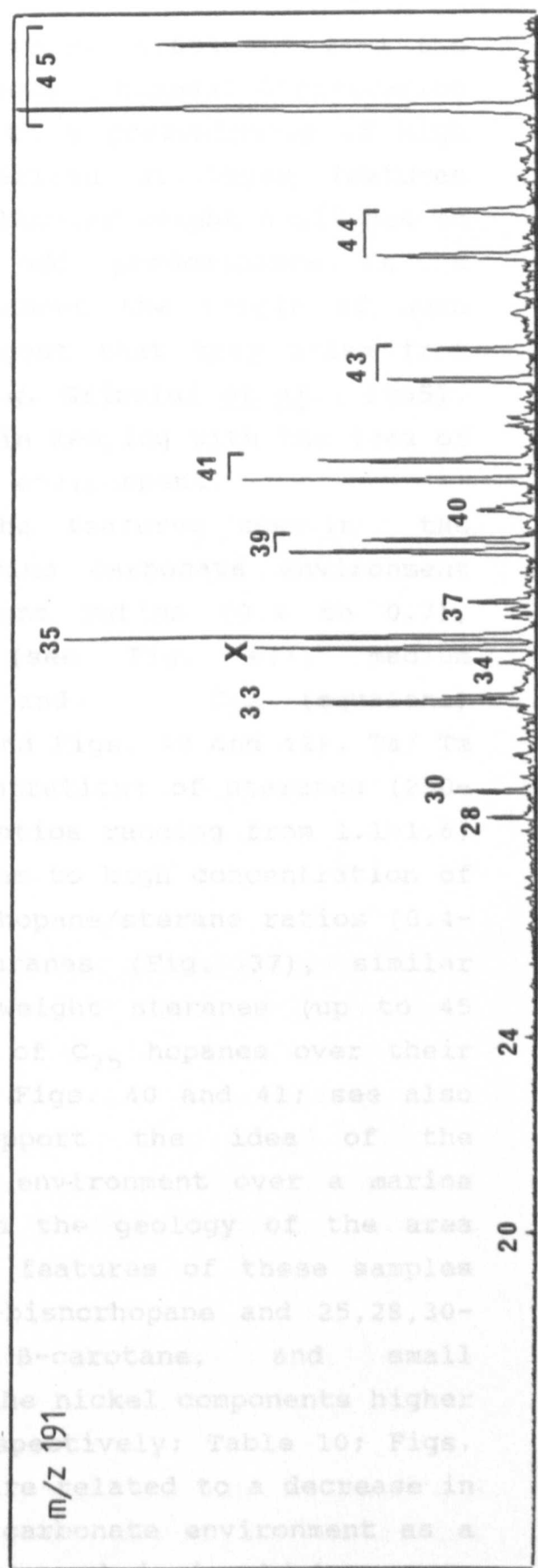
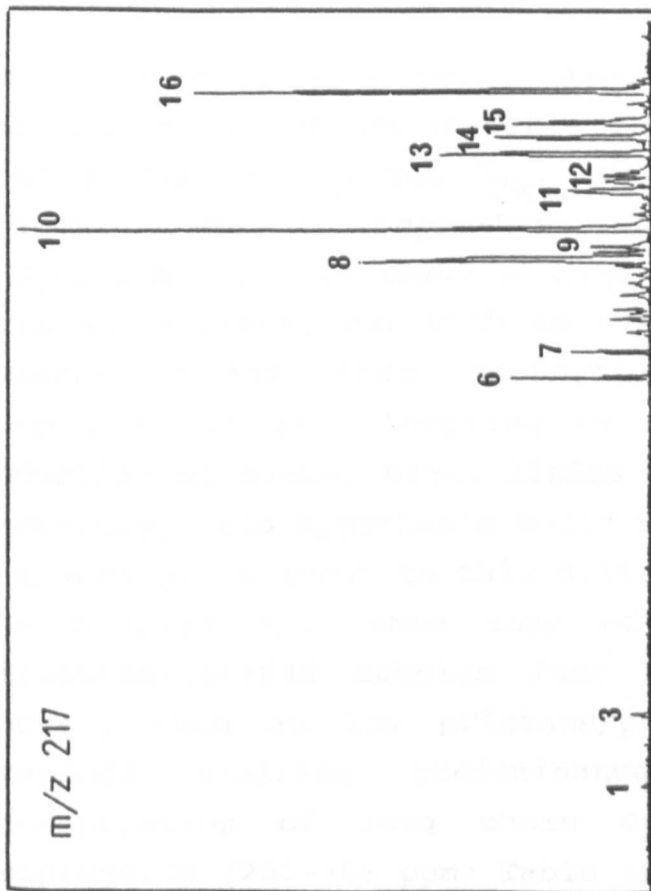
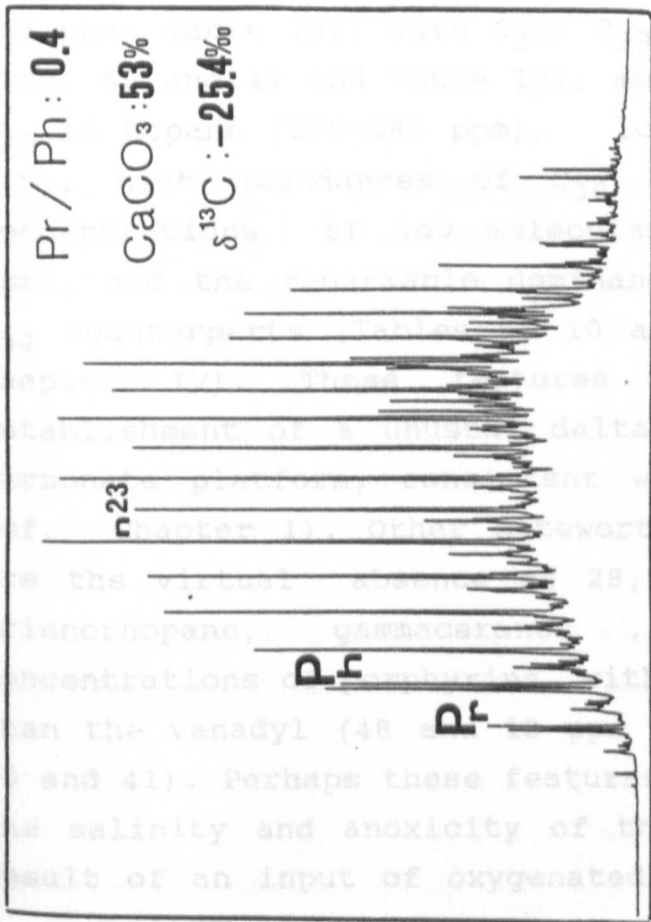


Figure 40- Lithological log of a well from Cassiporé basin, showing the stratigraphic position of a marine deltaic with carbonate influence organic-rich sample (AFS-36) for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

steranes and hopane . Fig. 41 on the other hand, shows the gas chromatograms and m/z 191 and m/z 217 mass chromatograms of sample MAS-10 (sample 44 in Fig. 38 and Table 9), as an example of the Tertiary sedimentary succession of the Maranhão basin. As can be observed, the samples from this environment can be differentiated from the other groups using diagnostic markers thought to be specific for higher plant contributions, namely the presence of 18 α (H)-oleanane (peak X; oleanane index ranging from 48 to 60; Table 10; Figs. 40 and 41) and of significant abundances of the Des-E C₂₄ tetracyclic terpane (peak 24), relative to the tricyclic terpanes, along with a high waxy content for the immature sample (saturates around 42%; Table 9 and Figs. 40, 41; see also Chapter IV); 18 α (H)-oleanane was first identified (Hills and Whitehead, 1966) in an oil from the Niger delta. Further work by several authors has suggested an origin from precursors in higher plants of the angiosperm family (Ekweozor et al., 1979a and b). More recently, it has been reported to occur in an increasing number of samples, but always appears to be linked to terrestrial inputs in predominantly Tertiary basins, mainly of deltaic nature (Taranaki delta, New Zealand; Beaufort-Mackenzie delta, Canada; Po Basin, Italy; Niger delta, Nigeria; Grantham et al., 1983; Philp and Gilbert, 1986; Riva et al., 1986; Brooks, 1986). The occurrence of high abundances of the C₂₄ Des-E tetracyclic terpane relative to the tricyclic terpanes (Fig. 40) appears also to be an indicator of a significant input of higher plant material (see chapter IV). This compound has also been reported in high relative abundance in coals and oils derived predominantly from terrigenous source material, an observation that suggests its use as a marker of higher plant input (Philp and Gilbert, 1986; Abdullah et al., 1988). Hence, the presence of high abundances of 18 α (H)-oleanane and the C₂₄ tetracyclic terpane in samples APS-36 and MAS-10 , is consistent with their deltaic origin.

The n-alkane distribution in the more immature of the samples is unusual, with significant content of high molecular

Figure 41- Gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms for the marine deltaic with carbonate influence sample MAS-10 from Maranhão basin (for peak assignments and quantitation see appendices I and II).



weight components. A third sample (around 0.60% Ro) from the Pará basin (not shown in Table 9) shows a bimodal distribution with maxima at C₂₂ and C₂₈, but with a predominance of high molecular weight components. Comparison of these features suggests a variable input of high molecular weight n-alkanes to this environment, but with an even/odd predominance. In the absence of any other information about the origin of such components it is tempting to suggest that they arise from reduction of higher plant lipids (e.g. Grimaldi *et al.*, 1985). Certainly, this hypothesis would be in keeping with the idea of a higher plant input to this deltaic environment.

The samples also show some of the features seen in the carbonate-derived samples (see marine carbonate environment above), such as low pristane/phytane ratios (0.4 to 0.7), even/odd n-alkane predominance (see Fig. 41), medium concentration of long chain C₂₅ and C₃₀ (squalane) isoprenoids (200-308 ppm; Table 10 and Figs. 40 and 41), Ts/Tm less than 1; medium to high concentrations of steranes (250-333 ppm; Table 10), with C₂₇/C₂₉ ratios ranging from 1.1-1.6; Figs. 40 and 41 and Table 10), medium to high concentration of C₃₀ αβ hopane (270-383 ppm), low hopane/sterane ratios (0.4-1.5), high abundances of C₃₀ steranes (Fig. 37), similar concentrations of low molecular weight steranes (up to 45 ppm), and the remarkable dominance of C₃₅ hopanes over their C₃₄ counterparts (Tables 9, 10 and Figs. 40 and 41; see also chapter IV). These features support the idea of the establishment of a unusual deltaic environment over a marine carbonate platform, consistent with the geology of the area (cf. Chapter I). Other noteworthy features of these samples are the virtual absence of 28,30-bisnorhopane and 25,28,30-trisnorhopane, gammacerane, β-carotane, and small concentrations of porphyrins, with the nickel components higher than the vanadyl (48 and 12 ppm respectively; Table 10; Figs. 40 and 41). Perhaps these features are related to a decrease in the salinity and anoxicity of the carbonate environment as a result of an input of oxygenated waters bringing high amounts

of clay minerals and organic debris from the river system. The significant relative abundances of diasteranes (peaks 6 and 7 in Figs. 40 and 41) in these immature sediments (R_o around 0.55%; see also other maturity parameters in Table 9), tend to support such an assumption, since such compounds are believed to arise from reduction of the rearrangement products of steranes, through catalytic effects of acidic clay minerals (Rubinstein et al., 1975)

In summary, the samples of this group contain features that are consistent with the establishment of a deltaic environment over a marine carbonate platform. The most marked are;

- 1) presence in high abundances of $18\alpha(H)$ -oleanane;
- 2) significant abundance of C_{24} tetracyclic Des-E hopane;
- 3) dominance of phytane over pristane, linked with even/odd n-alkane predominance;
- 4) tendency for abundant high molecular weight n-alkanes;
- 5) medium concentrations of regular C_{25} and C_{30} isoprenoids;
- 6) high concentrations of low molecular weight steranes;
- 7) medium to high relative abundance of diasteranes;
- 8) medium concentrations of steranes and hopanes;
- 9) low hopane/sterane ratios;
- 10) dominance of C_{35} hopanes over their C_{34} counterparts;

Only a few of these features (e.g. 1, 2 and 4) have been reported for samples from the Niger delta, Nigeria (Ekweozor et al., 1979a and b), Mahakam delta, Indonesia (Grantham et al., 1983), and Congo delta, Angola basin (Connan et al., 1988). Presumably this reflects the unusual depositional environment of the samples which also show many of the carbonate features not seen in these literature examples.

2.2.6 Open Marine Highly Anoxic With Dominance of Calcareous Mudstone Lithology.

The organic-rich sediments of this group, ranging in age from Turonian to Coniacian, are widespread along the Brazilian continental margin (Fig. 42).



Figure 42- Location map showing the basins from which samples from open marine highly anoxic environment with dominance of calcareous mudstone lithology were investigated.

The samples investigated were obtained from Cassiporé (sample 49), Ceará (samples 45-48), Sergipe/Alagoas (sample 50) and Campos (sample 51) basins (Fig. 42 and Table 11).

As examples, Fig. 43 shows two geochemical well logs (CES-50, Ceará basin and CAU-3, Sergipe/Alagoas basin) showing the stratigraphic position of the Turonian/Santonian organic-rich horizons in these wells together with their Van Krevelen type diagram. Fig. 43 and Tables 11 and 12 indicate that the Turonian/Coniacian sedimentary succession comprises mainly well laminated calcareous grey shales (CaCO_3 ranging from 15-48%), containing moderate to high organic carbon content (TOC up to 5.0%) and good hydrocarbon source potential (up to 20 kg Hc/ton of rock) largely arising from type II kerogen (hydrogen index ranging from 300-550 mg Hc/g organic carbon). The organic petrology data identify the organic matter as being

Table 11: Geological and Geochemical Data For Sediments From Marine Highly Anoxic Environment with Predominance of Calcareous Mudstone Lithology.

WELLS	CES-50	CES-56	CES-19	CES-28	APS-29	CAU-3	RJS-225
Sample Number	45	46	47	48	49	50	51
Sample Nature	Cuttings	Cuttings	Core	Core	Cuttings	Cuttings	Cuttings
Depth (m)	1461	1710	1950	1911	4320	700	1902
Age	Turonian/ Santonian	Turonian/ Santonian	Turonian/ Santonian	Turonian/ Santonian	Turonian/ Santonian	Turonian/ Santonian	Coniacian
Lithology	Calcareous Grey Shale	Calcareous Grey Shale	Calcareous Grey Shale	Calcareous Grey Shale	Calcareous Grey Shale	Calcareous Grey Shale	Calcareous Grey Shale
CaCO ₃ (%)	15	24	18	22	48	15	18
Sulphur (%)	0.37	0.45	0.3	0.3	0.4	0.32	0.35
TOC (%)	3.2	3.0	2.5	2.8	4.0	2.5	1.7
S ₂ (kgHC/Ton rock)	15	14	9	8	19	13	6
HI (mgHC/gTOC)	470	512	356	368	475	520	346
T-MAX (°C)	411	412	421	426	425	412	440
Ro (%)	0.47	0.46	0.54	0.48	0.63	0.45	0.55
SCI	5.0	-	5.0	5.0	6.0	-	5.0
EDM (ppm)	1900	1780	1400	1340	3570	940	968
Pr/Ph	0.5	0.8	0.8	0.8	0.7	0.7	0.9
Pr/nC ₁₇	1.4	1.2	1.6	1.0	0.8	0.9	0.7
Ph/nC ₁₈	1.5	0.9	1.3	1.4	0.8	0.9	0.7
nC ₁₇ /C ₃₁	1.2	1.2	1.3	1.2	2.1	1.4	2.3
δ ¹³ C whole extract	-28.2	-27.8	-27.0	-27.2	-25.1	-27.8	-26.9
Saturates (%)	22	25	28	31	34	23	39
Aromatics (%)	11	13	16	19	17	10	14
NSO (%)	67	62	56	50	49	67	47
Amorphous (%)	90	90	85	85	85	85	80
Herbaceous (%)	5	5	5	5	10	10	10
Woody+Coaly (%)	5	5	10	10	5	5	10

TABLE 12- Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples From Sediments From Marine Highly Anoxic Environment with Predominance of Calcareous Mudstone Lithology.

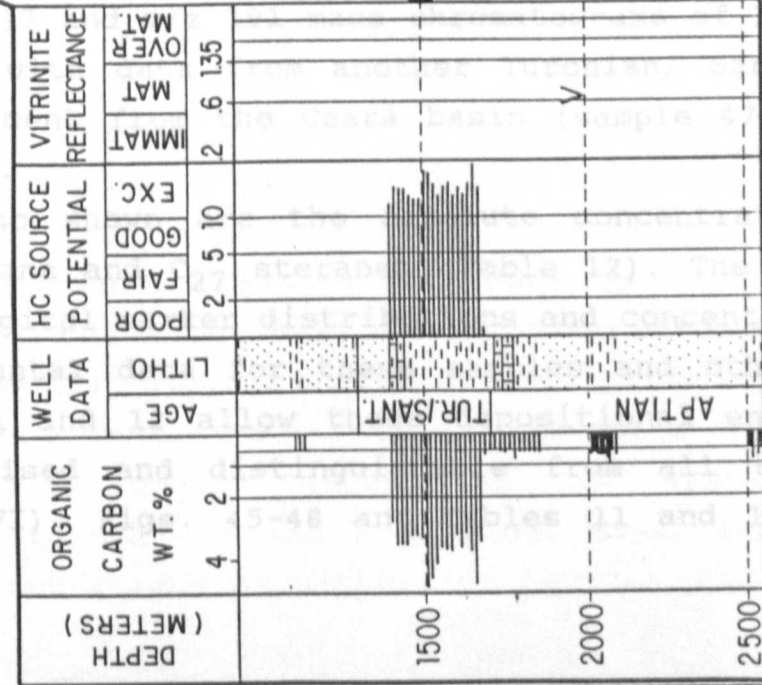
ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 3-6%	T.O.C.: 2-5%	n-ALKANES MAXIMA: ≈C ₂₁	C ₂₇ STERANE: ⁶ 30-200ppm	C _{30αβ} HOPANE: ¹¹ 30-70ppm	NICKEL: 130-1700ppm
HYDROGEN: 0.4-0.6%	S ₂ : ¹ 8-20	SATURATES: 20-39%	C ₂₇ /C ₂₈ : ⁷ 0.8-1.3	GAMMACERANE ¹² INDEX: 0-25	VANADYL: 30-4000ppm
NITROGEN: 0.05-0.10%	HI: ² 300-550mg/g	Pr/Ph: 0.5-0.9	DIASTERANE ⁸ INDEX: 10-30	BISNORHOPANE ¹³ up to 120ppm	AMORPHOUS: 80-90%
SULPHUR: 0.3-0.6%	R ₀ : 0.4-0.63%	I-C ₂₈ +I-C ₃₀ : ⁴ 70-170ppm	4-Me STERANE ⁹ INDEX: 20-40	TRISNORHOPANE ¹⁴ up to 130ppm	HERBACEOUS: 5-10%
CaCO ₃ : 15-48%	δ ¹³ C: ³ -27 to -28.2	β-CAROTANE: ⁵ 10-50ppm	HOPANES/ STERANES: 0.3-0.9	C ₃₄ /C ₃₅ HOPANES: 0.6-1.1	WOODY/COALY: 5-10%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (‰)
4. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₈) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (β) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in RIC chromatogram over peak area of sterane standard in RIC.
14. Peak area of C₂₇ 25,28,30-trisnorhopane (T) in RIC chromatogram over peak area of sterane standard in RIC.
15. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 44 to 47.

1-CES-50



1-CAU-3-SE

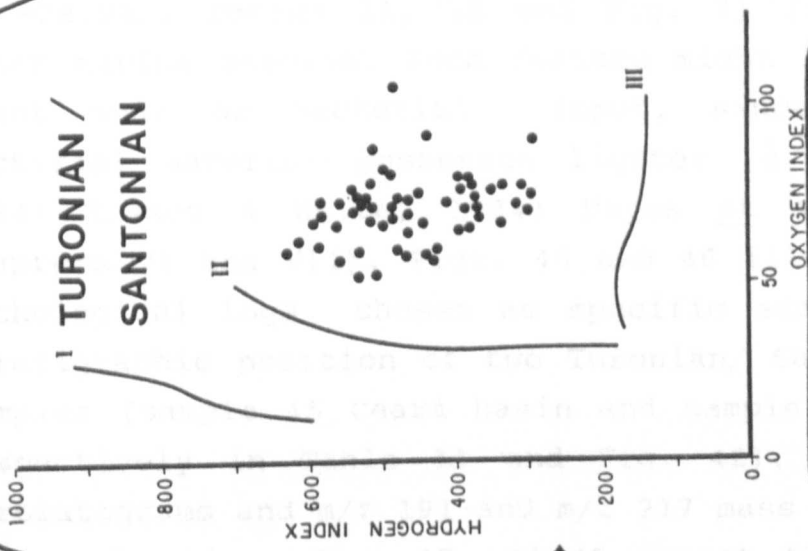
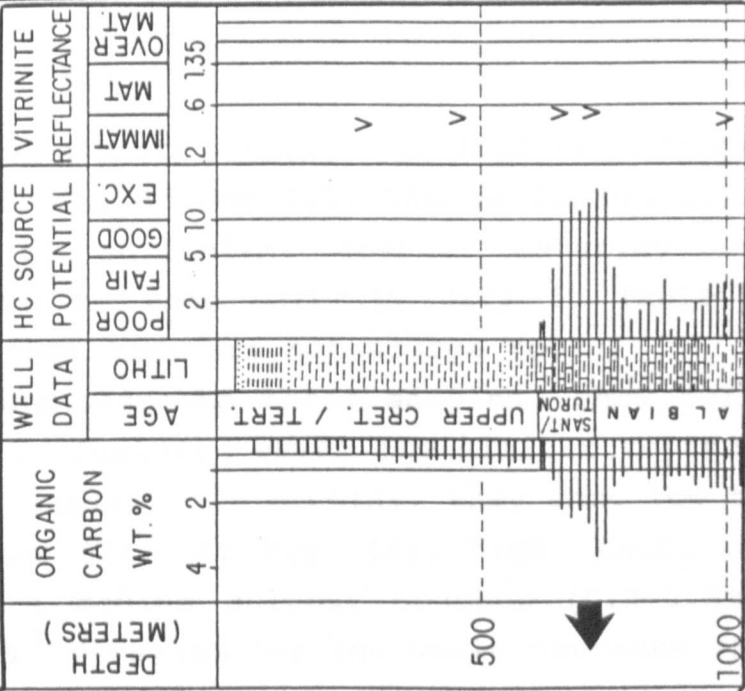


Figure 43- Geochemical logs of two wells from Ceará (CES-50) and Sergipe/ Alagoas (CAU-3) basins, showing the stratigraphic position of a typical open marine highly anoxic (with dominance of calcareous lithology) organic-rich sedimentary succession and the hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram, of samples from the Santonian/Turonian.

composed of almost entirely of lipid-rich material (amorphous plus herbaceous around 95%; Tables 11 and 12). Nevertheless, the lack of sufficient thermal maturity in the Brazilian marginal basins (see maturity data in Table 11 and Fig. 43) indicates that they are not source rocks.

In many respects these samples show bulk, elemental and geochemical features which are similar to those of the marine carbonate samples. In general, they show low to medium content of saturates (22-39%; Fig. 44), high CaCO_3 (ranging from 15-48%), and a medium sulphur content (0.3-0.6%; Tables 11 and 12). The $\delta^{13}\text{C}$ values for the whole extracts (Fig. 7 and Tables 11, 12) are unusual, since they show lighter $\delta^{13}\text{C}$ values (up to -28.2%; Tables 11, 12 and Fig. 7) if compared with the other marine samples. Such feature might suggest enhanced plant and/or bacterial input, since higher plant and bacterial material possesses lighter $\delta^{13}\text{C}$ values (Sofer, 1984; Tissot & Welte, 1984; Hayes *et al.*, 1987; see also chapters VI and VII). Figs. 45 and 46 illustrate two typical lithological logs chosen as specific examples, showing the stratigraphic position of two Turonian/Santonian organic-rich samples (sample 45 Ceará basin and sample 49, Cassiporé basin respectively in Table 11 and Fig. 42). Also shown are gas chromatograms and m/z 191 and m/z 217 mass chromatograms of the alkane fraction. Fig. 47 and 48 repeat the gas chromatograms and m/z 217 and m/z 191 mass chromatograms of Figs. 45 and 46, together with data from another Turonian/Santonian organic-rich sediment from the Ceará basin (sample 47 in Fig. 42 and Table 11).

Also shown are the absolute concentrations of 28,30-bisnorhopane and C_{27} steranes (Table 12). The similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and others reported in Tables 11 and 12 allow these depositional environment to be characterised and distinguishable from all the others (cf. Chapter VI). Figs. 45-48 and Tables 11 and 12 indicate that

some molecular features are again, in some respects, similar to those of the marine carbonate samples (see above).

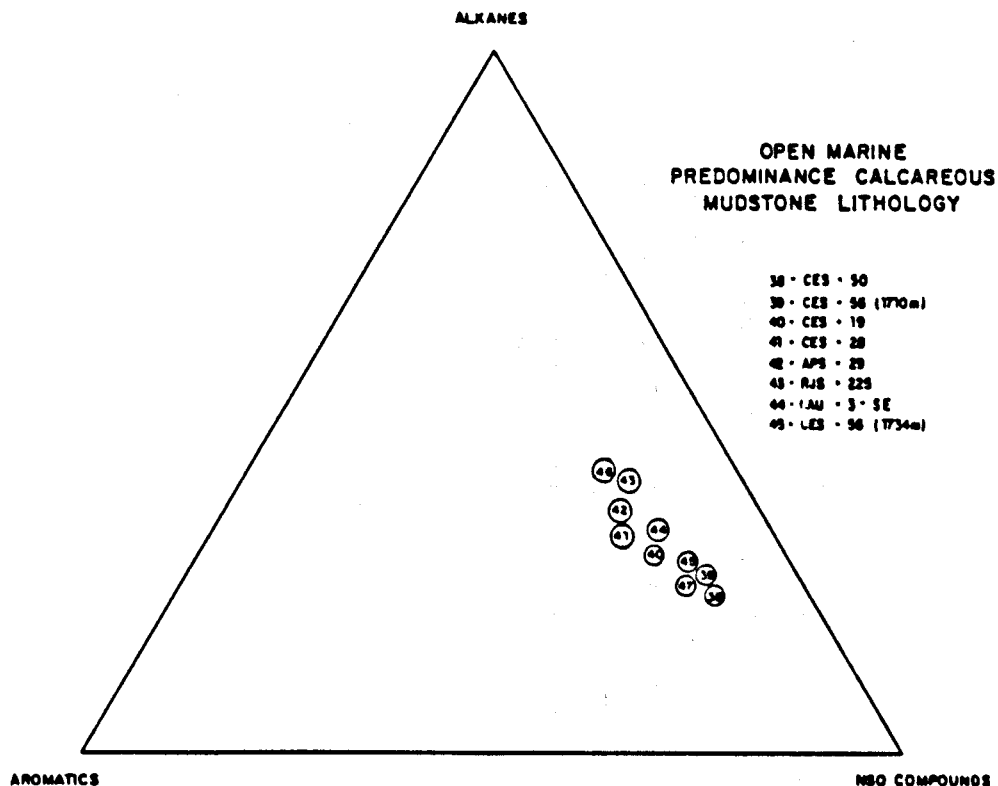


Figure 44- Relative abundance of alkanes, aromatics and NSO compounds in extracts from rock samples derived from open marine highly anoxic depositional environment with dominance of calcareous lithology .

Similarities include dominance of phytane over pristane (Pr/ Ph ratios ranging from 0,5 to 0.9), maximum in the n-alkanes around C₂₁ (Figs. 45-47), presence of low to medium concentrations of β-carotane (10-50 ppm) and the C₂₅ and C₃₀ isoprenoids (70-170 ppm; Table 12), presence of gammacerane in similar abundance (gammacerane index up to 25; peak 40, Figs 45, 46, 48 and Table 12), low hopane/ sterane ratios (0.3 to 0.9; Table 12), Ts/ Tm < 1 (Fig. 48), tendency of dominance of C₃₅ hopanes over their C₃₄ counterparts (peaks 45 and 44 respectively, in Figs. 46 and 48), low relative abundances of diasteranes (peaks 6 and 7 in Figs. 45-47 and Table 12), and high concentrations of nickel (up to 1746 ppm) and vanadyl (up

Figure 45- Lithological log of a well from Ceará basin, showing the stratigraphic position of an open marine highly anoxic (with dominance of calcareous lithology) organic-rich sample (CES-50) for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and bisnorhopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

1-CES-50

DEPTH (METERS)	ORGANIC CARBON WT. %	WELL DATA	
		AGE	LITHO
1500	4	TUR/SANT	[Patterned Lithology]
2000	2		
2500		APTIAN	[Patterned Lithology]

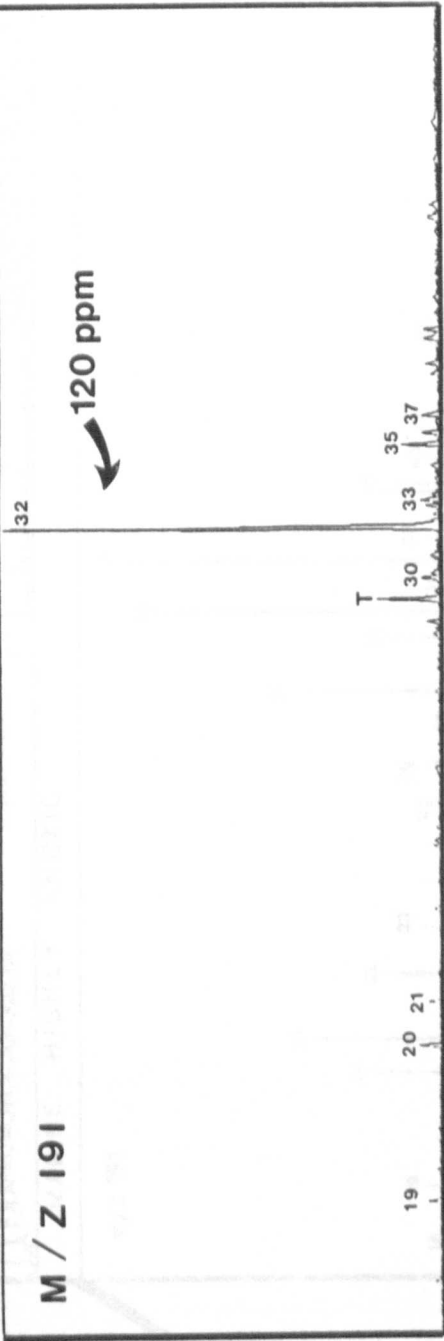
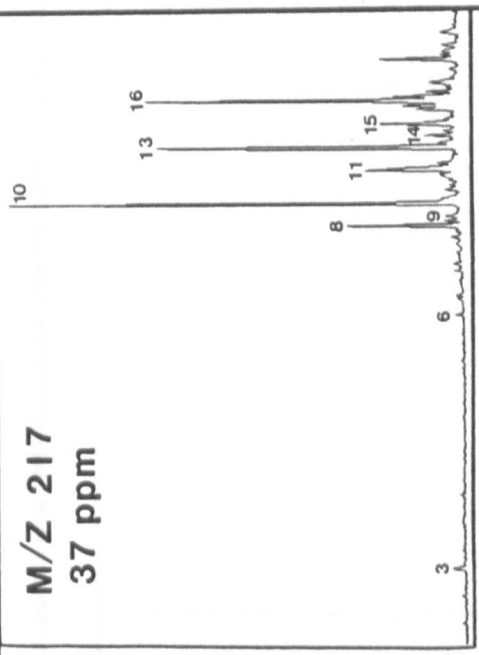
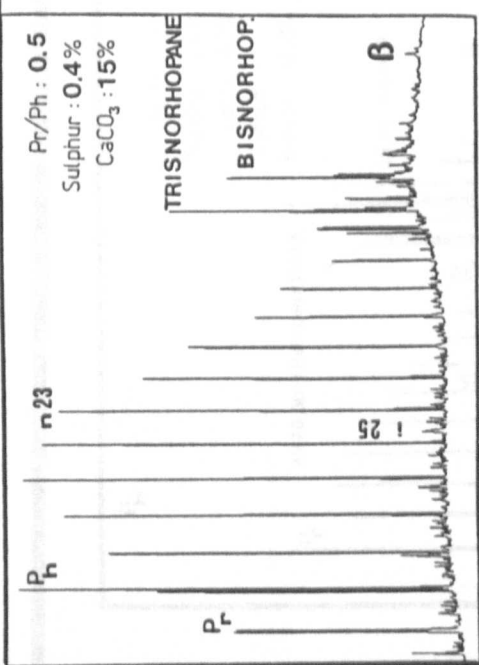
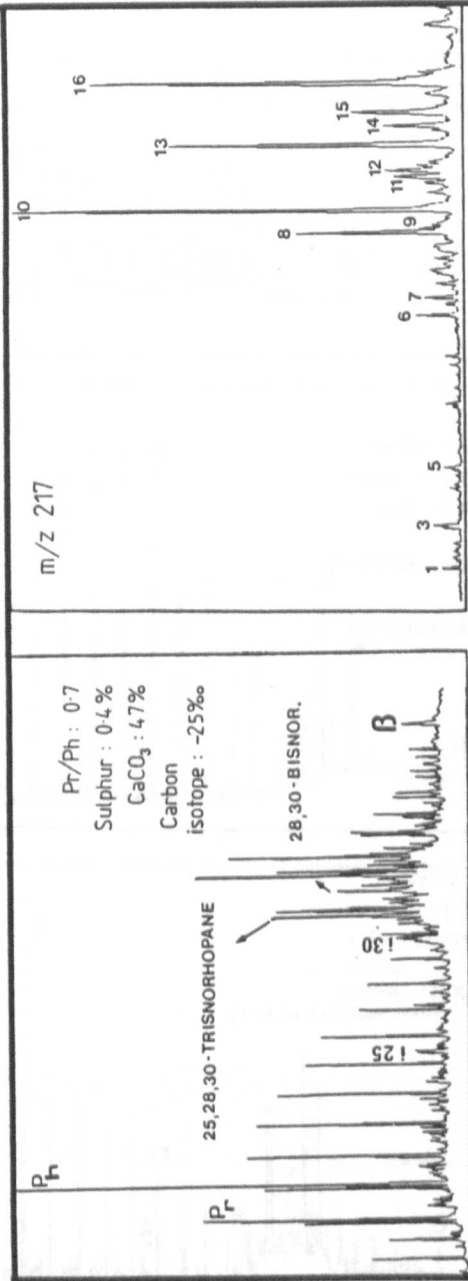
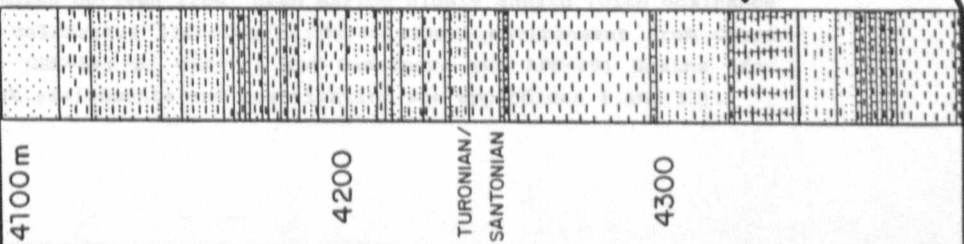


Figure 46. Mass spectrum of sample 1-CES-50 showing the isotopic composition of the sample with reference to the standard sample (100%) for comparison. The peak and elemental composition are shown in the table.

APS-29

CAMPANIAN



MARINE HIGHLY ANOXIC

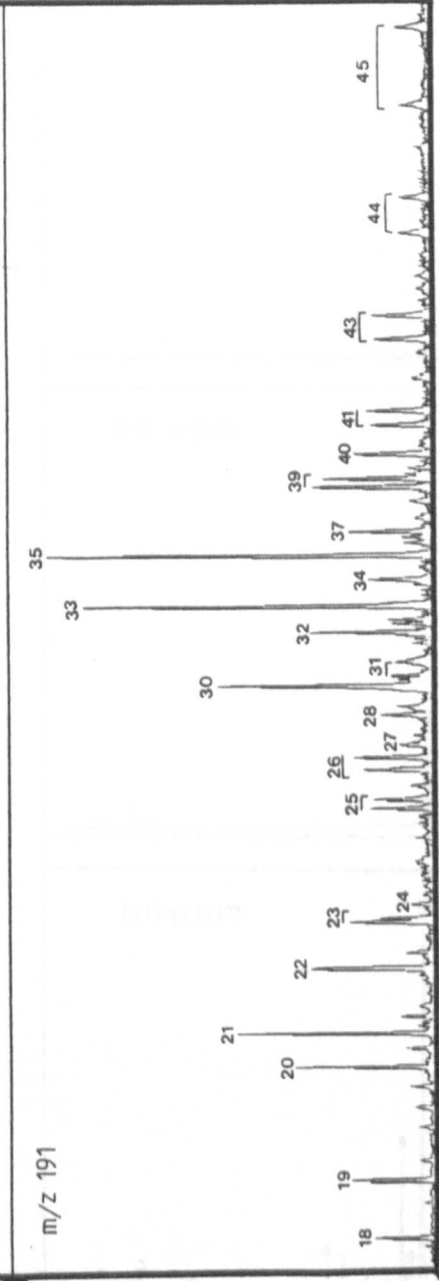


Figure 46- Lithological log of a well from Cassiporé basin, showing the stratigraphic position of an open marine highly anoxic (with dominance of calcareous lithology) organic-rich sample (APS-29) for which gas chromatogram of total alkanes, bulk and elemental parameters and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments see appendix I).

GAS CHROMATOGRAM

M / Z 217

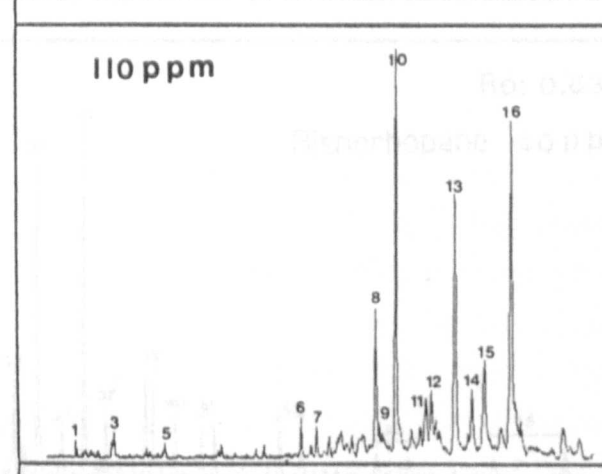
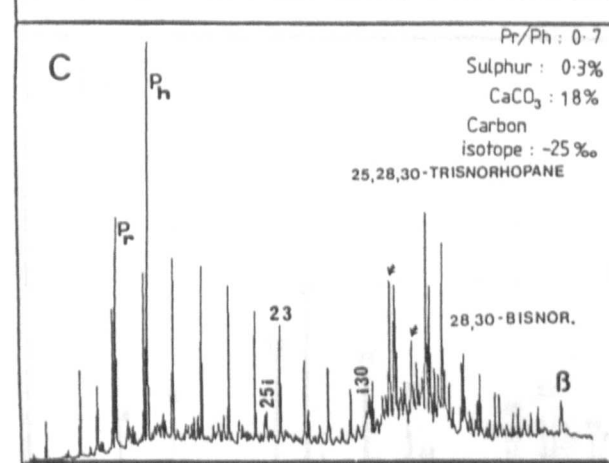
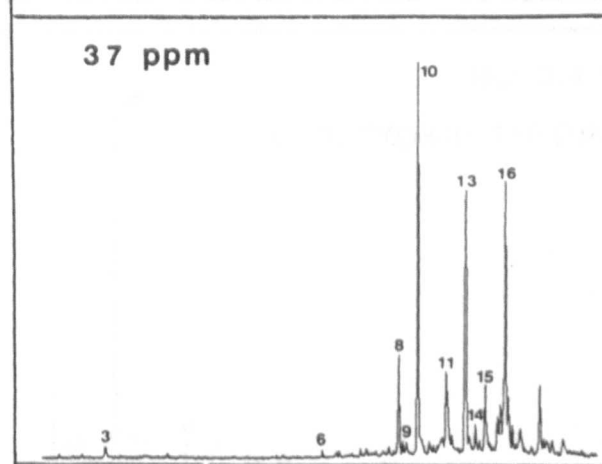
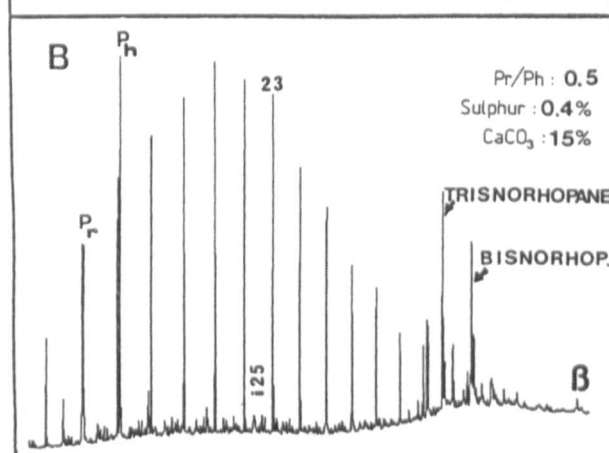
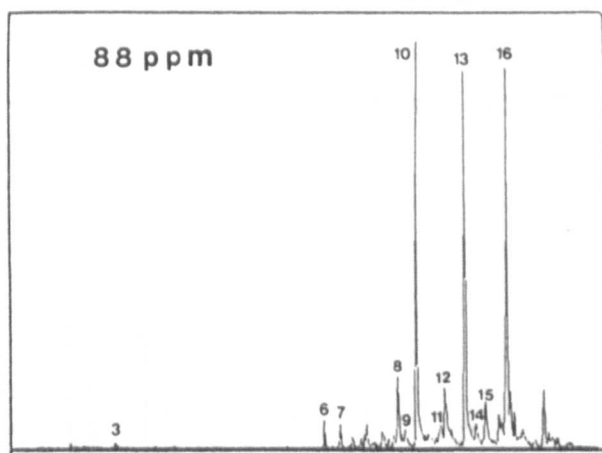
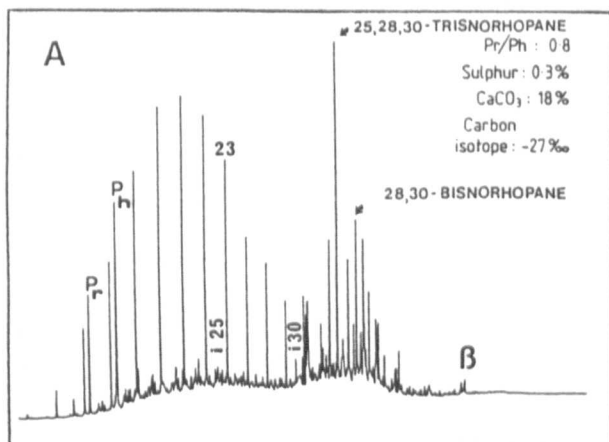


Figure 47- Gas chromatograms of total alkanes, bulk and elemental parameters, partial m/z 217 chromatograms and absolute concentration of steranes of three organic-rich rock samples derived from open marine highly anoxic (with dominance of calcareous lithology) depositional environment from Ceará (A: CES-19; B: CES-50) and Cassiporé (C: APS-29) basins (for peak assignments and quantitation see appendices I and II).

M/Z 191

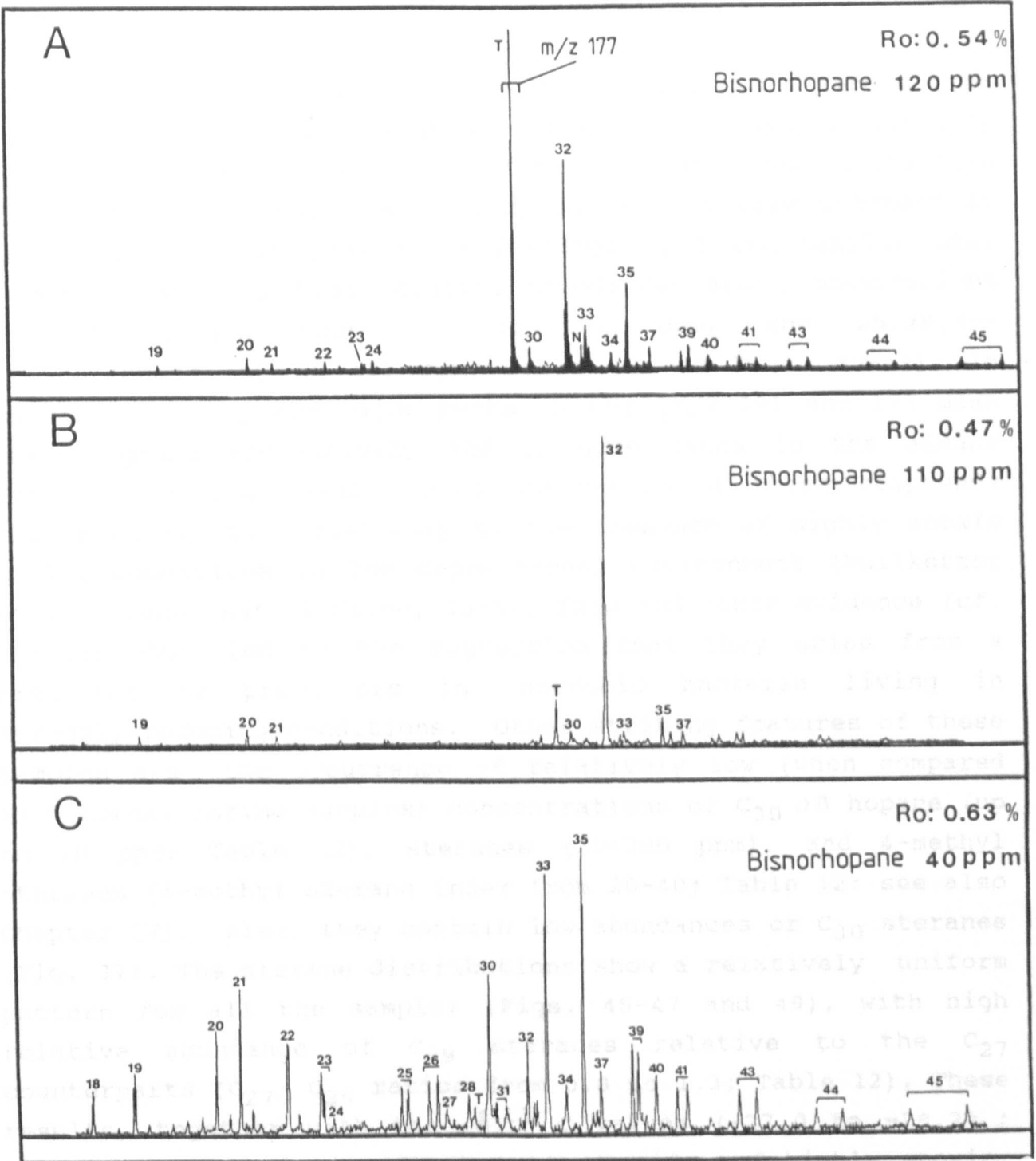


Figure 48- Partial m/z 191 chromatograms of total alkanes, vitrinite reflectance data and absolute concentration of bisnorhopane for the same samples as Fig. 47 (for peak assignments and quantitation see appendices I and II).

to 3790 ppm) porphyrins. The Ni/ Ni + V=O ratio ranges from 0.3-0.93. All these features suggest an enhanced salinity towards hypersaline conditions of the sea water during the time of deposition of this sedimentary succession (see Chapters IV and VI). The most remarkable features of these samples are, however, the very high relative abundances and concentrations of 28,30-bisnorhopane (up to 120 ppm) and 25,28,30-trisnorhopane (up to 130 ppm; Table 12 and Figs. 45-48). In most cases, they are major peaks in the m/z 191 and 177 mass chromatograms respectively and in some cases in the alkane fractions (Figs. 45-48). High abundances of these compounds have been related previously to the presence of highly anoxic marine conditions in the depositional environment (Rullkötter et al., 1984; Katz & Elrod, 1985). This and other evidence (cf. Chapter IV), led to the suggestion that they arise from a precursor or precursors in anaerobic bacteria living in strongly reducing conditions. Other striking features of these samples are the occurrence of relatively low (when compared with normal marine samples) concentrations of C₃₀ αβ hopane (up to 70 ppm; Table 12), steranes (30-200 ppm), and 4-methyl steranes (4-methyl sterane index from 20-40; Table 12; see also Chapter IV). Also, they contain low abundances of C₃₀ steranes (Fig. 37). The sterane distributions show a relatively uniform pattern for all the samples (Figs. 45-47 and 49), with high relative abundance of C₂₉ steranes relative to the C₂₇ counterparts (C₂₇/ C₂₉ ratios from 0.8 to 1.3; Table 12). These results, together with the δ¹³ C values (-27.0 to -28.2‰; Tables 11, 12 and Fig. 7) suggest the idea of highly anoxic, hypersaline, marine depositional environment where a huge anaerobic bacterial population was present. This could explain the lighter δ¹³ C values, as well as, the anomalous concentrations of 28,30-bisnorhopane and 25,28,30-trisnorhopane and paucity of steranes.

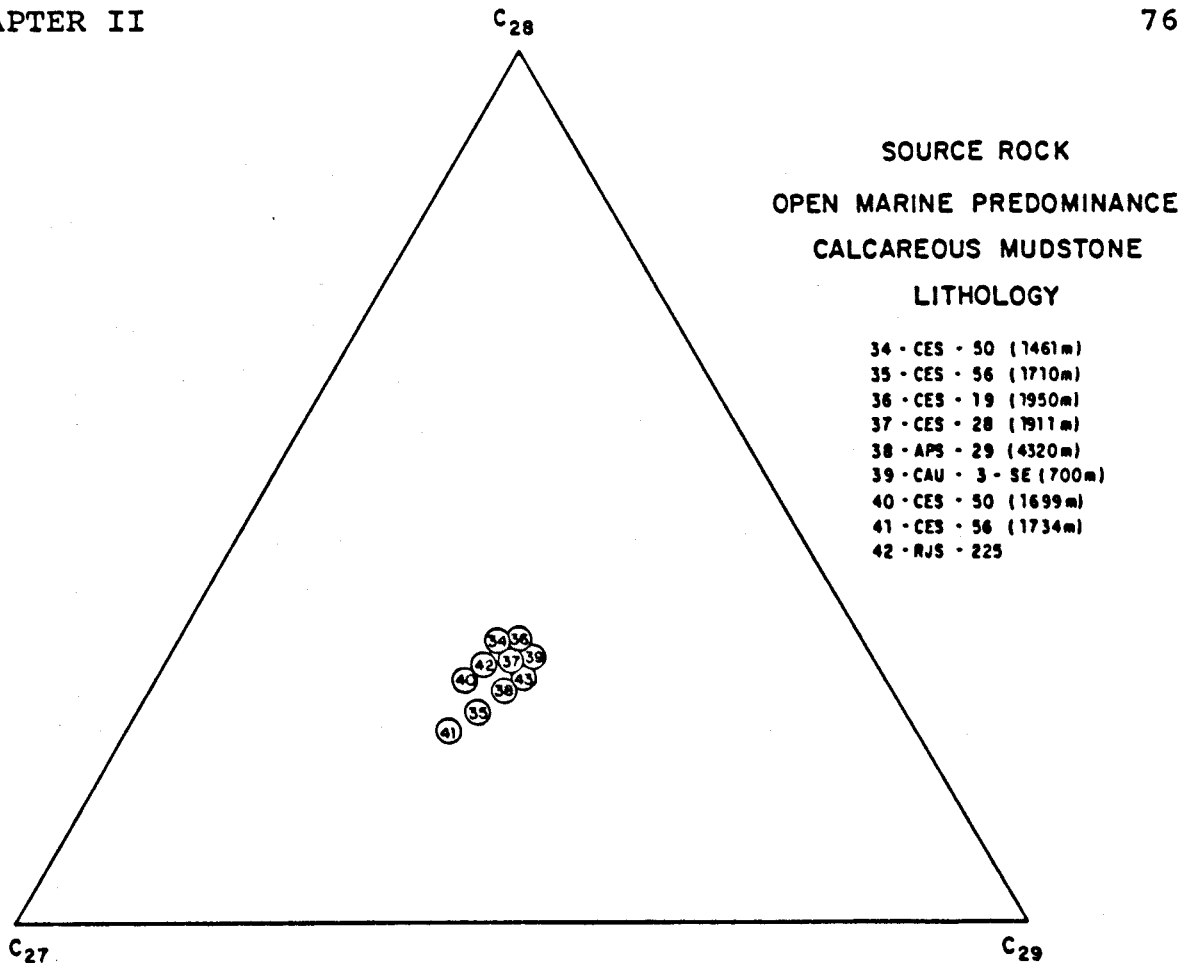


Figure 49-Carbon number (C27, C28, C29) distributions of $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20R steranes for samples from open marine highly anoxic environment with dominance of calcareous mudstone lithology

In summary, the most marked geochemical features that characterise this highly anoxic open marine depositional environment with dominance of calcareous mudstone lithology are;

- 1) high CaCO_3 ;
- 2) medium to high sulphur content;
- 3) significantly lighter $\delta^{13}\text{C}$ values ;
- 4) dominance of phytane over pristane;
- 5) maximum in the n-alkanes around C_{21}
- 6) presence of low to medium concentrations of β -carotane and the C_{25} and C_{30} isoprenoids

- 7) presence of gammacerane;
- 8) low concentrations of C₃₀ αβ hopane and steranes.
- 9) low hopane/ sterane ratios;
- 10) low abundance of 4-methyl steranes;
- 11) tendency for dominance of C₃₅ hopanes over their C₃₄ counterparts ;
- 12) very low relative abundances of diasteranes and C₃₀ steranes;
- 13) high concentrations of nickel and vanadyl porphyrins, with the ratio Ni/Ni + V=0 ranging from 0.3-0.93;
- 14) very high relative abundances and concentrations of 28,30-bisnorhopane and 25,28,30-trisnorhopane and,
- 15) high abundances of C₂₉ steranes relative to the C₂₇ counterparts.

Similar geochemical features have been identified in highly anoxic marine depositional environments with dominance of calcareous mudstone lithology in the Monterey Formation in California (Katz and Elrod, 1983; Curiale *et al* 1985), Cenomanian/Turonian sediments from Oued Bahloul, Tunisia and Danish Central Graben, North Sea (Farrimond, 1987) and Pleistocene and Jurassic shales from the Norwegian continental shelf, North Sea (Rullkötter *et al.*, 1982; Volkman *et al.*, 1983), and Oxfordian shales in the North Sea (Niels Telnaes personal communication).

2.2.7 Open Marine Anoxic With Dominance of Siliciclastic Lithology.

The sediments of this sequence, ranging in age from Aptian to Paleocene, appear also to be widespread in the Brazilian continental margin (Fig. 50) . They were detected in local areas of the Ceará (samples 54 and 58) , Potiguar (sample 57) Sergipe/Alagoas (samples 55 and 56) and Espirito Santo (samples 52 and 53) basins in the equatorial, central and eastern areas (Fig. 50 and Table 13).

Table 13: Geological and Geochemical Data For Sediments From Marine Anoxic Environment with Predominance of Siliciclastic Lithology.

WELLS	ESS-46	ESS-24	CES-42	ALS-30	ALS-27	RNS-15	CES-42
Sample Number	52	53	54	55	56	57	58
Sample Nature	Cuttings	Cuttings	Core	Cuttings	Cuttings	Core	Core
Depth (m)	3210	3264	2550	1900	2301	1428	2400
Age	Turonian/ Santonian	Campanian	Aptian	Paleocene	Turonian/ Santonian	Santonian	Aptian
Lithology	Dark Grey Shale	Dark Grey Shale	Black Shale	Dark Grey Shale	Calcareous Grey Shale	Dark Grey Shale	Black Shale
CaCO ₃ (%)	13	6	12	15	20	17	10
Sulphur (%)	0.35	0.6	0.7	0.3	0.35	0.35	0.38
TOC (%)	1.2	4.4	2.5	1.6	2.0	1.4	2.0
S ₂ (KgHC/Ton rock)	2.5	16.0	6.0	6.0	17.0	2.3	5.0
HI (mgHC/gTOC)	123	358	270	368	876	164	249
T-MAX (°C)	438	429	435	431	442	431	427
Ro (%)	0.70	0.60	0.55	0.50	0.55	0.50	0.52
SCI	6.5	5.5	5.5	-	-	4.5	-
EOM (ppm)	820	1501	2500	1377	1540	433	2720
Pr/Ph	1.3	1.3	1.4	1.1	-	1.0	1.3
Pr/nC ₁₇	0.9	0.9	1.9	1.3	1.9	1.0	1.8
Ph/nC ₁₈	0.7	0.8	1.6	1.3	1.8	1.5	1.4
nC ₁₇ /C ₃₁	2.2	3.3	1.6	1.4	1.3	1.9	1.5
δ ¹³ C whole extract	-26.0	-25.6	-26.5	-26.4	-26.0	-26.4	-26.5
Saturates (%)	34	44	28	29	42	27	20
Aromatics (%)	20	14	18	21	15	12	14
NSO (%)	46	42	54	50	43	61	66
Amorphous (%)	80	60	80	40	80	90	60
Herbaceous (%)	5	10	5	55	5	5	20
Woody+Coaly (%)	15	30	15	5	15	5	20



Figure 50- Location map showing the basins from which samples from open marine anoxic environment with dominance of siliciclastic lithology were investigated

Fig. 51 shows a geochemical well log (ALS-30, Sergipe/Alagoas basin), with the Van Krevelen type diagram, as an example of the organic-rich sedimentary succession derived from this environment. Overall, the sediments of this group comprise mainly dark grey shales containing moderate to high organic carbon (TOC up to 4.4%) and a high hydrocarbon source potential (up to 17 kg Hc/ ton of rock) largely arising from type II kerogen (hydrogen index ranging from 123 to 876 mg Hc/ g organic carbon). The organic petrography indicate a mixture of amorphous, herbaceous and woody plus coaly organic matter (Tables 13 and 14). The immature character of these sediments in the Brazilian marginal basins (see maturity data in Table 13 and Fig. 51), indicate that they are not potential source rocks.

see Figs. 41 to 43 and Appendices.

TABLE 14- Elemental, Bulk and Biological Marker Parameters of Rocks and Extracts of Samples From Sediments Derived from Marine Anoxic Environment with Predominance of Siliciclastic Lithology in the Brazilian Marginal Basins.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/TYPE ORGANIC MATTER
CARBON: 2.8-4.4%	T.O.C.: 1.2-4.4%	n-ALKANES MAXIMA: C ₁₇ -C ₁₉	C ₂₇ STERANE: ⁶ 20-400ppm	C _{30αβ} HOPANE: ¹¹ 50-800ppm	NICKEL: 0-800ppm
HYDROGEN: 0.55-0.63%	S ₂ : ¹ 2.5-17	SATURATES: 20-44%	C ₂₇ /C ₂₈ : ⁷ 1.5-2.5	GAMMACERANE ¹² INDEX: 0-5.0	VANADYL: 0-130ppm
NITROGEN: 0.10-0.15%	HI: ² 123-876mg/g	Pr/Ph: 1.0-1.5	DIASTERANE ⁸ INDEX: 30-80	BISNORHOPANE ¹³ INDEX: 0-5.0	AMORPHOUS: 60-80%
SULPHUR: 0.3-0.7%	R ₀ : 0.50-0.70%	I-C ₂₅ +I-C ₃₀ : ⁴ 40-180ppm	4-Me STERANE ⁹ INDEX: 10-20	HOPANE/STERANE ¹⁴ 1.5-3.0	HERBACEOUS: 5-10%
CaCO ₃ : 6-20%	δ ¹³ C: ³ -25.6 TO -26.5	β-CAROTANE: ⁵ undetected	C ₂₁ + C ₂₂ ¹⁰ STERANES: 25-35ppm	C ₃₄ /C ₃₅ HOPANES: 1.1-1.3	WOODY/COALY: 10-30%

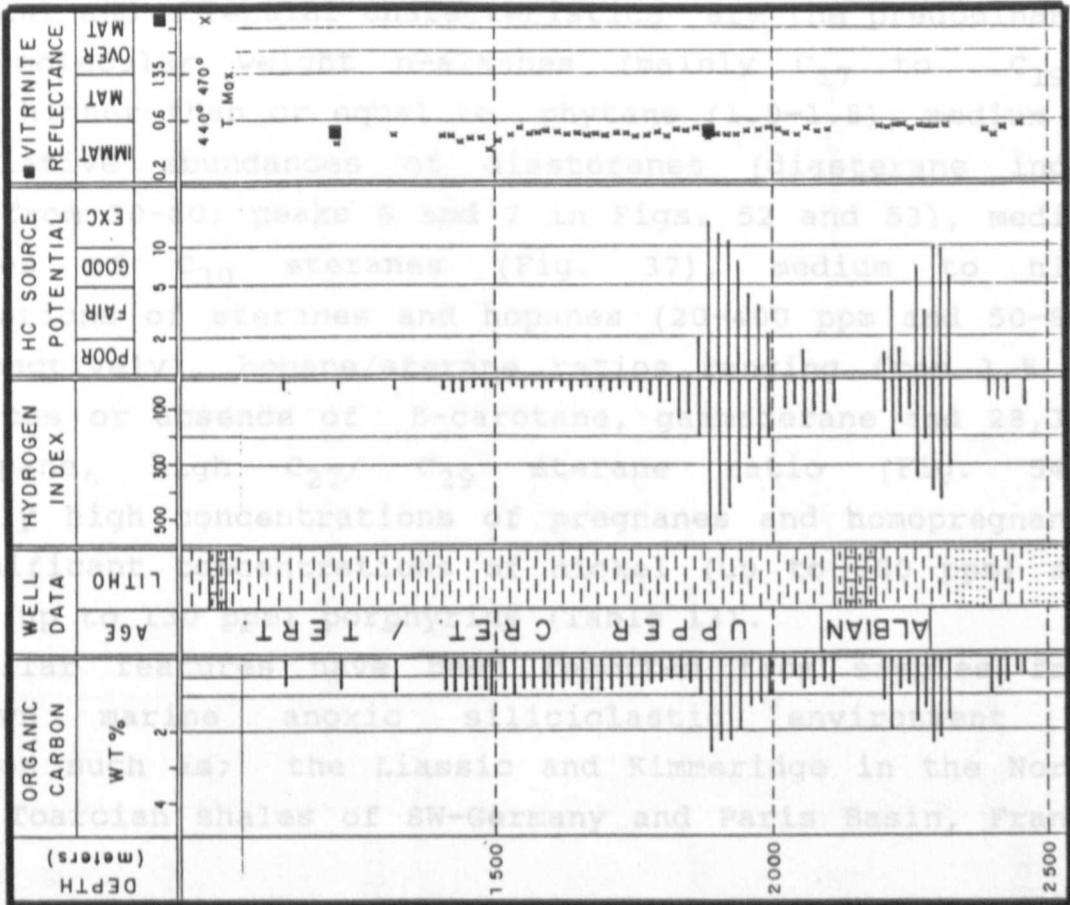
MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (‰)
4. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (I-C₂₅) and squalane (I-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (8) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13B,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21B(H)-hopane (35) X100.
13. Peak area of C₃₅ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21B(H)-hopane (35) X100.
14. Peak area of C₃₀ 17α,21B(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
15. Peak areas of C₃₄ 22R and 22S 17α,21B(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 51 to 52 and Appendices.

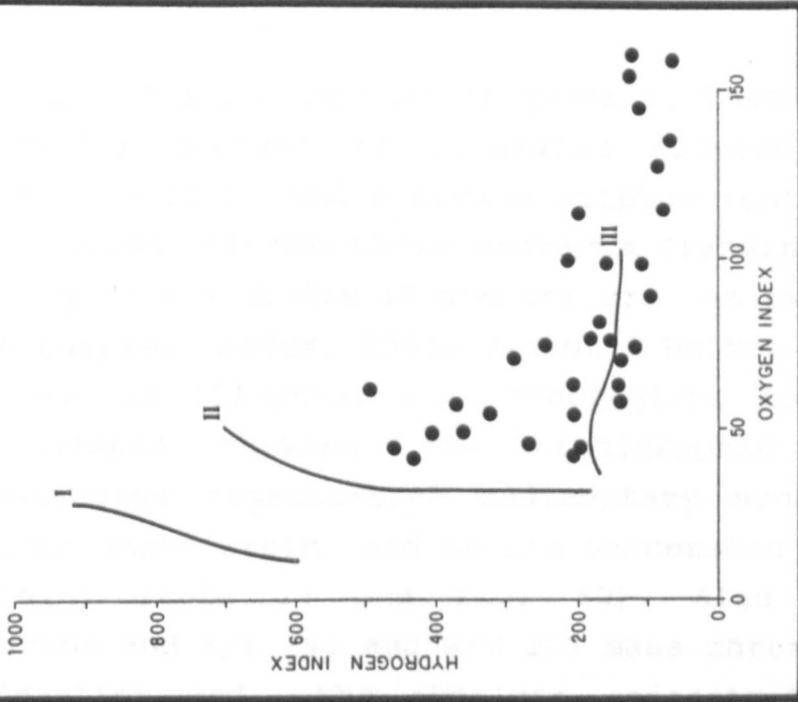
Figure 51- Geochemical log of a well from Sergipe/ Alagoas basin, showing the stratigraphic position of the upper Cretaceous open marine anoxic (with dominance of siliciclastic lithology) organic-rich sedimentary succession and the hydrogen index (S_2 / TOC) vs oxygen index (S_3 / TOC), presented on van Krevelen type diagram, for samples from the whole well.

ALS 30



VAN KREVELEN TYPE DIAGRAM

WELL: ALS-30



Tables 13 and 14 indicate that in general, these sediments have low to medium content of saturates (20-44%), low CaCO_3 (ranging from 6-20%), and a medium sulphur content (0.3-0.7%). The $\delta^{13}\text{C}$ values for the whole extracts (ranging from -25.6 to -26.5‰; Fig. 7 and Tables 13 and 14) are, as expected, typical of marine samples (Sofer, 1984; Tissot & Welte, 1984).

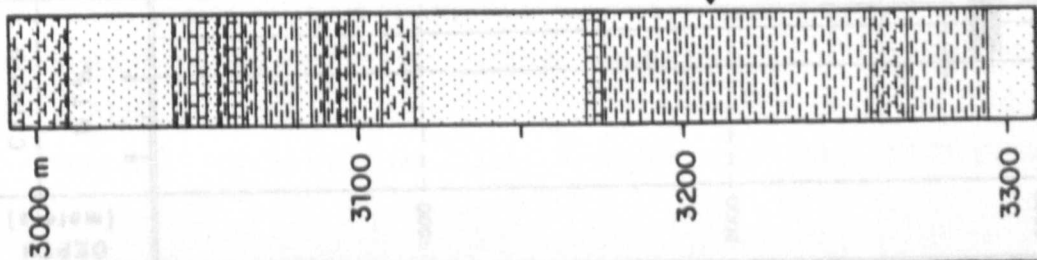
Figs. 52 and 53 illustrates a lithological log chosen as a specific example, showing the stratigraphic position of an upper Cretaceous organic-rich sedimentary succession (sample 52, Espirito Santo basin) and Aptian succession (sample 58 from Ceará basin; Table 13 and Fig. 50). Also shown are gas chromatograms and m/z 191 and m/z 217 mass chromatograms of the alkane fraction and the absolute concentration of C_{30} $\alpha\beta$ hopane and C_{27} steranes (Table 12). Taken overall, the geochemical and molecular features of these samples can essentially only be considered as characteristic in the sense that most of the major features ascribed as diagnostic of the other depositional environments are not present. The main geochemical and molecular characteristics are the predominance of low molecular weight n-alkanes (mainly C_{17} to C_{19}), pristane higher than or equal to phytane (1.0-1.5), medium to high relative abundances of diasteranes (diasterane index ranging from 30-80; peaks 6 and 7 in Figs. 52 and 53), medium abundances of C_{30} steranes (Fig. 37), medium to high concentrations of steranes and hopanes (20-400 ppm and 50-800 ppm respectively), hopane/sterane ratios ranging from 1.5 to 3.0, traces or absence of β -carotane, gammacerane and 28,30-bisnorhopane, high $\text{C}_{27}/\text{C}_{29}$ sterane ratio (Fig. 54), relatively high concentrations of pregnanes and homopregnanes and significant concentrations of nickel (up to 800 ppm) and vanadyl (up to 130 ppm) porphyrins (Table 13).

Similar features have been reported from samples from well-known marine anoxic siliciclastic environment of deposition such as; the Liassic and Kimmeridge in the North Sea and Toarcian shales of SW-Germany and Paris Basin, France

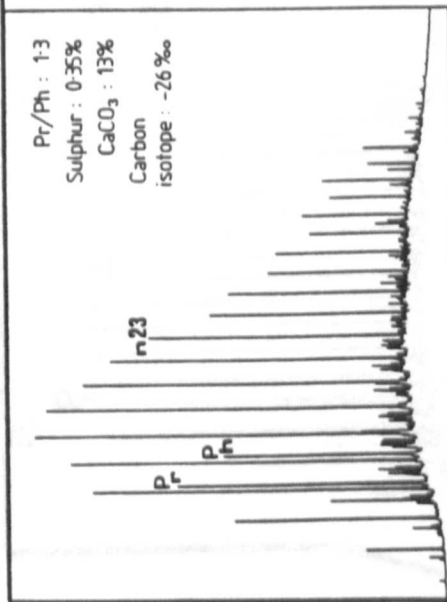
Figure 52- Lithological log of a well from Espirito Santo basin, showing the stratigraphic position of the upper Cretaceous open marine anoxic (with dominance of siliciclastic lithology) organic-rich sample (ESS-46) for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

ESS-46

MAAS/CAMPANIAN



Pr/Ph : 1:3
Sulphur : 0.35%
CaCO₃ : 13%
Carbon
isotope : -26 ‰



M/Z 191
57 ppm

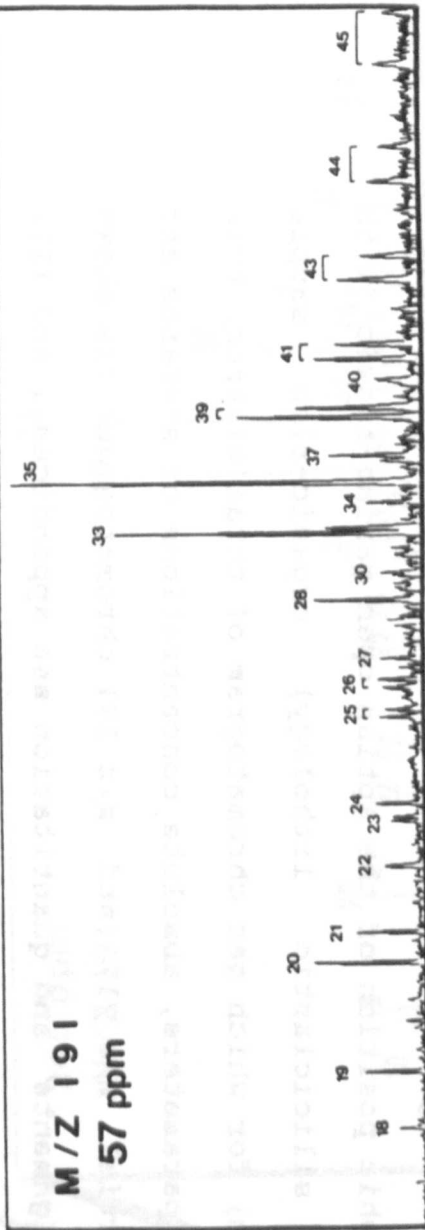
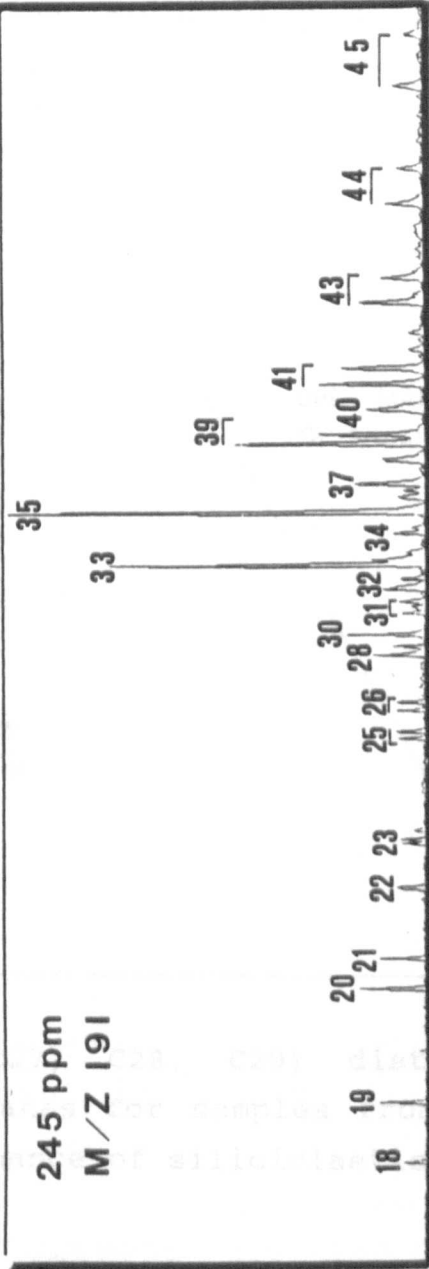
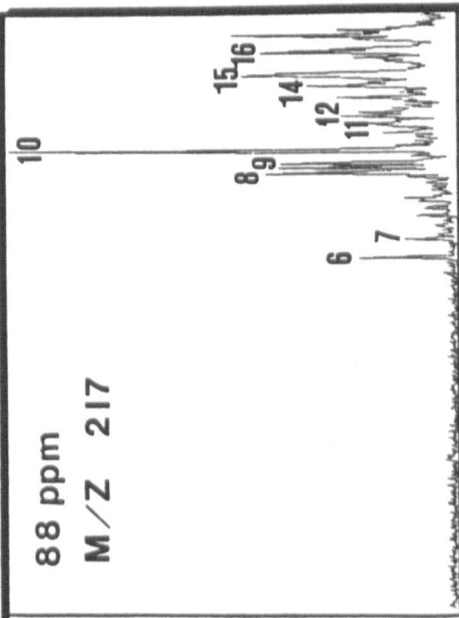
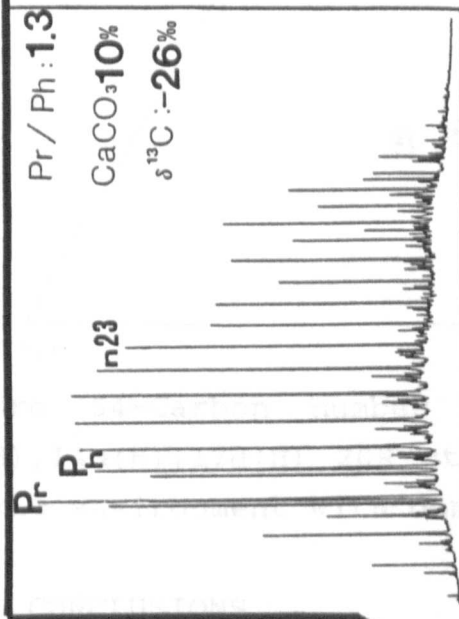


Figure 53- Lithological log of a well from Ceara basin, showing the stratigraphic position of the Aptian open marine anoxic (with dominance of siliciclastic lithology) organic-rich sample (CES-42, 2400m) for which gas chromatogram of total alkanes, bulk and elemental parameters, absolute concentrations of steranes and hopane and partial m/z 217 and m/z 191 chromatograms are shown (for peak assignments and quantitation see appendices I and II).

CES 42

DEPTH (Meters)	ORGANIC CARBON WT%	WELL DATA	
		AGE	LITHO
1500	~1.5	OLIG.	...
2000	~1.5	ECC. SUP.	...
2500	~1.5	SAN.	...
		ALB/MAAS	...
		CON.	...
		AN	...
		AP	...
		TI	...
		AN	...



(Mackenzie et al., 1980 and 1984; Moldowan et al., 1986).

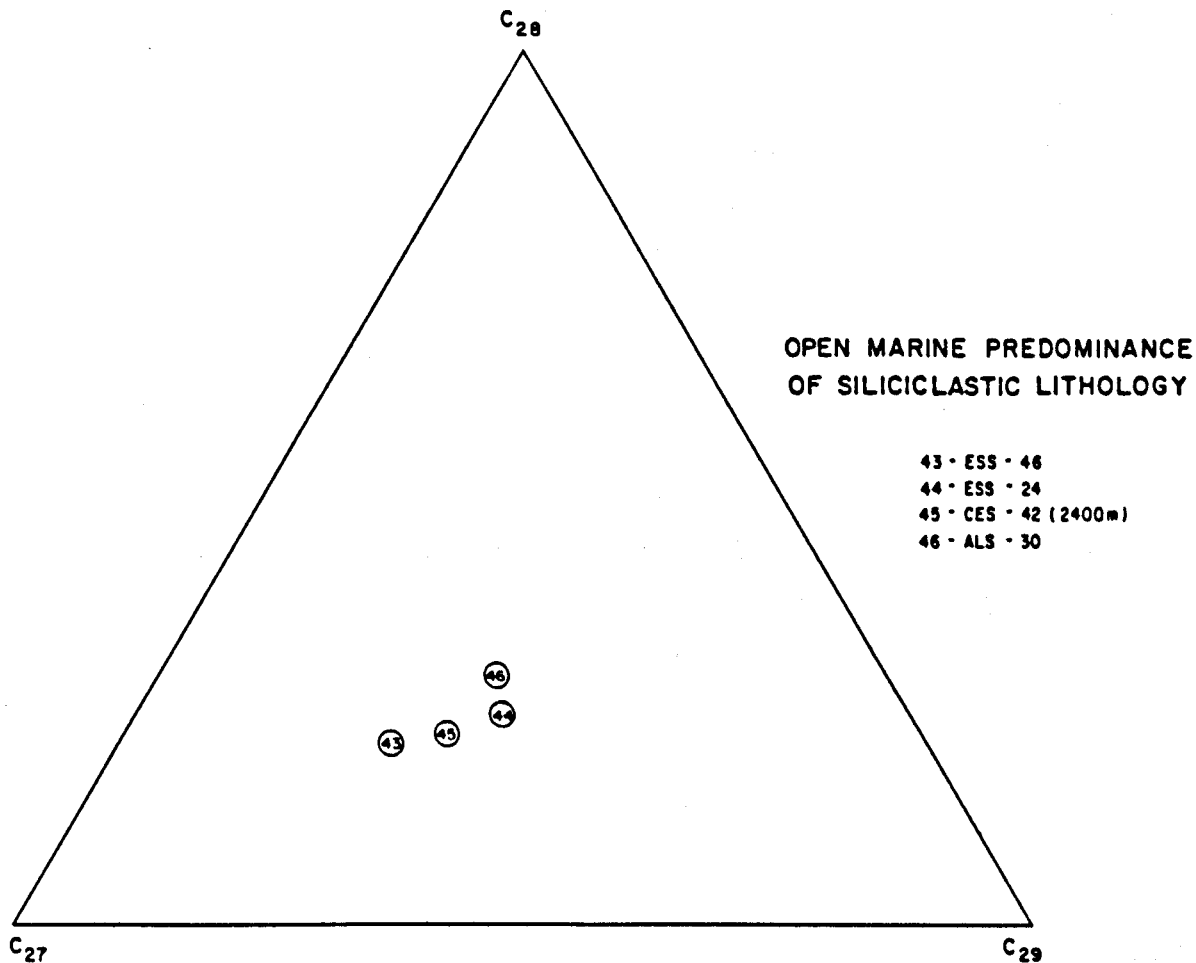


Figure 54-Carbon number (C27, C28, C29) distributions of $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20R steranes for samples from open marine anoxic environment with dominance of siliciclastic lithology

2.3 CONCLUSIONS

The present investigation shows the value of a multidisciplinary approach (geological, geochemical and molecular marker) in the assessment and characterisation of depositional environments organic-rich sediments. It supports and extends previous investigations which have used molecular parameters and provides reference information which can be tested against samples from other basins in Brazil and elsewhere in the world.

The results summarised in Tables 1 to 14 reveal

significant differences among the organic-rich sediments from Brazilian marginal basins, which can be related to seven depositional regimes, namely I-lacustrine freshwater; II-lacustrine saline water; III-marine evaporitic; IV-marine carbonate; V-marine deltaic with carbonate influence; VI-open marine highly anoxic, with dominance of calcareous mudstone lithology and VII-open marine anoxic, with dominance of siliciclastic lithology (Fig. 55). It is clear that no single geochemical or biological marker property is sufficient to characterise and assess in detail a specific environment of deposition. Nevertheless, consideration of various properties can provide diagnostic criteria, especially when a deuteriated internal standard is used in a quantitative biological marker approach (ppm of rock extract). For example, low pristane/phytane ratios, linked with even/odd n-alkane dominance, and high concentrations and relative abundances of 2,6,10,14,18-pentamethyleicosane, squalane, β -carotane and gammacerane appear to be related indirectly to the salinity of the original water column. Hence, the highest concentrations and abundances of these biological markers occur in the hypersaline samples. Very high concentrations of bacterially derived hopanoids (up to 2000 ppm of C_{30} $\alpha\beta$ hopane) and steroids (up to 4000 ppm of C_{27} steranes) also appear to be linked to high salinity. In some cases the single presence of high relative abundances of specific compounds can be diagnostic of particular environments (e.g. $18\alpha(H)$ -oleanane in the deltaic samples and 28,30-bisnorhopane and 25,28,30-trisnorhopane in the marine highly anoxic samples. On the other hand, the absence of biological marker compounds diagnostic of specific source inputs, are further shown to be useful. For example, C_{30} steranes and dinosteranes, held to be an indicator of a marine origin (Moldowan et al., 1985; Summons et al., 1987), were not found in the Brazilian non-marine samples (groups I and II). Porphyrins also can play an important role in the assessment of environment of deposition (e.g. predominance of vanadyl species in marine carbonate

ORGANIC-RICH

SEDIMENTS

LEGEND:

- LACUSTRINE FRESHWATER
- ◐ LACUSTRINE SALINE WATER
- ▲ MARINE EVAPORITIC
- MARINE CARBONATE
- ★ MARINE DELTAIC
- ◇ OPEN MARINE CALCAREOUS MUDSTONE
- ☆ OPEN MARINE SILICICLASTIC

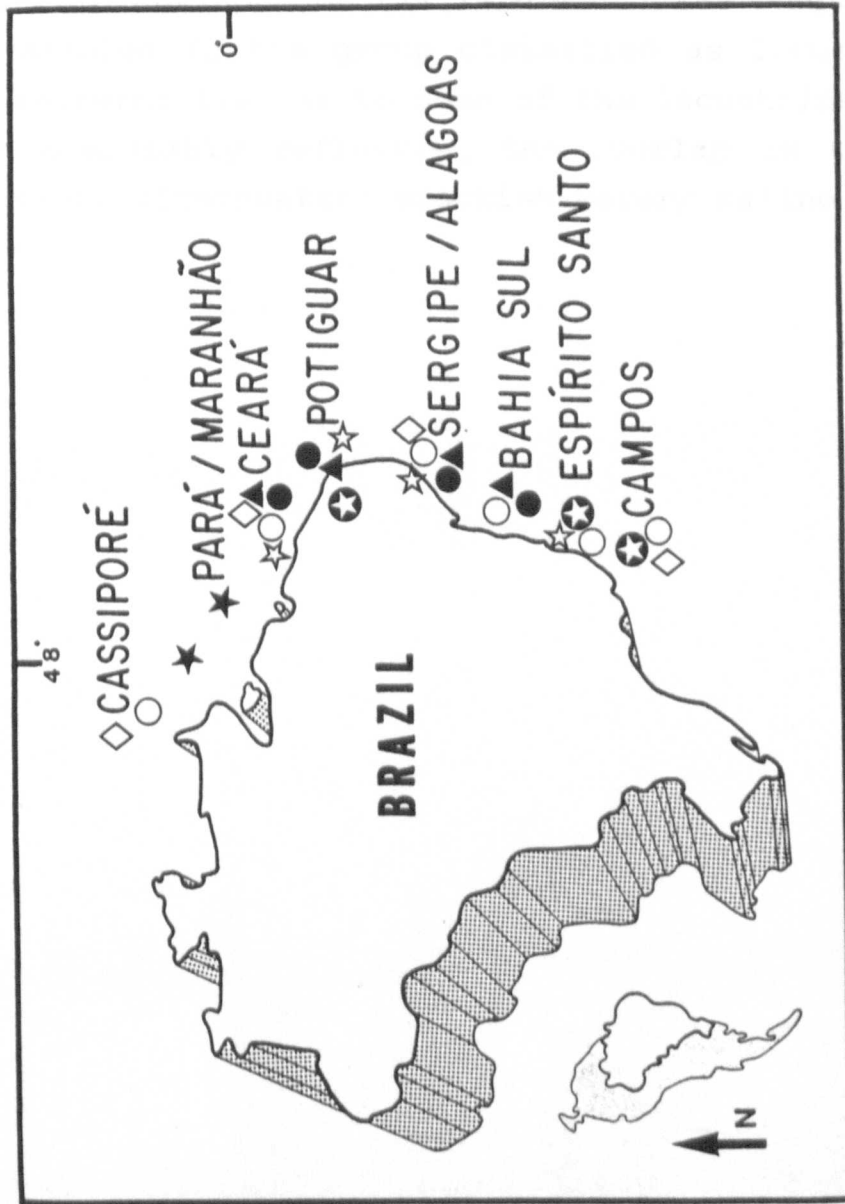
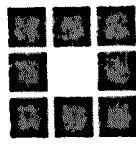


Figure 55- Location map of the Brazilian marginal basins showing the distribution of organic-rich sediments in accordance with their proposed depositional environment.

environment). Nevertheless, the results also show the difficulties in trying to characterise or distinguish depositional environments from the geochemical features. Overall, the impression is that although the "end members" of specific depositional environments have a diagnostic group of characteristics there must inevitable be overlap. This can be seen, for example, in comparing some of the samples in the lacustrine saline group with some of the samples in the marine evaporitic group, where distinguishing features in the biological markers blurred. This is, perhaps, not surprising since a hypersaline lake environment might be expected to have similar chemical conditions to those in a transitional marine evaporitic environment (as in Brazil; see Chapter I). Likewise, some samples in the group classified as lacustrine freshwater show features similar to some of the lacustrine saline samples, again presumably reflecting the overlap in the environmental conditions (freshwater/ brackish water/ saline water.



CHAPTER III

CHAPTER III

GEOCHEMICAL AND BIOLOGICAL MARKER ASSESSMENT OF DEPOSITIONAL ENVIRONMENTS USING BRAZILIAN OILS

This chapter describe a combined geochemical, molecular and statistical characterisation of a wide selection of oils from the major Brazilian marginal basins. The results reveal significant differences in the oils which enable them to be divided into five groups. The distinction appears to reflect differences in the depositional environment of the source rocks. Each group is correlated with source rocks laid down in a different depositional regime, namely lacustrine freshwater, lacustrine saline water, marine evaporitic, marine carbonate and marine deltaic with carbonate influence (see Chapter II).

3.1 INTRODUCTION

The assessment and differentiation of the depositional palaeoenvironments of petroleum source rocks using molecular parameters from oil samples is increasing in importance and application. Both geochemical evidence and biological marker distributions enable the distinction of marine and non-marine oils (e.g. Mackenzie et al., 1984; Moldowan et al., 1985; McKirdy et al., 1986; Peters et al., 1986). In addition, recent evidence shows that such features can provide diagnostic criteria for the distinction of oils derived from source rocks deposited in different environments, such as lacustrine freshwater and hypersaline in China (e.g. Powell, 1986; Fu Jiamo et al., 1986), marine carbonate in Venezuela, Australia and Florida (Talukdar et al., 1986; McKirdy et al., 1984; Palacas et al., 1984) and lacustrine freshwater in Australia (McKirdy et al., 1986; Philp and Gilbert, 1986). It is evident that the components of a particular rock extract or oil are a reflection of the precursor compounds in the organisms which contributed organic matter at the time of sediment deposition, and thereby can provide information about the prevailing environmental conditions. Biological marker analysis of oils can therefore, be used in helping to ascertain which type of depositional environment source rocks had and in some cases the type of organisms which contributed to them.

In this study a combination of geochemical and statistical data for a number of oil samples have been used in an attempt to characterise the environments of deposition of the source rocks that gave rise to them. A succession of putative source rocks deposited in different environments exists within the Brazilian marginal basins (Chapter II; Mello et al., 1984, 1988a). Specifically, the elemental and bulk properties, and biological marker distributions of about fifty oil samples recovered from reservoirs ranging from lower Neocomian to Oligocene within the major Brazilian basins were investigated.

In order to try to minimise differences due to the effects of maturation and the effects of biodegradation, water washing, gravity segregation and loss of volatiles, only oils which were comparatively unaffected by such processes and with medium to high API values were selected (as far as possible). In summary 31 of the oils (Table 2 in "Introduction"), chosen to be representative of the total, were selected for a more detailed GC-MS and metastable ion GC-MS study to measure the concentrations of specific biological marker compounds by addition of a deuteriated sterane standard.

3.2 RESULTS

The results reveal significant differences in the characteristics of the oils, best described in terms of a classification into five groups (I to V). The n-alkane distributions and pristane/phytane ratios were determined from GC analysis of the saturate fractions. The molecular properties, based on the distributions and abundances of acyclic isoprenoids (C_{25} and C_{30}), β -carotane, sterane and terpane families were determined by GC-MS analysis. In the following sections, each group of oils is considered in turn.

3.2.1 Group I oils

These oils are confined to the Ceará (1), Potiguar (5, 7 and 8), Sergipe/Alagoas (4 and 6) and Bahia Sul (2 and 3) basins (Table 1 and Fig. 1). They are pooled mainly in sandstone reservoirs belonging to lacustrine freshwater facies with ages ranging from lower Neocomian to Aptian (Table 1). Considered as a whole, the bulk and elemental data reveal a set of common characteristics, such as low sulphur concentrations ($< 0.1\%$, except BAS-48), high wax contents (saturates $> 60\%$; Fig. 2), n-alkane distributions with abundant high molecular weight components and odd predominance, pristane dominant over

Table 1 : Geological and Geochemical Data For Oils Used in the Assessment of Lacustrine Freshwater Depositional Environment

Wells	CES-8	BAS-48	BAS-64	PIR-4	RNS-53	RB-12	AG-16D	SE-1
Sample Number	1	2	3	4	5	6	7	8
Depth (m) (reservoir)	1696	2780	2340	1841	2289	2306	2172	1340
Age (reservoir)	Aptian	Neocomian	Neocomian	Neocomian	Aptian	Neocomian	Aptian	Neocomian
Lithology (reservoir)	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone
$^{\circ}$ API	39	30	30	36	30	38	28	32
Sulphur (%)	0.01	0.30	0.02	0.08	0.10	0.10	0.10	0.08
Pr/Ph	1.8	2.2	1.9	2.0	1.3	2.2	2.1	2.0
Pr/nC ₁₇	0.3	0.6	0.3	0.3	0.8	0.5	0.3	0.7
Ph/nC ₁₈	0.13	0.23	0.18	0.18	0.40	0.30	0.17	0.30
nC ₁₇ /C ₃₁	2.3	2.2	2.0	3.1	3.2	2.9	2.4	3.3
$\delta^{13}\text{C}$ whole oil ‰	-28.6	-28.1	-29.3	-28.7	-29.0	-	-28.9	-31.2
$\delta^{13}\text{C}$ saturates ‰	-29.6	-28.5	-30.4	-29.7	-28.9	-	-29.7	-31.9
$\delta^{13}\text{C}$ aromatics ‰	-27.0	-27.4	-27.7	-27.1	-27.9	-	-27.3	-29.4
V /Ni ratio	0.05	-	0.02	0.02	-	0.02	-	-
Saturates (%)	73	71	69	66	69	80	60	63
Aromatics (%)	16	16	19	24	14	13	22	21
NSO (%)	11	13	12	10	17	7	18	16

phytane (values 1.3), low n-C17/n-C31 (< 3.3) and V/Ni ratios (< 0.05; Tables 1 and 2).



Figure 1- Location map showing the areas which group I oils were investigated.

All the oils have $\delta^{13}C$ values equals to/ or lighter than - 28.1 for the whole oil, -28.5 for the saturate fraction and - 27.0% for the aromatic fraction (Tables 1 and 2 and Fig. 3).

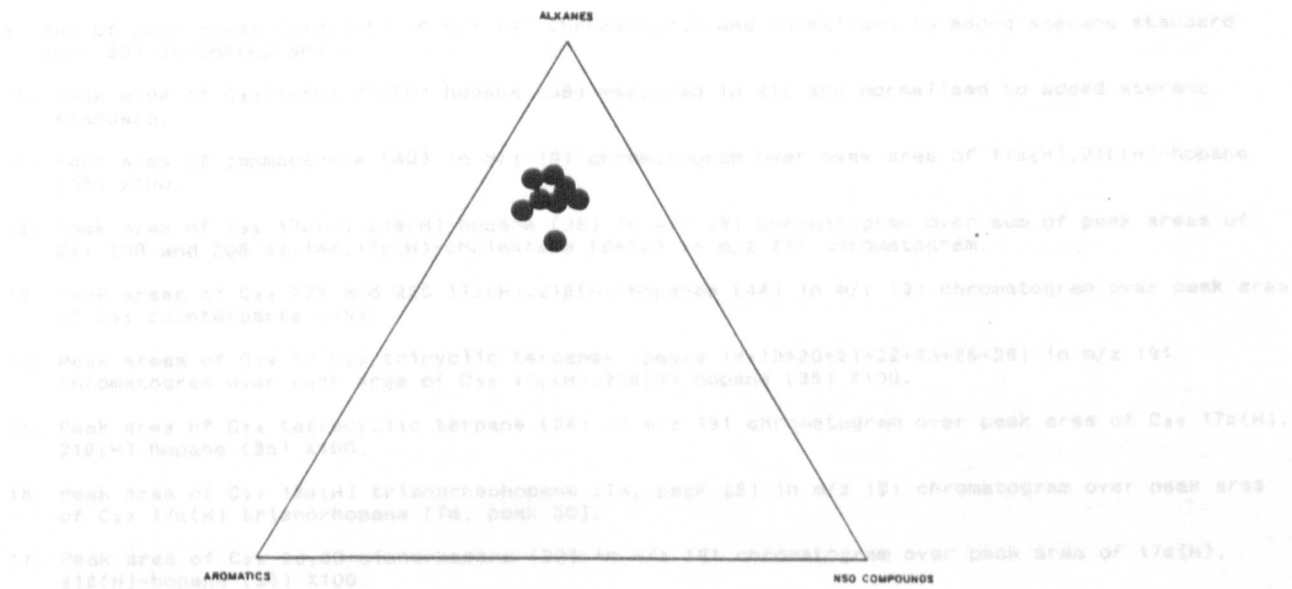


Figure 2- Relative abundance of alkanes, aromatics and NSO compounds in group I oils.

* See Fig. 1, 2 and Appendices.

TABLE 2 - Bulk and Biological Marker Parameters for Oils from Lacustrine Freshwater Environment.

BULK	ALKANES	STERANES	TRITERPANES	TRITERPANES
°API: 28-39	n-ALKANES MAXIMA: C ₂₁ -C ₂₃	C ₂₇ STERANE: ⁵ 0-64ppm	C _{30αβ} HOPANE: ¹⁰ 80-420ppm	TRICYCLIC ¹⁴ INDEX: 35-126
SULPHUR: 0.01-0.10	SATURATES: 60-80%	C ₂₇ /C ₂₉ : ⁶ 1.6-2.8	GAMMACERANE ¹¹ INDEX: 18-37	TETRACYCLIC ¹⁵ INDEX: 5.0-9.0
V/N1: 0.02-0.05	Pr/Ph: 1.3-2.2	DIASTERANE ⁷ INDEX: 20-40	18α(H)OLEANANE undetected	Ts/Tm: ¹⁶ 0.72-2.20
δ ¹³ C ¹ -28.1 to -31.2	I-C ₂₉ +I-C ₃₀ : ³ Tr-370ppm	4-Me STERANE ⁸ INDEX: 18-48	HOPANE/STERANE ¹² INDEX: 6.1-15	BISNORHOPANE ¹⁷ INDEX: undetected
δ ¹³ C ² -27.9 to -31.9	β-CAROTANE: ⁴ undetected	C ₂₁ + C ₂₂ STERANES: traces	C ₃₄ /C ₃₅ HOPANES: 1.2-1.7	C ₂₉ /C ₃₀ HOPANES: 50-82

MEASUREMENT PROCEDURES

1. PDB (%) Whole oil fraction.
2. PDB (%) Saturates fraction.
3. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₃) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
4. Peak area (β) in RIC trace and normalised to added sterane standard.
5. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
6. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
7. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
8. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
10. Peak area of C₃₀17α(H),21β(H) hopane (35) measured in RIC and normalised to added sterane standard.
11. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
12. Peak area of C₃₀ 17α(H),21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
13. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak area of C₃₅ counterparts (45).
14. Peak areas of C₁₉ to C₂₉ tricyclic terpanes (peaks 18+19+20+21+22+23+25+26) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
15. Peak area of C₂₄ tetracyclic terpene (24) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
16. Peak area of C₂₇ 18α(H) trisnorhopane (Ts, peak 28) in m/z 191 chromatogram over peak area of C₂₇ 17α(H) trisnorhopane (Tm, peak 30).
17. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
18. Peak area of C₂₉ 17α(H),21β(H)-hopane (33) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H)-hopane (35) X100.

* See Fig . 5 and Appendices.

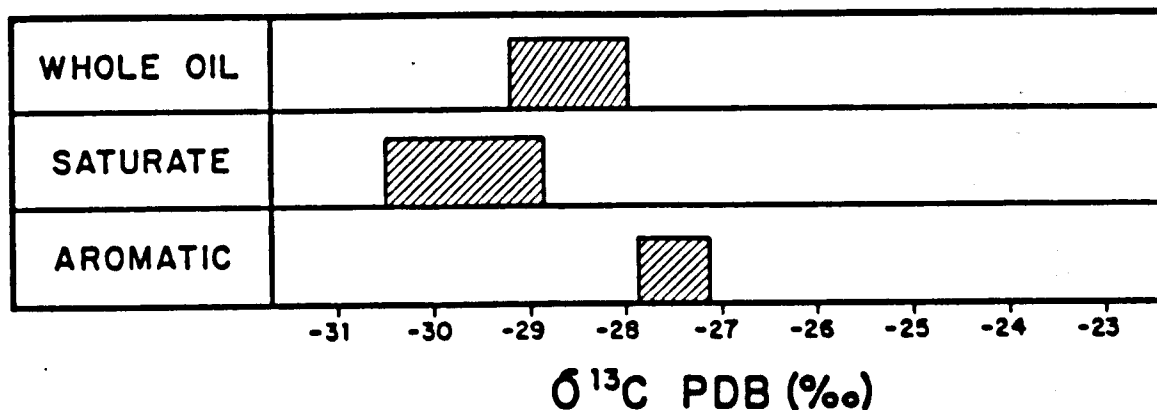
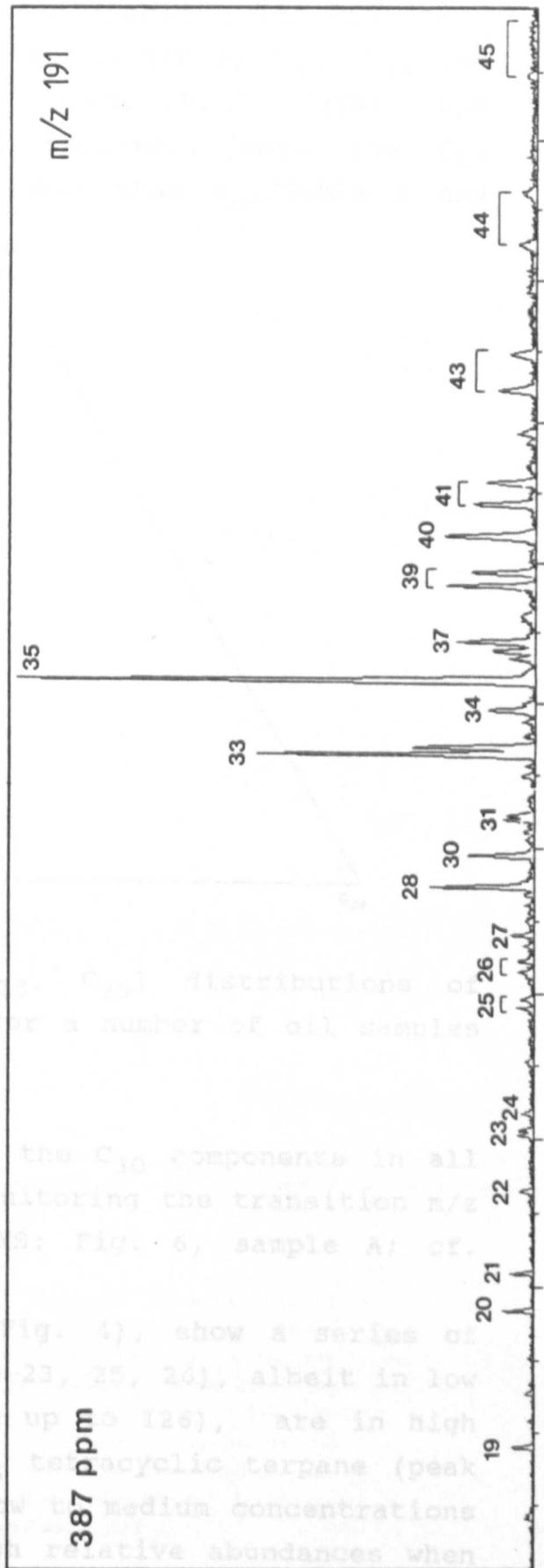
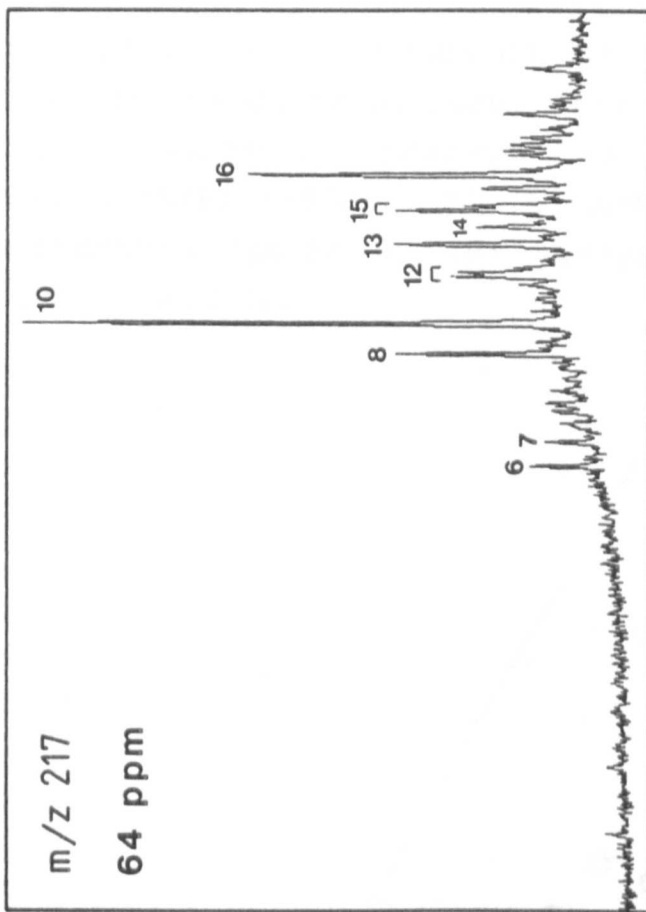
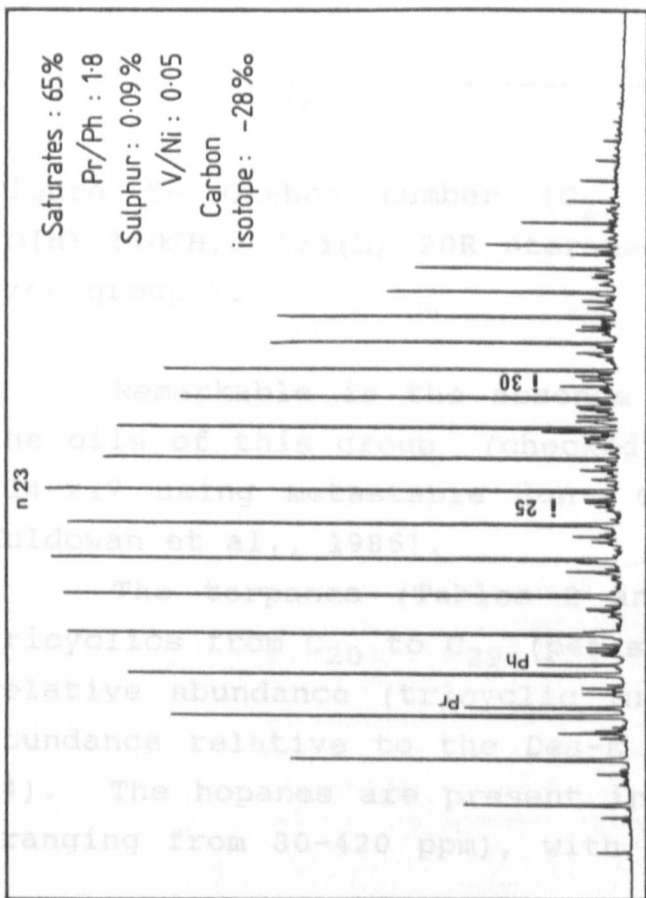


Figure 3- Variation of carbon isotopic data of whole oil and saturate and aromatic fractions for group I oils.

The specific biological markers examined are mainly represented by the long chain acyclic isoprenoids, sterane and terpane families (Tables 2 and Fig. 4). Representative GC and GC-MS traces of a typical example of this consistent group are shown in Fig. 4. The presence of C₂₅ and C₃₀ acyclic isoprenoids had to be confirmed by mass chromatography in some cases using m/z 183, 239 and 253, since they were present in low relative abundance in these samples. In others, the C₂₅ (2,6,10,14,18 and/or 2,6,10,15,19 pentamethyleicosanes) and C₃₀ (squalane) components were identified in the RIC traces (cf. Fig. 4) and quantified (Table 2). Generally, they have low concentrations with a maximum value of 370 ppm (Table 2). The steranes were assigned by mass chromatography, using m/z 217, 231 and 259 for steranes including C₂₁ and C₂₂ components (peaks 1 to 5), 4-methylsteranes and diasteranes, respectively. In general, the oils have very low concentrations of steranes (up to 64 ppm), with 4-methyl steranes (4 α , 20 R and S, mainly C₃₀; not shown) present in concentrations similar to, but less than, those of steranes (Tables 2 and Fig 4). Diasteranes are in low to medium relative abundance (diasterane index up to 40), and the low molecular weight steranes are

Figure 4- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms and absolute concentrations of steranes and hopane of a typical group I oils, from Ceará basin (CES-8; for peak assignments and quantitation see appendices I and II).



present in low to trace concentrations (Table 2 and Fig. 4) . The sterane distributions, represented mainly by C_{27} , C_{28} and C_{29} homologues present as ($5\alpha(H),14\alpha(H),17\alpha(H)$ and $5\alpha(H),14\beta(H),17\beta(H)$, 20 R and S isomers), show the C_{27} components (peaks 8, 10) always higher than C_{29} (Table 2 and Figs. 4 and 5).

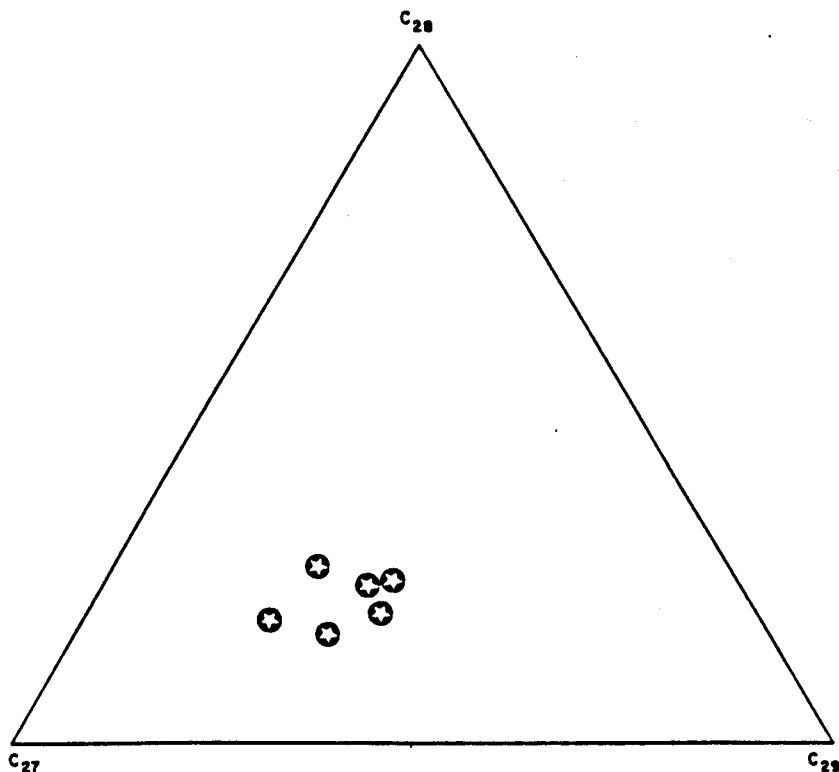


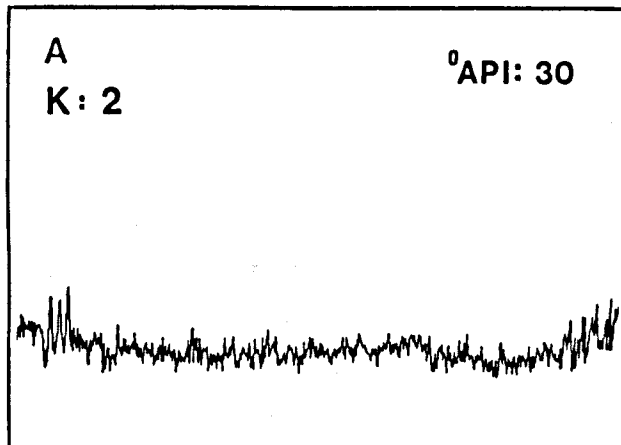
Figure 5- Carbon number (C_{27} , C_{28} , C_{29}) distributions of $5\alpha(H),14\alpha(H),17\alpha(H)$ 20R steranes for a number of oil samples from group I.

Remarkable is the absence of the C_{30} components in all the oils of this group (checked monitoring the transition m/z 414-217 using metastable ion GC-MS; Fig. 6, sample A; cf. Moldowan et al., 1985).

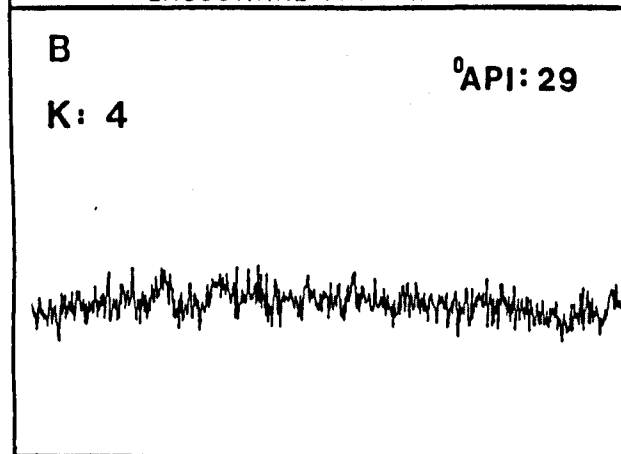
The terpanes (Tables 2 and Fig. 4), show a series of tricyclics from C_{20} to C_{29} (peaks 19-23, 25, 26), albeit in low relative abundance (tricyclic index up to 126), are in high abundance relative to the Des-E C_{24} tetracyclic terpane (peak 24). The hopanes are present in low to medium concentrations (ranging from 80-420 ppm), with high relative abundances when

OIL SAMPLES M/Z

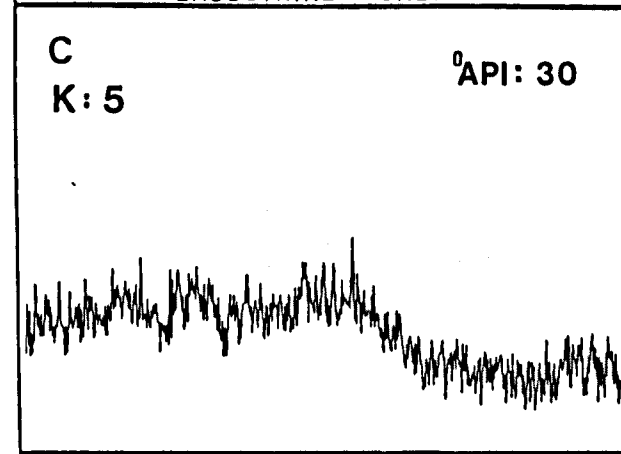
414 - 217



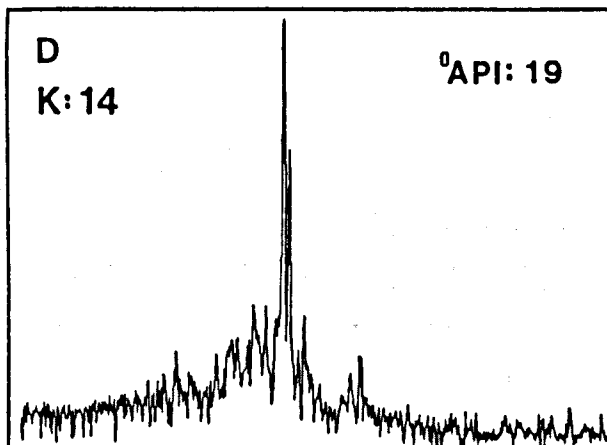
LACUSTRINE FRESHWATER



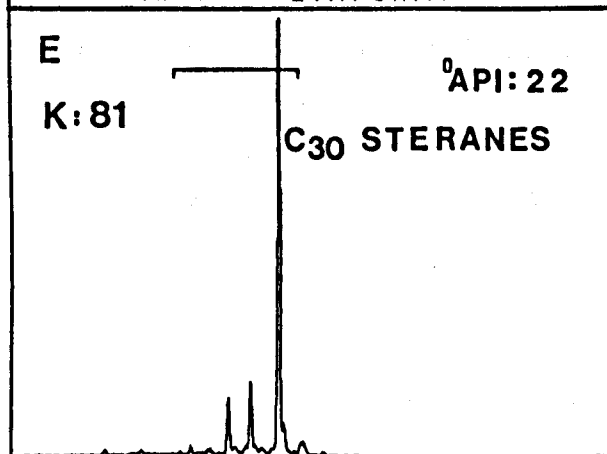
LACUSTRINE SALINE



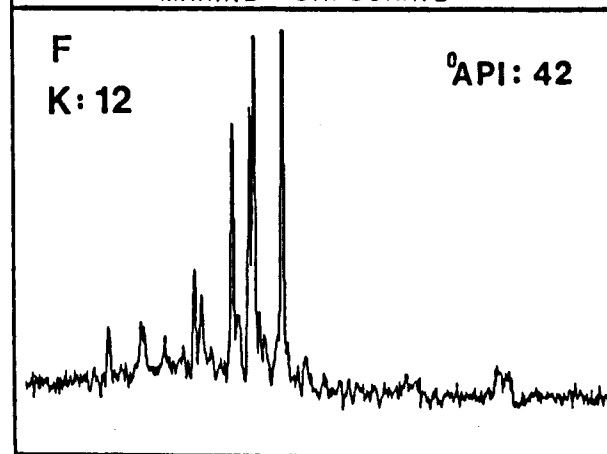
LACUSTRINE SALINE



MARINE EVAPORITIC



MARINE CARBONATE



MARINE DELTAIC

Figure 6- Mass chromatograms from metastable ion monitoring of transition m/z 414-217 of alkane fractions (K indicates amounts relative to added deuteriated standard), and API data from oils from different depositional environments from Brazilian marginal basins ; A: lacustrine freshwater (group I, BAS-64); B: lacustrine saline water (group II, RJS-305); C: lacustrine saline water (group II, RJS-41); D: marine evaporitic (group III, CES-8); E: marine carbonate (group IV, APS-27); F: marine deltaic with carbonate influence (group V, PAS-9).

compared with the steranes (hopane/ sterane ranging from 6.1-15) with the C_{30} $17\alpha(H),21\beta(H)$ component (peak 35) dominant in the typical C_{27} to C_{35} range (C_{28} absent and C_{31} to C_{35} with 22 S and R isomers; Table 2, Fig. 4). Minor amounts of C_{29} and C_{30} $17\beta(H),21\alpha(H)$ hopanes (moretanenes; peaks 34, 37), are also present; the C_{27} hopanes Ts and Tm($18\alpha(H)$ 22,29,30-trisnorneohopane and $17\alpha(H)$ 22,29,30-trisnorhopane, peaks 28 and 30), are present with $Ts/Tm > 1$ (except Bas-48; Table 2 and Fig. 4). A feature is the presence, in low to medium relative abundance, of gammacerane(peak 40). The use of a standard and an efficient GC column (DB-1701, 60 m), allowed its identification, with complete separation from the C_{31} hopanes.

3.2.2 Group II oils.

The oils belonging to group II are confined to the eastern and southern areas of the margin, in Espirito Santo (9-12) and Campos (14-18) basins, respectively (Table 3 and Fig. 7).



Figure 7- Location map showing the areas which group II oils were investigated.

Table 3: Geological and Geochemical Data For Oils Used in the Assessment of Lacustrine Saline Water Depositional Environment.

Wells	ESS-38	LP-3	RI-29	ESS-26	SM-35	RJS-305	RJS-49	RJS-41	RJS-139	GP-1
Sample Number	9	10	11	12	13	14	15	16	17	18
Depth (m) (reservoir)	1947	1524	1047	2700	1422	3166	2857	2210	2814	2880
Age (reservoir)	Aptian	Paleocene	Albian	Albian	Aptian	Albian	Neocomian	Aptian	Neocomian	Eocene
Lithology (reservoir)	Sandstone	Sandstone	Carbonate	Carbonate	Sandstone	Carbonate	Coquina	Sandstone	Coquina	Sandstone
γ API	25	30	20	35	20	29	32	30	30	30
Sulphur (%)	0.30	0.30	0.90	0.30	0.31	0.30	0.23	0.30	0.26	0.22
Pr/Ph	1.7	1.6	1.4	1.6	1.8	1.7	1.5	1.6	1.6	1.5
Pr/nC ₁₇	0.9	0.9	1.1	0.8	1.2	0.7	0.9	0.5	0.7	0.8
Ph/nC ₁₈	0.55	0.60	0.80	0.60	0.80	0.50	0.70	0.80	0.50	0.60
nC ₁₇ /C ₃₁	3.0	6.0	2.8	6.5	1.8	4.2	5.0	3.0	6.5	6.0
$\delta^{13}C$ whole oil ‰	-26.7	-25.5	-24.5	-25.2	-25.6	24.7	-23.4	-25.0	-22.7	-25.0
$\delta^{13}C$ saturates ‰	-27.4	-24.2	-25.1	-25.4	-26.7	-25.8	-24.3	-25.4	-23.7	-
$\delta^{13}C$ aromatics ‰	-26.1	-24.0	-24.4	-24.4	-25.4	-24.3	-23.0	-24.4	-22.3	-
V /Ni ratio	0.22	-	0.30	-	0.42	0.42	0.40	0.42	-	-
Saturates (%)	50	60	49	65	52	62	60	51	60	58
Aromatics (%)	25	25	20	20	19	18	25	19	21	20
NSO (%)	25	15	31	15	29	20	15	30	19	22

They occur in reservoir rocks deposited in non-marine and marine facies which range from Neocomian to Eocene in age (Table 2). Their geochemical features (Tables 3, 4) include medium sulphur contents (0.22% to 0.31%, excluding RI-29 which is biodegraded), medium to high V/Ni ratios (0.22% to 0.42%), and $^{\circ}\text{API}$ ranging from 20 to 32 (Tables 3 and 4). The compositional data show a tendency for a small reduction in saturates content (49-65%; Table 3 and Fig. 8) relative to the group I oils, as well as for a slight increase in the aromatics. The n-alkane predominance, around C_{17} to C_{21} , tends to increase the $n\text{-C}_{17} / n\text{-C}_{31}$ ratios (up to 6.5). The pristane/phytane ratios are high (1.4-1.8) and are accompanied by a slight odd over even preference in the n-alkanes .

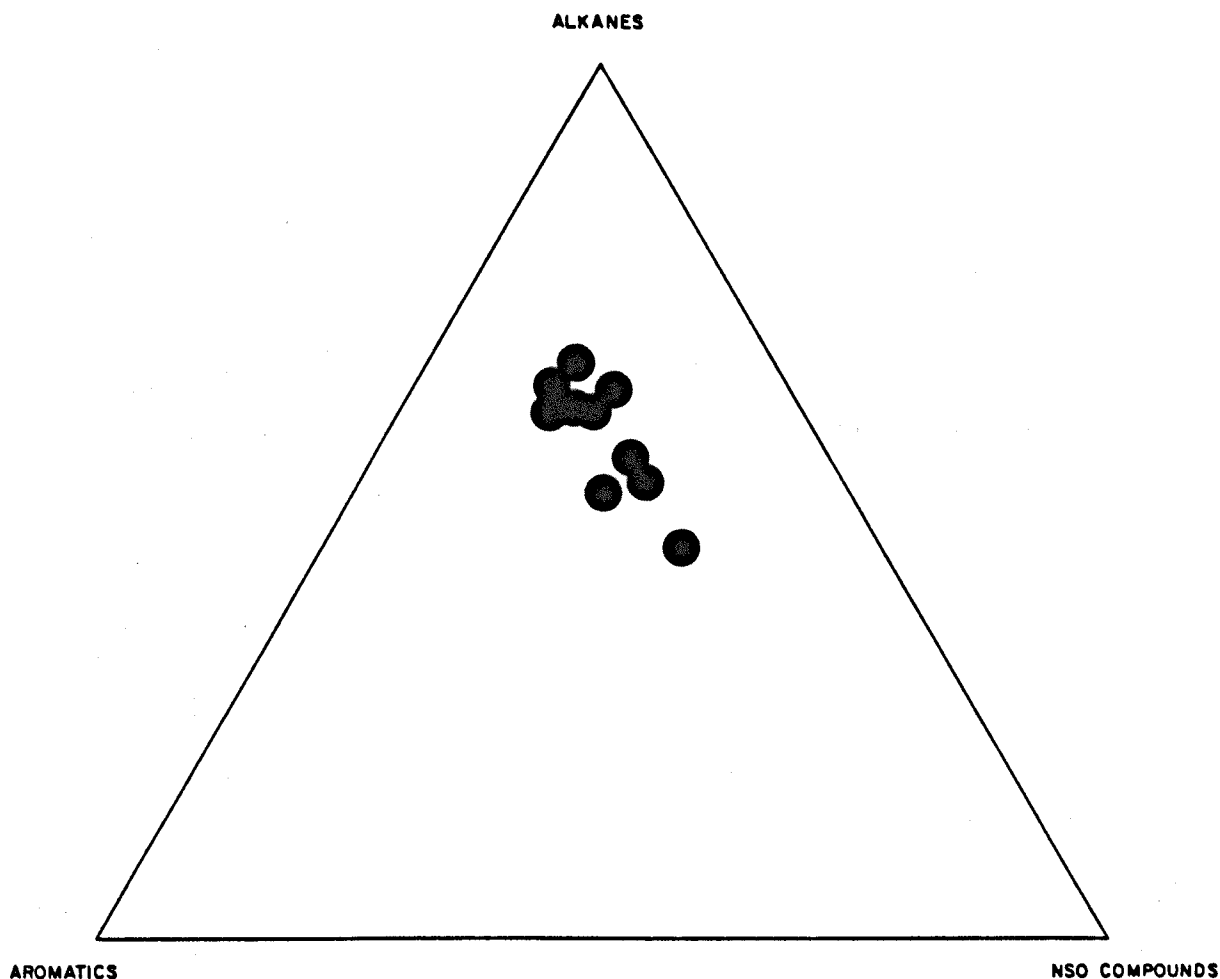


Figure 8- Relative abundance of alkanes, aromatics and NSO compounds in group II oils.

TABLE 4 - Bulk and Biological Marker Parameters for Oils from Lacustrine Saline Water Environment.

BULK	ALKANES	STERANES	TRITERPANES	TRITERPANES
°API: 20-32	n-ALKANES MAXIMA: C ₁₉ -C ₂₁	C ₂₇ STERANE: ⁵ 0-190ppm	C _{30αβ} HOPANE: ¹⁰ 620-1128ppm	TRICYCLIC ¹⁴ INDEX: 110-198
SULPHUR: 0.22-0.31	SATURATES: 49-65%	C ₂₇ /C ₂₉ : ⁶ 1.1-2.2	GAMMACERANE ¹¹ INDEX: 20-37	TETRACYCLIC ¹⁵ INDEX: 6.0-9.0
V/Ni: 0.22-0.42	Pr/Ph: - 1.4-1.8	DIASTERANE ⁷ INDEX: 30-53	18α(H)OLEANANE undetected	T ₈ /T _m : ¹⁶ 0.40-0.90
δ ¹³ C ¹ -22.7 to -26.7	I-C ₂₅ +I-C ₃₀ : ³ 380-700ppm	4-Me STERANE ⁸ INDEX: 30-150	HOPANE/STERANE ¹² INDEX: 5-12	BISNORHOPANE ¹⁷ INDEX: 4-15
δ ¹³ C ² -23.7 to -27.4	β-CAROTANE: ⁴ Cr-165ppm	C ₂₁ + C ₂₂ ⁹ STERANES: Cr-30ppm	C ₃₄ /C ₃₅ ¹³ HOPANES: 1.3-1.6	C ₂₉ /C ₃₀ ¹⁸ HOPANES: 60-77

MEASUREMENT PROCEDURES

1. PDB (%) Whole oil fraction.
2. PDB (%) Saturates fraction.
3. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
4. Peak area (β) in RIC trace and normalised to added sterane standard.
5. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
6. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
7. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
8. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
10. Peak area of C₃₀ 17α(H),21β(H) hopane (35) measured in RIC and normalised to added sterane standard.
11. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
12. Peak area of C₃₀ 17α(H),21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
13. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).
14. Peak areas of C₁₉ to C₂₉ tricyclic terpanes (peaks 18+19+20+21+22+23+25+26) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
15. Peak area of C₂₄ tetracyclic terpene (24) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
16. Peak area of C₂₇ 18α(H) trisnorhopane (T₈, peak 28) in m/z 191 chromatogram over peak area of C₂₇ 17α(H) trisnorhopane (T_m, peak 30).
17. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
18. Peak area of C₂₉ 17α(H),21β(H)-hopane (33) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H)-hopane (35) X100.

* See Figs.10 to 11 and Appendices.

The $\delta^{13}\text{C}(\text{‰})$ values spanning a range of relatively heavy values of -22.7 to -26.7 for the whole oil, -23.7 to -27.4 for the saturate fraction and between -22.3 and -26.1 for the aromatics (Tables 3 and 4; Fig. 9).

These oils have higher relative abundances and concentrations of the long chain acyclic C_{25} and C_{30} isoprenoids than the oils in group I (up to 700 ppm; Table 4 and Figs. 10 and 11). That the $i\text{-C}_{25}$ component is mainly 2,6,10,14,18-pentamethyleicosane was confirmed using m/z 253 chromatograms (as well as m/z 239 and 183). β -Carotane occurs, generally in low to medium concentration (ranging from traces to 165 ppm; Table 4 and Figs. 10 and 11).

LACUSTRINE SALINE OILS

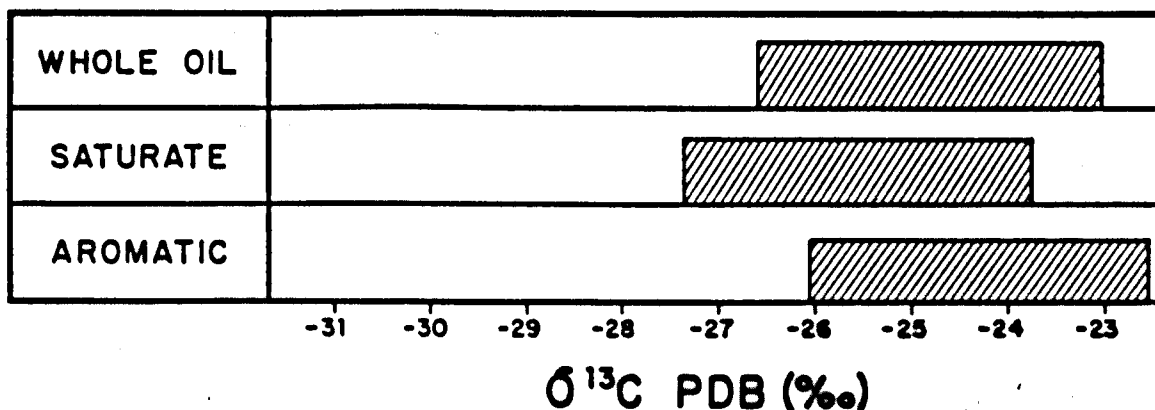


Figure 9- Variation of carbon isotopic data of whole oil and saturate and aromatic fractions for group II oils.

Figure 10- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane of a typical sample, from group II oils, from Campos basin (RJS-41; for peak assignments and quantitation see appendices I and II).

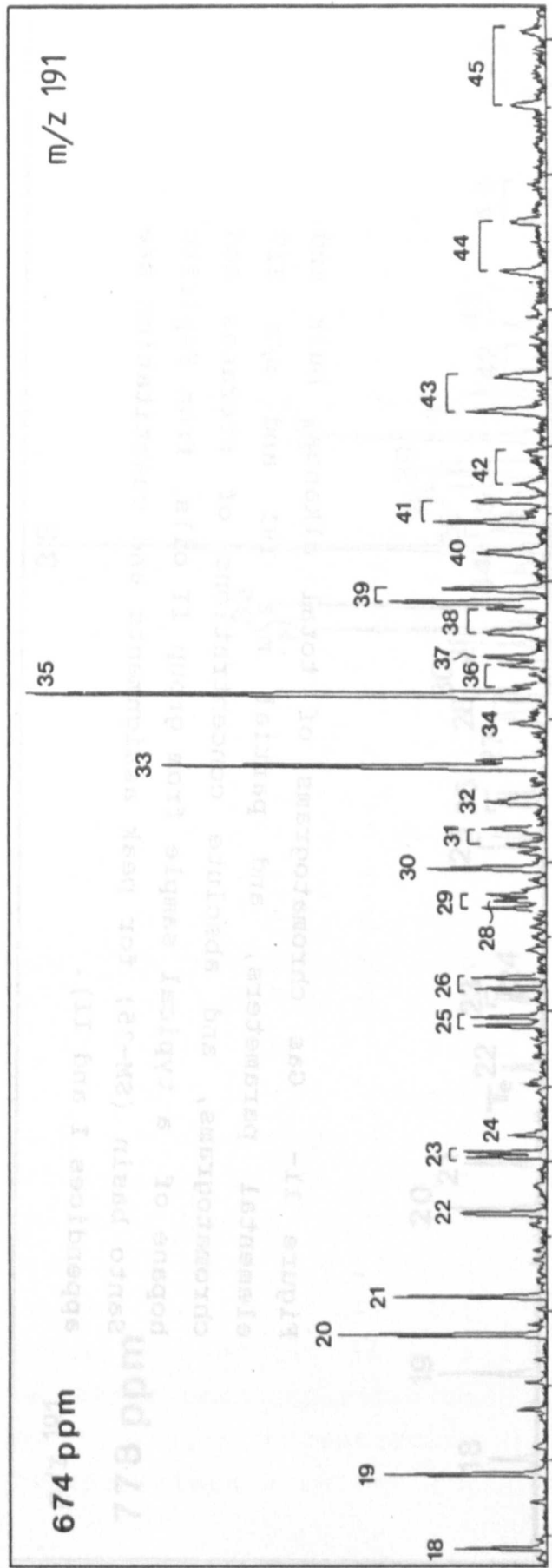
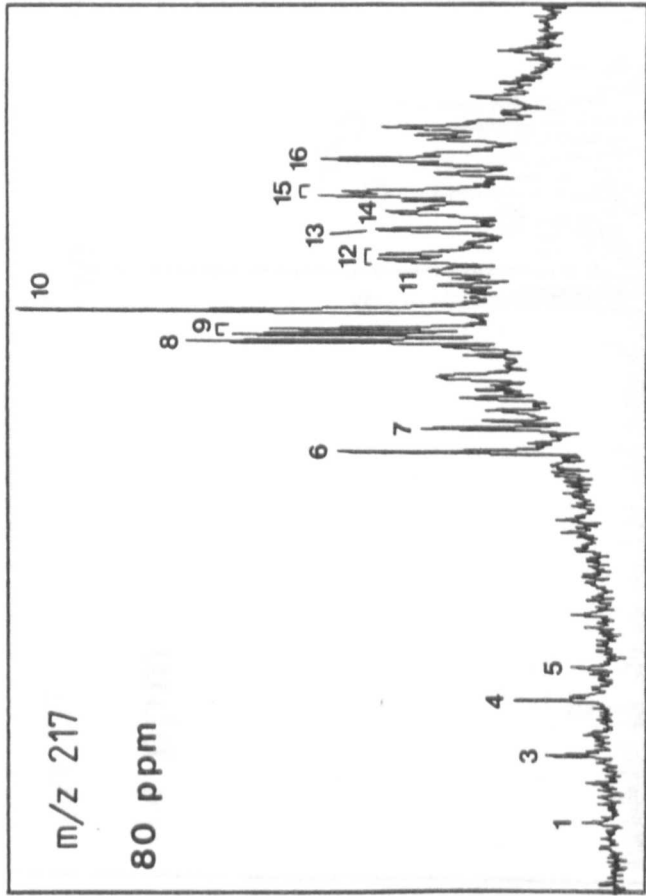
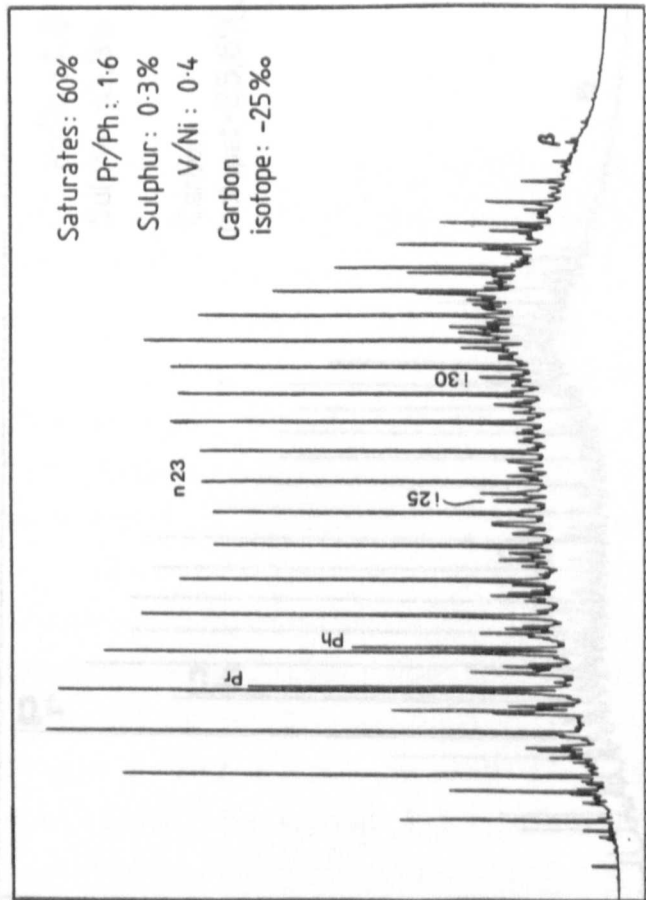
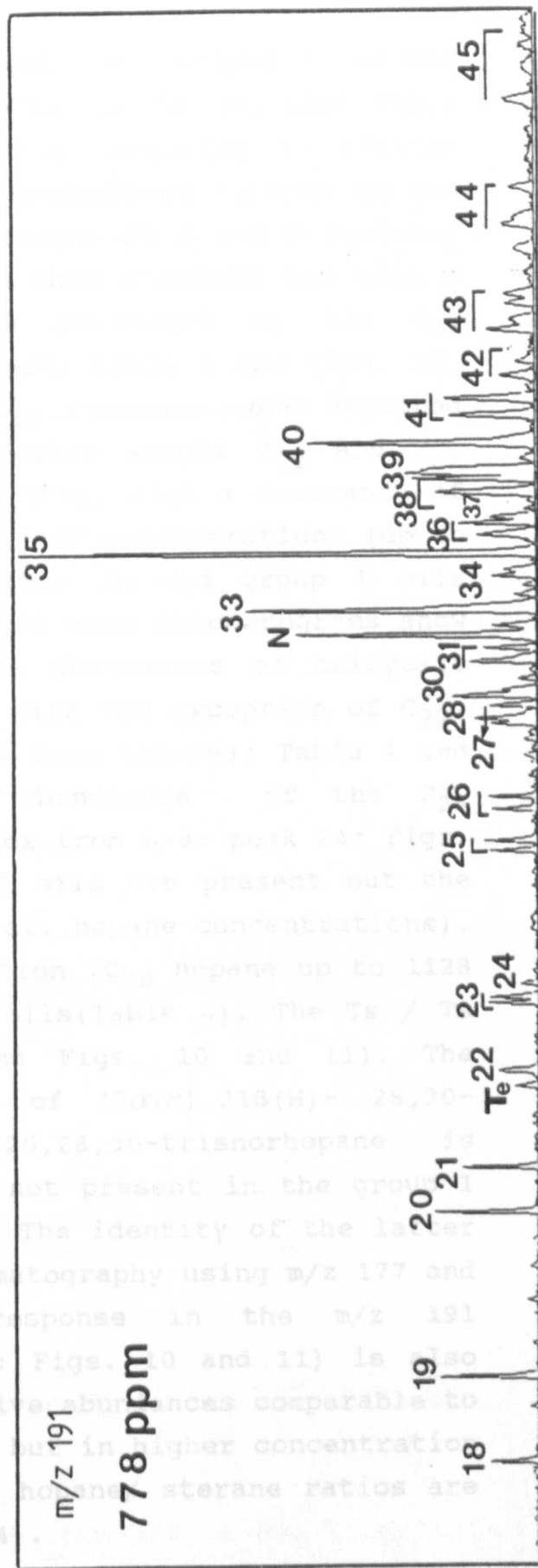
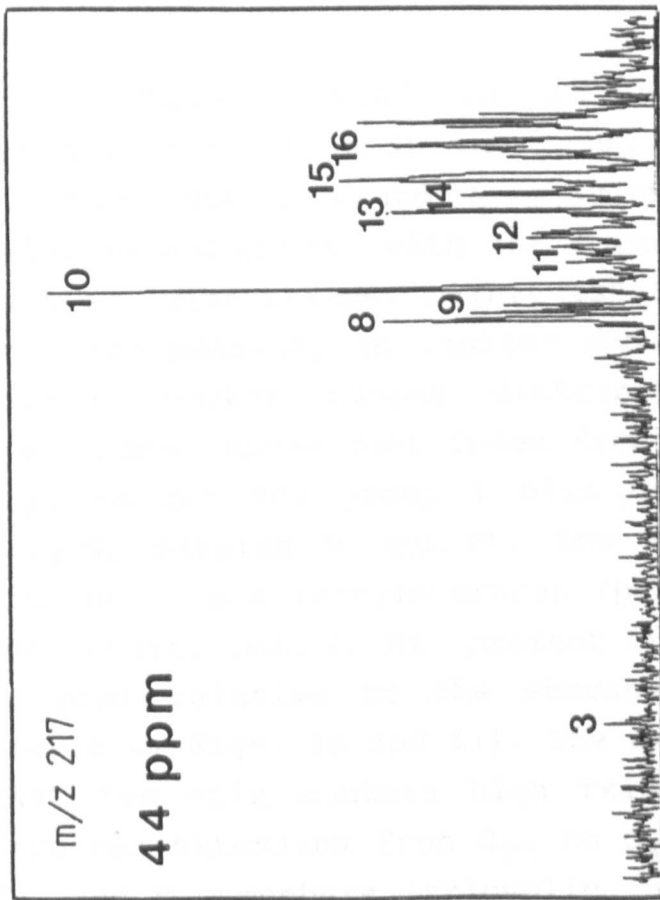
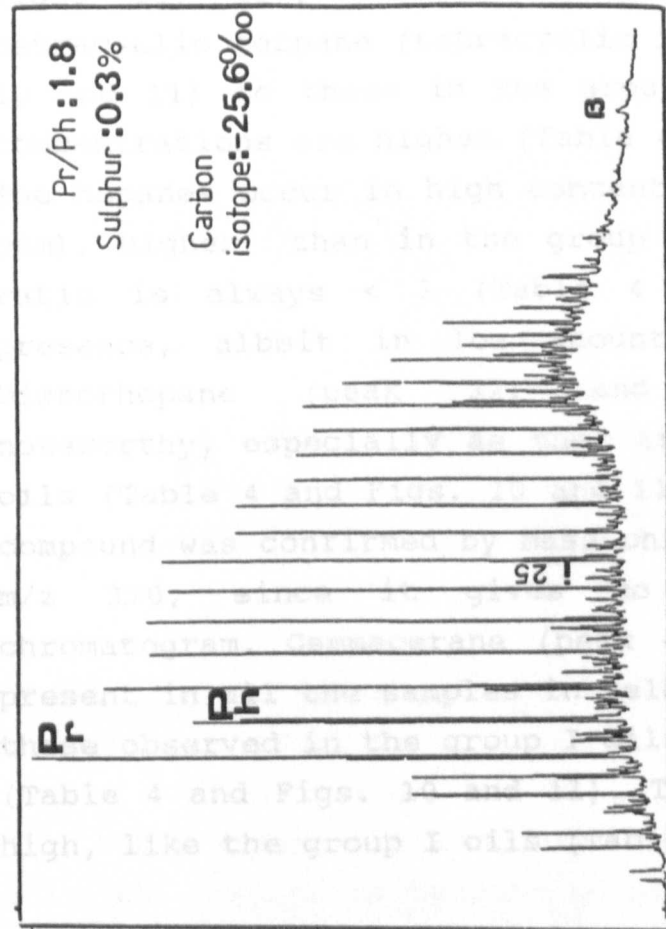


Figure 11- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane of a typical sample from group II oils, from Espirito Santo basin (SM-35; for peak assignments and quantitation see appendices I and II).



Steranes tend to be present in slightly higher concentrations than in the group I oils (up to 190 ppm; Table 4), with steranes and 4-methylsteranes occurring in similar relative abundance, with the former predominant in most of the samples. Diasteranes, mainly $13\beta(H)$, $17\alpha(H)$ 20 S and R isomers, are also present, in smaller amounts than steranes but with a similar carbon number distribution dominated by the C_{27} components (diasterane index from 30-53; Table 4 and figs. 10, 11). As for the group I oils no C_{30} steranes were detected (Fig. 6, samples B and C). Low molecular weight C_{21} and C_{22} steranes and 4-methylsteranes (peaks 1-5), with a dominance of the latter, tend to be present in higher concentrations (up to 30 ppm) relative to the steranes than in the group I oils (Table 4; Figs. 10 and 11). The m/z 191 mass chromatograms show that the oils contain high relative abundances of tricyclic terpanes extending from C_{20} to C_{35} , with the exception of C_{22} , C_{27} and C_{32} members (tricyclic index from 110-198; Table 4 and Figs. 10, 11). Similar relative abundances of the C_{24} tetracyclic terpene (tetracyclic index from 6-9; peak 24; Figs. 10 and 11) to those in the group I oils are present but the concentrations are higher (Table 4; cf. hopane concentrations). The hopanes occur in high concentration (C_{30} hopane up to 1128 ppm), higher than in the group I oils (Table 4). The T_s / T_m ratio is always < 1 (Table 4 and Figs. 10 and 11). The presence, albeit in low amounts, of $17\alpha(H)$, $21\beta(H)$ - 28,30-bisnorhopane (peak 32) and 25,28,30-trisnorhopane is noteworthy, especially as they are not present in the group I oils (Table 4 and Figs. 10 and 11). The identity of the latter compound was confirmed by mass chromatography using m/z 177 and m/z 370, since it gives no response in the m/z 191 chromatogram. Gammacerane (peak 40; Figs. 10 and 11) is also present in all the samples in relative abundances comparable to those observed in the group I oils, but in higher concentration (Table 4 and Figs. 10 and 11). The hopane/ sterane ratios are high, like the group I oils (Table 4).

3.2.3 Group III oils

Oils in this group occur in Bahia Sul (26), Sergipe/Alagoas (24,25 and 27), Potiguar (19-21) and Ceará (22 and 23) basins, being pooled in reservoirs ranging from Pre-Cambrian to Paleocene (Table 5 and Fig. 12).

Their geochemical characteristics include medium to high sulphur contents (0.3 to 1.5%), medium V/Ni ratios(around 0.2), and $\delta^{13}\text{C}(\%)$ values within the narrow range of -25.4 to -26.6 for whole oil, -26.4 to -27.3 for saturates and -25.4 to -26.4 for the aromatic fraction (Tables 5, 6 and Fig. 13).

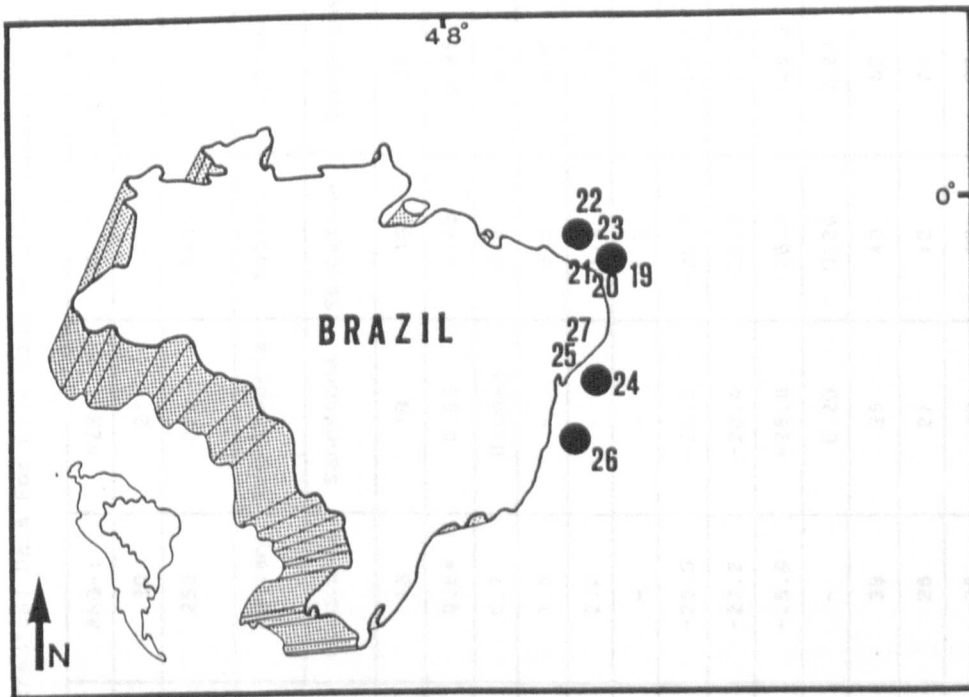


Figure 12- Location map showing the areas which group III oils were investigated.

The amounts of saturates range from 35% to 59% (Fig. 14) with NSO components tending to be higher than aromatics (Tables

Table 5: Geological and Geochemical Data For Oils Used in the Assessment of Marine Evaporitic Depositional Environment

Wells	RNS-10	ARG-1	FZB-1	CES-8	CES-41	SES-77	TM-5	BAS-11	CP-578
Sample Number	19	20	21	22	23	24	25	26	27
Depth (m) (reservoir)	1953	256	376	1475	2764	1998	999	1915	623
Age (reservoir)	Albian	Aptian	Pre-Cambrian	Aptian	Aptian	Aptian	Aptian	Paleocene	Pre-Cambrian
Lithology (reservoir)	Carbonate	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Sandstone	Basement
γ API	19	18	19	19	30	29.8	26	32	28
Sulphur (%)	1.30	0.64	0.63	1.46	0.35	0.33	0.30	0.44	0.35
Pr/Ph	0.6	0.7	Biodeg	0.5	0.6	0.8	0.6	0.8	0.9
Pr/nC ₁₇	0.5	1.5	-	0.5	0.5	0.5	0.7	0.8	0.5
Ph/nC ₁₈	1.2	2.0	-	1.2	1.0	0.8	2.6	1.0	0.6
nC ₁₇ /C ₃₁	7.2	-	-	7.5	5.7	-	6.3	7.0	2.1
$\delta^{13}C$ whole oil ‰	-25.4	-26.0	-25.6	-26.6	-26.5	-25.6	-25.5	-26.0	-26.1
$\delta^{13}C$ saturates ‰	-26.8	-27.2	-26.4	-27.3	-27.0	-26.5	-26.4	-27.0	-27.0
$\delta^{13}C$ aromatics ‰	-26.1	-25.8	-25.8	-26.4	-26.0	-25.4	-26.5	-26.2	-25.8
V /Ni ratio	0.27	-	0.20	0.20	0.23	-	0.23	-	-
Saturates (%)	35	39	35	40	60	43	44	67	49
Aromatics (%)	17	26	27	12	20	22	23	15	31
NSO (%)	48	35	38	48	20	34	34	18	20

TABLE 6- Bulk and Biological Marker Parameters for Oils from Marine Evaporitic Environment.

BULK	ALKANES	STERANES	TRITERPANES	TRITERPANES
°API: 18-32	n-ALKANES MAXIMA: C ₁₈ -C ₂₆	C ₂₇ STERANE: ⁸ 500-2080ppm	C _{30αβ} HOPANE: ¹⁰ 450-1510ppm	TRICYCLIC ¹⁴ INDEX: 12-60
SULPHUR: 0.3-1.46	SATURATES: 35-67%	C ₂₇ /C ₂₉ : ⁹ 1.2-1.6	GAMMACERANE ¹¹ INDEX: 34-120	TETRACYCLIC ¹⁵ INDEX: 1.2-4.0
V/Ni: 0.20-0.27	Pr/Ph: 0.5-0.9	DIASTERANE ⁷ INDEX: 6-18	18α(H)OLEANANE undetected	T ₈ /T _m : ¹⁶ 0.50-0.90
δ ¹³ C ¹ -25.4 to -26.6	I-C ₂₅ +I-C ₃₀ : ³ 127-1500ppm	4-Me STERANE ⁸ INDEX: 43-80	HOPANE/STERANE ¹² INDEX: 0.7-2	BISNORHOPANE ¹⁷ INDEX: 10-35
δ ¹³ C ² -26.4 to -27.3	β-CAROTANE: ⁴ 180-400ppm	C ₂₁ + C ₂₂ ⁹ STERANES: 10-60ppm	C ₃₄ /C ₃₅ ¹³ HOPANES: 0.67-1.5	C ₂₉ /C ₃₀ ¹⁸ HOPANES: 35-70

MEASUREMENT PROCEDURES

1. PDB (‰) Whole oil fraction.
2. PDB (‰) Saturates fraction.
3. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
4. Peak area (8) in RIC trace and normalised to added sterane standard.
5. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
6. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
7. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
8. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
10. Peak area of C₃₀ 17α(H),21β(H) hopane (35) measured in RIC and normalised to added sterane standard.
11. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
12. Peak area of C₃₀ 17α(H),21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
13. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).
14. Peak areas of C₁₈ to C₂₆ tricyclic terpanes (peaks 18+19+20+21+22+23+25+26) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
15. Peak area of C₂₄ tetracyclic terpene (24) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
16. Peak area of C₂₇ 18α(H) trisnorhopane (T₈, peak 28) in m/z 191 chromatogram over peak area of C₂₇ 17α(H) trisnorhopane (T_m, peak 30).
17. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
18. Peak area of C₂₉ 17α(H),21β(H)-hopane (33) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H)-hopane (35) X100.

* See Figs.15 to 16 and Appendices.

5 and 6). A close examination of the relative abundances of normal and branched alkanes shows a dominance of low molecular weight n-alkanes (around C_{18} - C_{20}), no predominance or/ and a slight even/odd n-alkane dominance, low pristane/phytane ratios (ranging from 0.5-0.9) and n- C_{17} /n- C_{31} ratios around 6.0 (except CP-578; Tables 5 and 6 and Fig. 15).

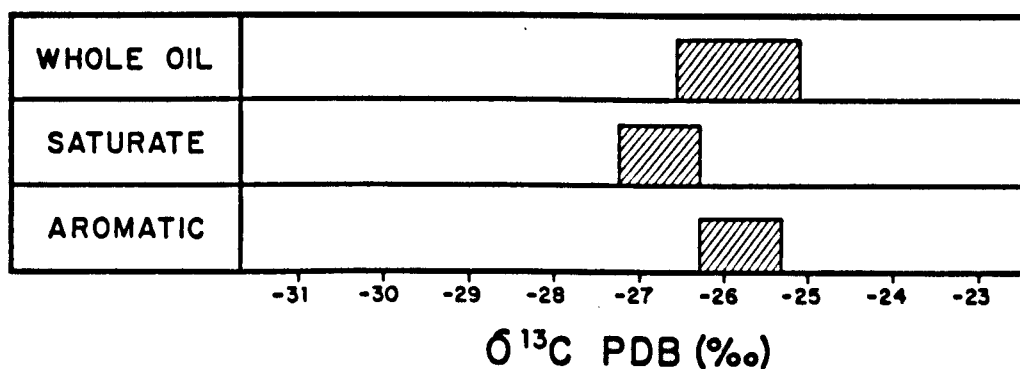


Figure 13- Variation of carbon isotopic data of whole oil and saturate and aromatic fractions for group III oils.

The distributions and concentrations of long chain isoprenoids (C_{25} regular and C_{30} , squalane), steranes and terpanes are similar within the group, but differ significantly from the other oil groups, for example in terms of the concentrations (Tables 6 and Figs. 15 and 16), except that the hopanes are also high in group II oils.

A high concentration of the C_{25} and C_{30} (squalane) isoprenoids (up to 1500 ppm; Table 6 and Fig. 15) is typical of these oils. The assignment of the i- C_{25} component as mainly 2,6,10,14,18-pentamethyleicosane ("regular") in two of the oils was made by coinjection of a synthesised standard. The 2,6,10,15,19 isomer ("irregular"), which could only be partly separated from the "regular" isomer, also appeared to be present, but in low abundance. Noteworthy is the presence, in

high concentrations, of components with carotenoid skeletons, i.e. mainly β -carotane (up to 400 ppm) with γ -carotane in lower abundance (Fig. 15 and Table 6).

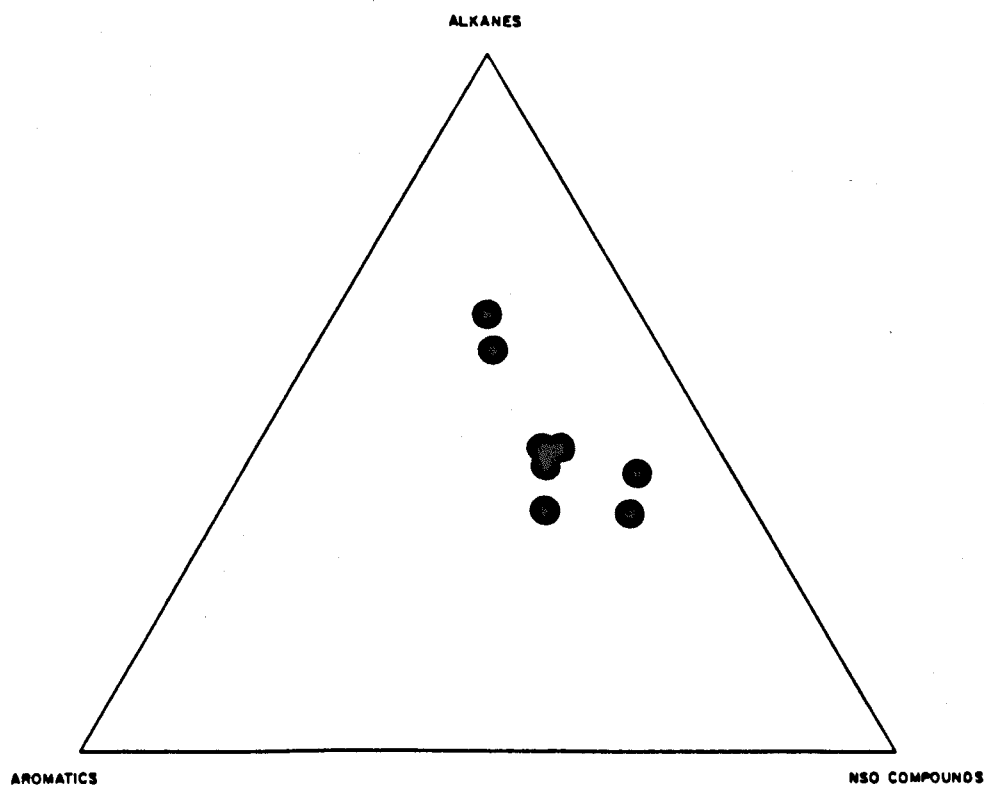


Figure 14- Relative abundance of alkanes, aromatics and NSO compounds in group III oils.

Steranes occur in the highest concentrations of all the groups (up to 2080 ppm; Table 6 and Fig. 15). The oils contain low relative abundances of diasteranes (diasterane index up to 18), and fairly similar abundances of 4-methyl steranes (mainly C_{30}) relative to steranes (but high concentrations). All the samples show a dominance of C_{27} components over their C_{28} and C_{29} counterparts (C_{27}/C_{29} ranging from 1.2-1.6; Table 6 and Fig. 15). Most of these samples show an unusually high abundance "for oils" of the 20 $R\alpha\alpha$ components (e.g. peak 10) relative to 20 S (e.g. peak 8) plus low abundances of the $\alpha\beta\beta$ components (e.g. peak 9; Fig. 15). Also notable is the

GAS CHROMATOGRAM

M / Z 217

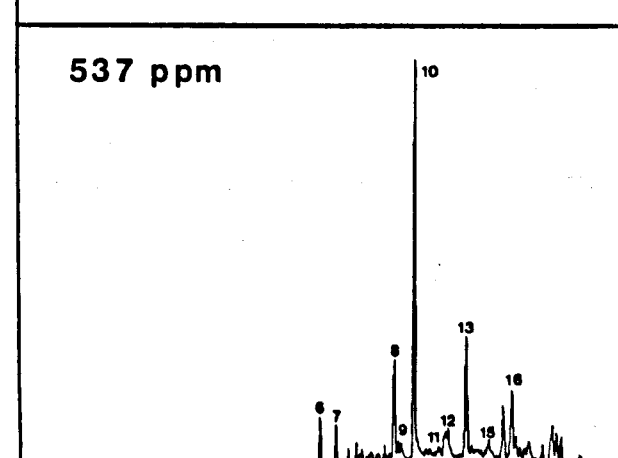
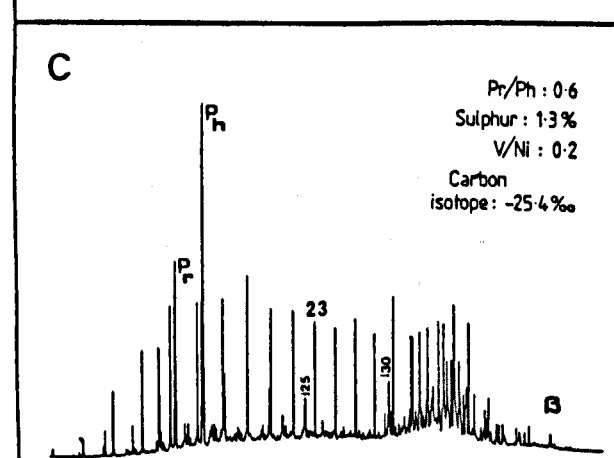
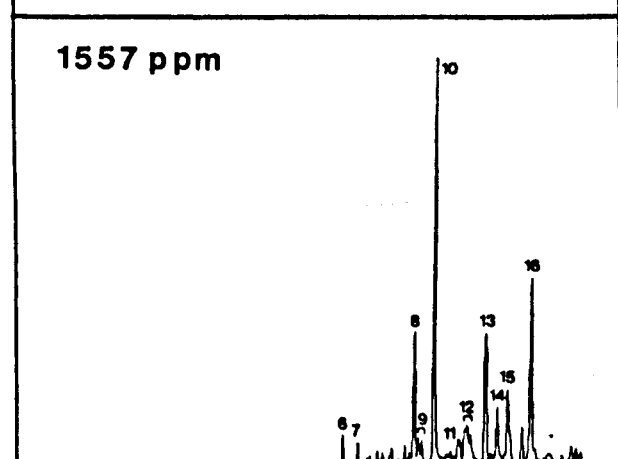
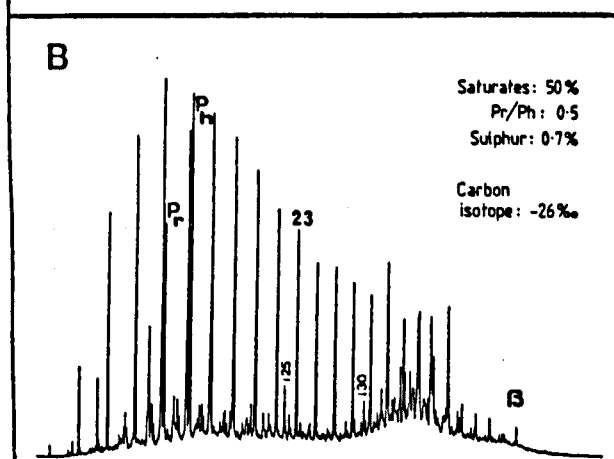
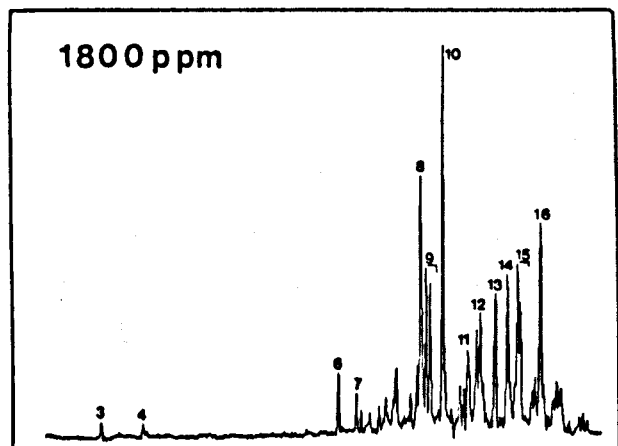
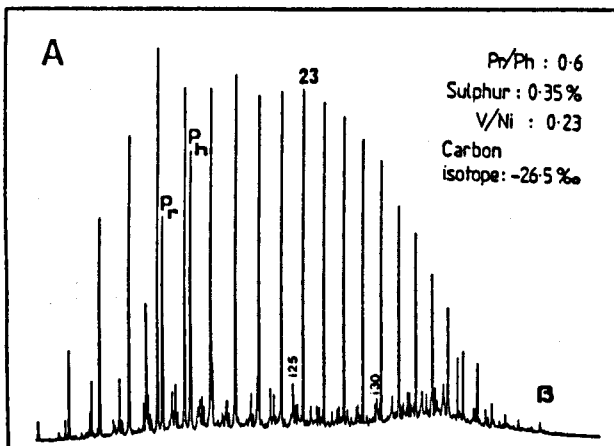


Figure 15- Gas chromatograms of total alkanes, bulk and elemental parameters, partial m/z 217 chromatograms and absolute concentration of steranes of three group III oil samples from Ceará (A: CES-41; B: CES-8) and Potiguar (C: RNS-10), basins (for peak assignments and quantitation see appendices I and II).

occurrence, although only in low concentrations, of C_{30} steranes which were not detected in samples of groups I and II (Fig. 6). In addition, the oils contain relatively high concentrations (up to 60 ppm) of low molecular weight steranes and 4-methylsteranes, although in low abundance relative to the C_{27} - C_{29} steranes (cf. Table 6 and Fig. 15).

Like the steranes, the terpanes are present in very high concentrations and on the average are the highest amongst the groups. The distributions of the tricyclic terpanes differ from groups II and IV (see below), since they are present in lower relative abundance (tricyclic index from 12-60) and contain no homologues higher than C_{29} ; Table 6 and Fig. 16). Overall, the characteristics of the m/z 191 mass fragmentograms (Fig. 16) for these oils include: a high relative abundance of gammacerane (sometimes the major peak; peak 40; gammacerane index up to 120), C_{35} hopanes sometimes higher than their C_{34} counterparts (peaks 45 and 44, respectively; Fig. 16 and Table 6), the presence of significant amounts of 28,30-bisnorhopane (peak 32; bisnorhopane index up to 35; Fig. 16) and high concentration of hopanes (C_{30} $\alpha\beta$ up to 1510 ppm), with high relative abundances of C_{29} to C_{35} $17\alpha(H), 21\beta(H)$ hopanes compared to their $17\beta(H), 21\alpha(H)$ counterparts (Table 3 and Fig. 6). It is interesting to note the low hopane/sterane ratios (ranging from 0.7-2.0; Table 6) for the samples of this group when compared to the oils from groups I and II. Like group II, the T_s/T_m ratios (peaks 28 and 30; Fig. 16) are always < 1 , in contrast to group I (Table 6). In addition, high amounts of another C_{27} hopane (25,28,30-trisnorhopane) are observed (m/z 177 and m/z 370 mass chromatograms).

3.2.4 Group IV oils

These oils are found only in Cassiporé (28) and Maranhão (29) basins in the extreme northern part of the continental margin (Fig. 17). Data for only two samples are given in tables 7 and 8; however, a third sample was available and the bulk,

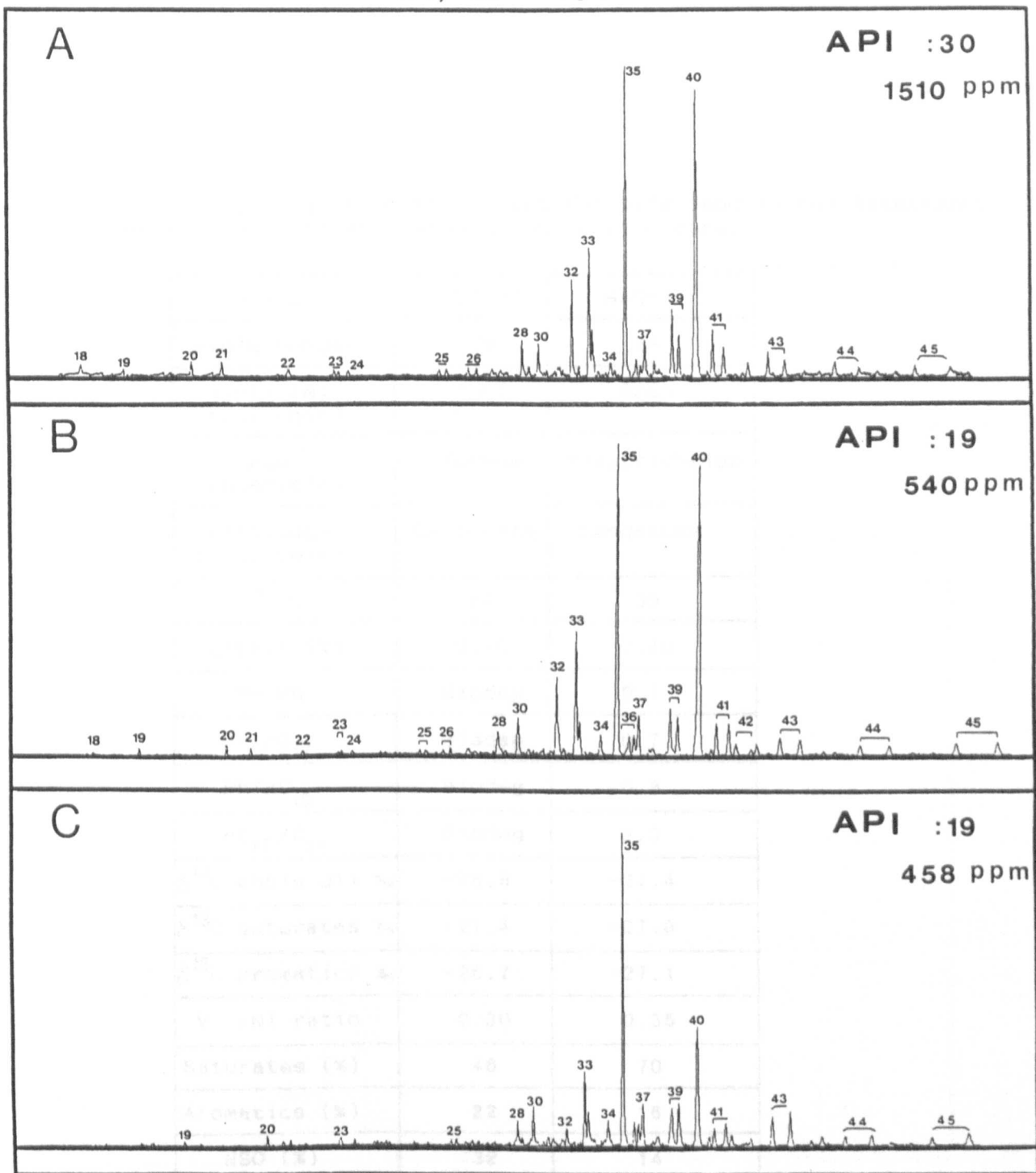


Figure 16- Partial m/z 191 chromatograms of total alkanes, API data and absolute concentration of hopane for the same samples as Fig. 15 (for peak assignments and quantitation see appendices I and II).

Table 7: Geological and Geochemical Data For Oils Used in the Assessment of Marine Carbonate Depositional Environment.

Wells	APS-27	MAS-5
Sample Number	28	29
Depth (m) (reservoir)	1107	2889
Age (reservoir)	Eocene	Maastrichtian
Lithology (reservoir)	Carbonate	Sandstone
$^{\circ}\text{API}$	22	39
Sulphur (%)	0.70	0.40
Pr/Ph	Biodeg	0.7
Pr/nC ₁₇	Biodeg	0.7
Ph/nC ₁₈	Biodeg	0.8
nC ₁₇ /C ₃₁	Biodeg	3.0
$\delta^{13}\text{C}$ whole oil ‰	-26.8	-27.4
$\delta^{13}\text{C}$ saturates ‰	-27.4	-27.6
$\delta^{13}\text{C}$ aromatics ‰	-26.7	-27.1
V /Ni ratio	0.30	0.35
Saturates (%)	46	70
Aromatics (%)	22	16
NSO (%)	32	14

elemental and biological marker ratios have been measured. Overall, they fall within the ranges given in Table 8. The biological marker concentrations have not yet been measured at Bristol in the same way as the other samples, although metastable ion monitoring studies have been carried out.

The oils are accumulated in reservoirs ranging from Maastrichtian to Tertiary age (Table 7). The bulk geochemical properties of these oils are, in most respects, similar to those of the group III oils (Table 7) with high sulphur contents and medium V/Ni ratios (0.4 to 0.7% and 0.3 to 0.35 respectively).

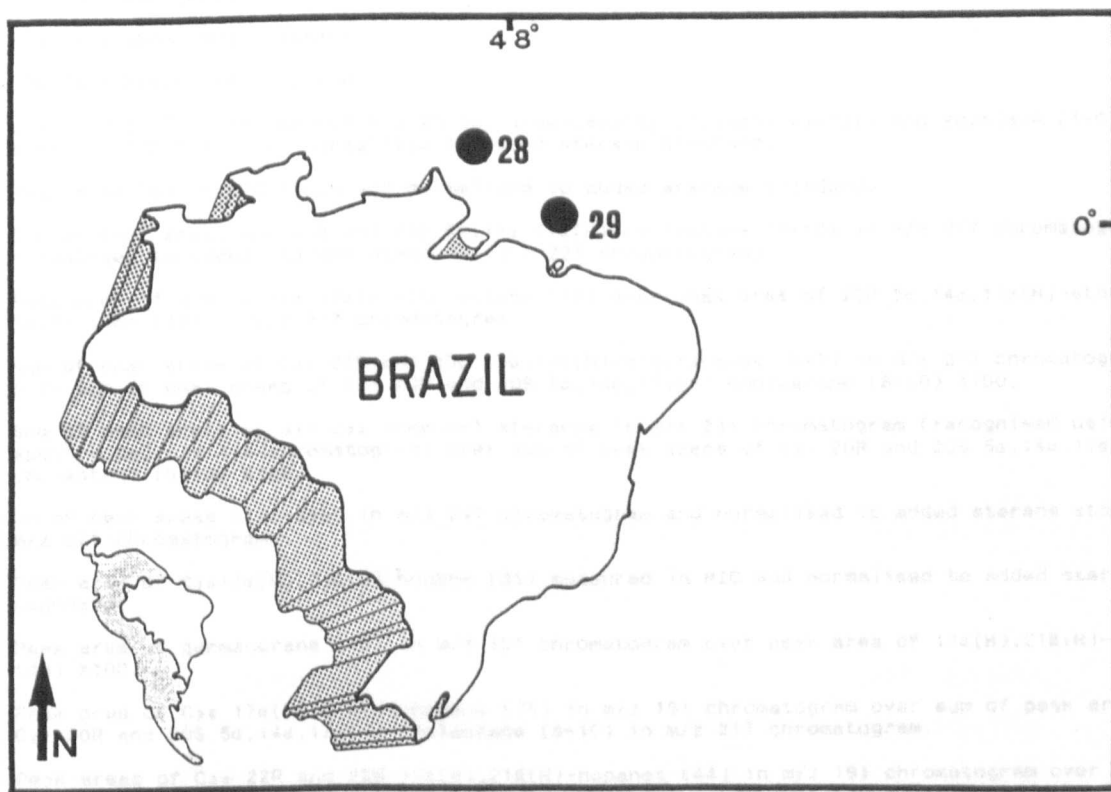


Figure 17- Location map showing the areas which group IV oils were investigated.

Their saturate fractions range from 46% to 70% , with aromatics and NSO components having similar values to each other (Table 7). The $\delta^{13}\text{C}(\%)$ values of the whole oils range from -26.8 to -27.4, around -27.5 for the saturate and -26.7 to -27.1 for the aromatic fraction (Tables 7 and 8 and Fig. 18).

TABLE 8- Bulk and Biological Marker Parameters for Oils from Marine Carbonate Environment.

BULK	ALKANES	STERANES	TRITERPANES	TRITERPANES
*API: 22-39	n-ALKANES MAXIMA: C ₂₀ -C ₂₂	C ₂₇ STERANE: ⁵ 42-250ppm	C ₃₀ αB HOPANE: ¹⁰ 130-285ppm	TRICYCLIC INDEX: 140-180 ¹⁴
SULPHUR: 0.4-0.7	SATURATES: 46-70%	C ₂₇ /C ₂₉ : ⁶ 1.5-2.0	GAMMACERANE INDEX: 15-20 ¹¹	TETRACYCLIC INDEX: 4.0-6.0 ¹⁸
V/Ni: 0.30-0.35	Pr/Ph: ≈0.7	DIASTERANE INDEX: 20-30 ⁷	18α(H)OLEANANE undetected	T ₈ /T _m : 0.70-0.80 ¹⁶
δ ¹³ C (‰): ¹ -26.8 to -27.4	I-C ₂₅ +I-C ₃₀ : ³ ≈467ppm	4-Me STERANE ⁸ INDEX: 20-80	HOPANE/STERANE ¹² INDEX: 1.5-2.3	BISNORHOPANE INDEX: 13-19 ¹⁷
δ ¹³ C (‰): ² -27.4 to -27.6	β-CAROTANE: ⁴ 11-42ppm	C ₂₁ + C ₂₂ STERANES: 14-54ppm ⁹	C ₃₄ /C ₃₅ HOPANES: 0.95-1.3 ¹³	C ₂₈ /C ₃₀ HOPANES: 66-86 ¹⁸

MEASUREMENT PROCEDURES

1. PDB (‰) Whole oil fraction.
2. PDB (‰) Saturates fraction.
3. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
4. Peak area (β) in RIC trace and normalised to added sterane standard.
5. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
6. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
7. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
8. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
10. Peak area of C₃₀17α(H),21β(H) hopane (35) measured in RIC and normalised to added sterane standard.
11. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
12. Peak area of C₃₀ 17α(H),21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
13. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).
14. Peak areas of C₁₉ to C₂₉ tricyclic terpanes (peaks 18+19+20+21+22+23+25+26) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
15. Peak area of C₂₄ tetracyclic terpene (24) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
16. Peak area of C₂₇ 18α(H) trisnorhopane (T₈, peak 28) in m/z 191 chromatogram over peak area of C₂₇ 17α(H) trisnorhopane (T_m, peak 30).
17. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
18. Peak area of C₂₈ 17α(H),21β(H)-hopane (33) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H)-hopane (35) X100.

* See Fig . 19 and Appendices.

Fig. 19 shows the GC traces, bulk and elemental data of two oil samples of this group. Sample A is biodegraded oil from Cassiporé basin (28), and sample B is a highly mature oil (39 °API) from Maranhão basin (29; Fig. 17). Also shown are the m/z 217 and 191 mass chromatograms and the absolute concentrations of steranes and C₃₀ αβ hopane (Fig. 19).

MARINE CARBONATE

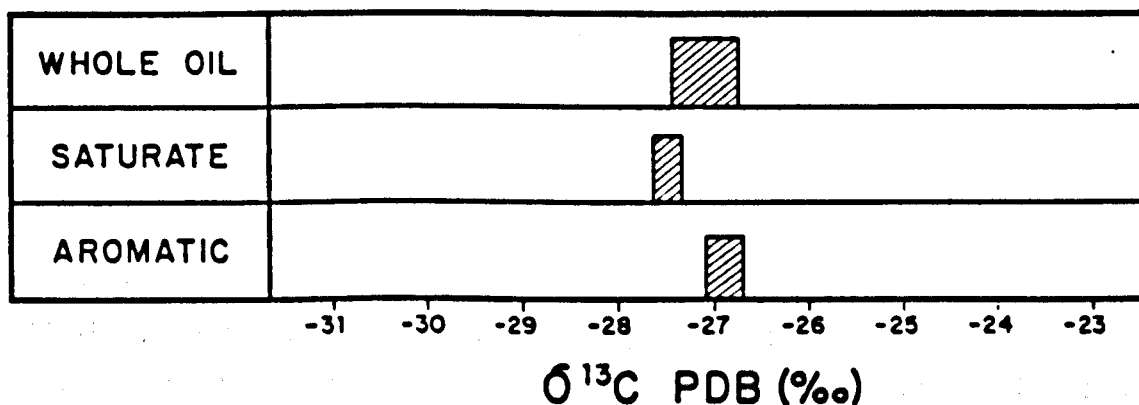
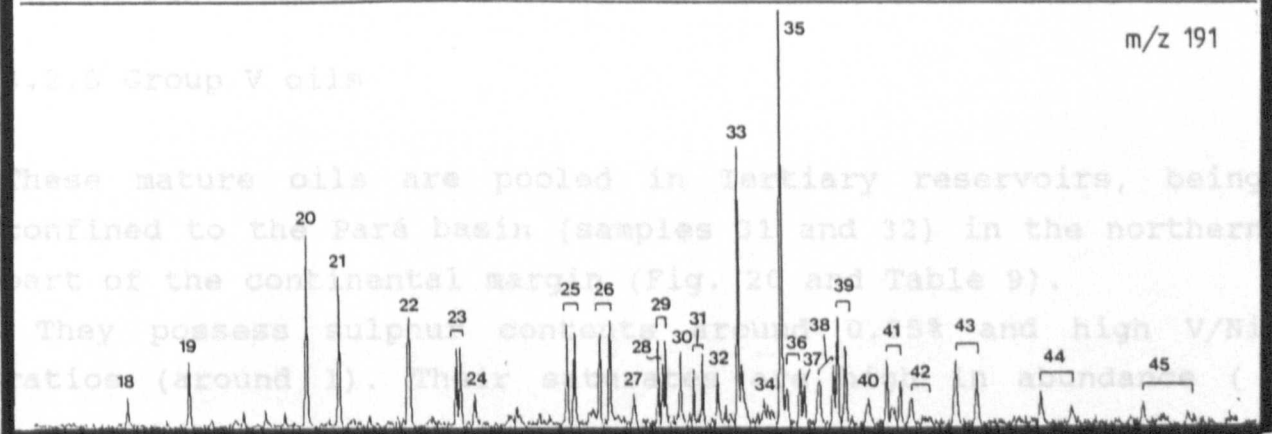
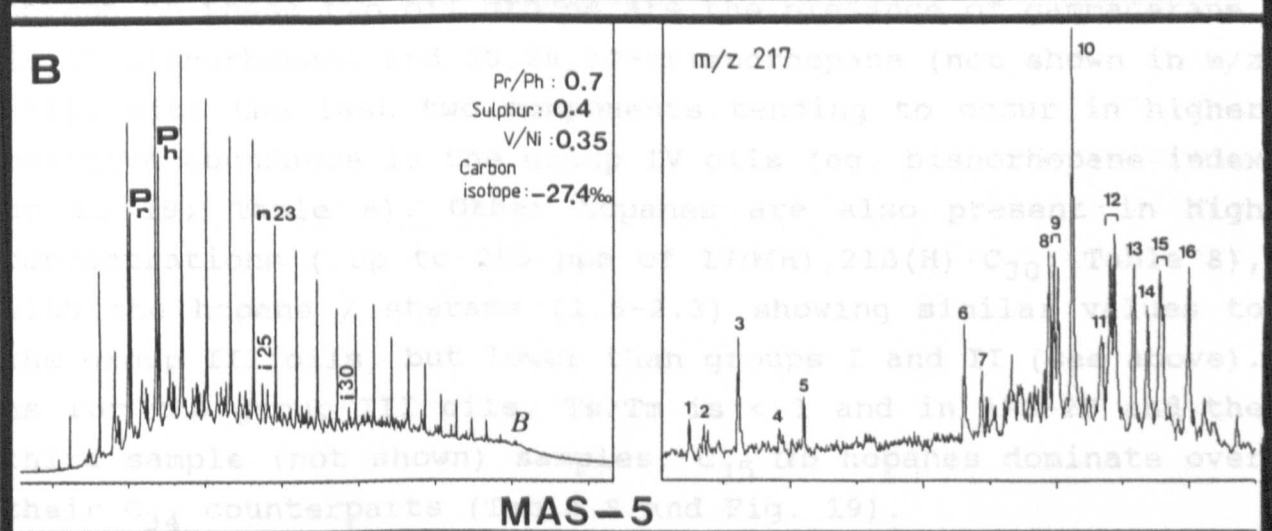
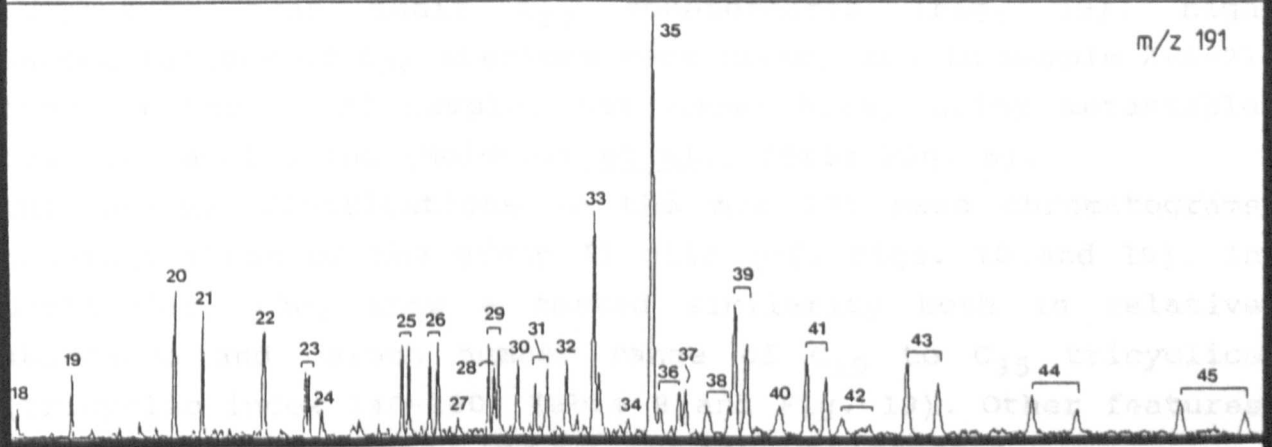
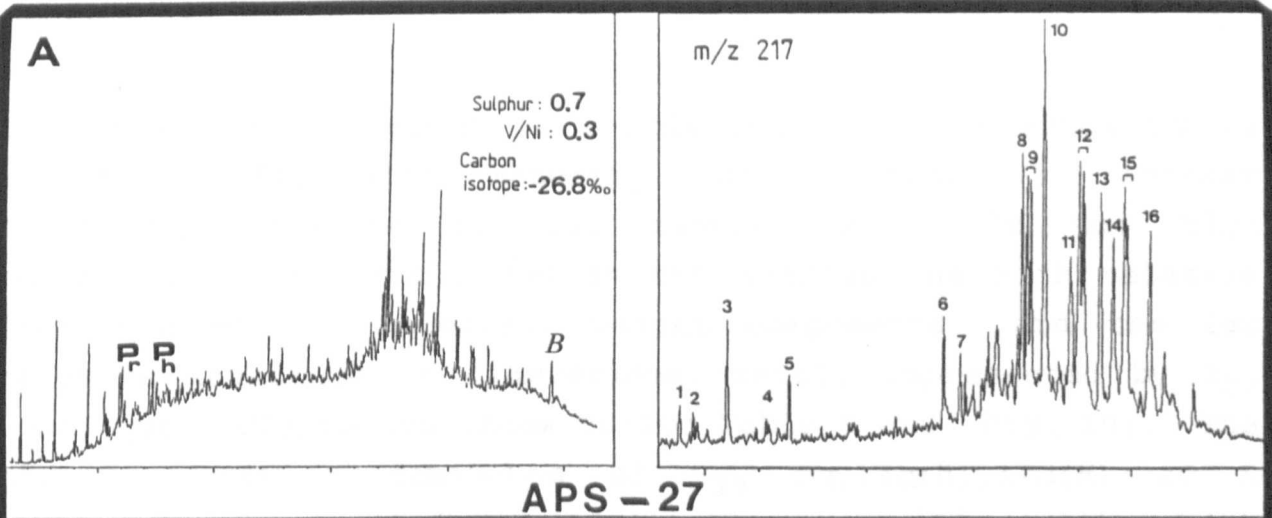


Figure 18- Variation of carbon isotopic data for whole oil and saturate and aromatic fractions for group IV oils.

The oils (sample 29 and the third oil, not shown), like those of group III, show a predominance of low molecular weight n-alkanes around C₂₀-C₂₂, with a dominance of phytane over pristane (Tables 7 and 8 and Fig. 19). The concentrations of the long chain C₂₅ regular and C₃₀(squalane) isoprenoids (around 467 ppm; Table 8 and Fig. 19) are also similar to those of the group III oils, where high concentrations are found (see group III and Table 8; Fig. 19). β-carotane occurs in low to medium concentrations (up to 42 ppm; Table 8).

Steranes are present in high concentration in two of the samples (APS-27 and the third sample), second only to their concentrations (up to 250 ppm; Table 8) in the group III oils.

Figure 19- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 mass chromatograms of two samples from group IV oils, from Cassiporé (sample A, APS-27) and Maranhão (sample B, MAS-5) basins (for peak assignments see appendix I).



The lower concentration in sample MAS-5 is suspected to be result of its high maturity (cf. chapter V). Another significant feature of the sample APS-27 is the high concentration (54 ppm), and in the samples the high relative abundance of low molecular weight components and the low relative abundance of diasteranes, mainly represented by C₂₇ homologues (diasterane index 20-30; Table 8 and Fig. 19). The steranes show a dominance of C₂₇ 5 α ,14 α (H),17 α (H) 20 R components over their C₂₉ counterparts (Fig. 19). High concentrations of C₃₀ steranes were recognised in sample APS-27 (and in the third sample, not shown here) using metastable reaction monitoring (Moldowan *et al.*, 1985; Fig. 6).

The terpane distributions in the m/z 191 mass chromatograms resemble those of the group II oils (cf. Figs. 10 and 19). In particular, they show a marked similarity both in relative abundance and carbon number range of C₁₉ to C₃₅ tricyclics (tricyclic index 140-180; Table 8 and Fig. 19). Other features common to these two oil groups are the presence of gammacerane, 28,30-bisnorhopane and 25,28,30-trisnorhopane (not shown in m/z 191), with the last two components tending to occur in higher relative abundance in the group IV oils (eg. bisnorhopane index up to 19; Table 8). Other hopanes are also present in high concentrations (up to 285 ppm of 17 α (H),21 β (H) C₃₀; Table 8), with the hopane / sterane (1.5-2.3) showing similar values to the group III oils, but lower than groups I and II (see above). As for the group III oils, Ts/Tm is < 1 and in APS-27 and the third sample (not shown) samples, C₃₅ $\alpha\beta$ hopanes dominate over their C₃₄ counterparts (Table 8 and Fig. 19).

3.2.5 Group V oils

These mature oils are pooled in Tertiary reservoirs, being confined to the Pará basin (samples 31 and 32) in the northern part of the continental margin (Fig. 20 and Table 9).

They possess sulphur contents around 0.35% and high V/Ni ratios (around 1). Their saturates are high in abundance (

Table 9: Geological and Geochemical Data For Oils Used in the Assessment of Marine Deltaic Depositional Environment with Marine Carbonate Influence.

Wells	PAS-9	PAS-11
Sample Number	31	32
Depth (m) (reservoir)	4291	4289
Age (reservoir)	Eocene	Eocene
Lithology (reservoir)	Carbonate	Carbonate
$^{\circ}\text{API}$	42	44
Sulphur (%)	0.35	0.35
Pr/Ph	0.7	1.1
Pr/nC ₁₇	0.4	0.5
Ph/nC ₁₈	0.7	0.4
nC ₁₇ /C ₃₁	1.6	3.6
$\delta^{13}\text{C}$ whole oil ‰	-24.4	-25.1
$\delta^{13}\text{C}$ saturates ‰	-25.1	-26.2
$\delta^{13}\text{C}$ aromatics ‰	-23.6	-24.3
V /Ni ratio	1.0	1.0
Saturates (%)	60	70
Aromatics (%)	31	18
NSO (%)	9	12

60%), compared with the aromatic and NSO fractions (Tables 9 and 10).



Figure 20- Location map showing the areas which group V oils were investigated.

The $\delta^{13}\text{C}(\%)$ values are -24.4 and -25.1 for the whole oils, -25.1 and -26.2 for the saturates, and -23.6 and -24.3 for the aromatic fraction (Tables 9 and 10 and Fig. 21).

MARINE DELTAIC

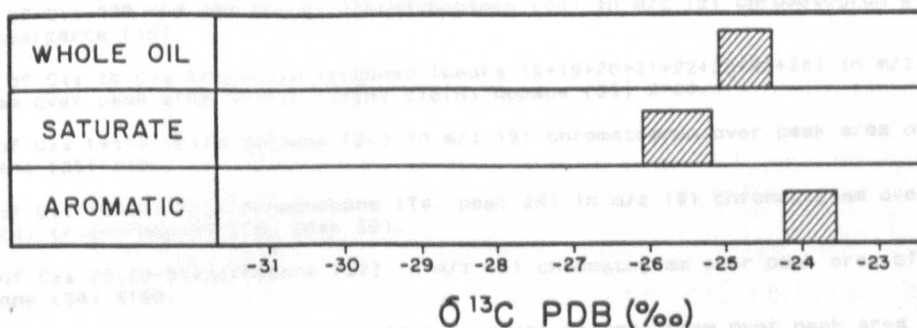


Figure 21- Variation of carbon isotopic data for whole oil and saturate and aromatic fractions for group V oils.

TABLE 10- Bulk and Biological Marker Parameters for Oils from Marine Deltaic Environment with Marine Carbonate Influence.

BULK	ALKANES	STERANES	TRITERPANES	TRITERPANES
*API: 42-44	n-ALKANES MAXIMA: C ₂₀ -C ₂₂	C ₂₇ STERANE: ⁵ 70-80ppm	C _{30α} B HOPANE: ¹⁰ 150-230ppm	TRICYCLIC ¹⁵ INDEX: 85-100
SULPHUR: 0.35%	SATURATES: 60-70%	C ₂₇ /C ₂₈ : ⁶ 2.0-3.0	GAMMACERANE ¹¹ INDEX: traces	TETRACYCLIC ¹⁶ INDEX: 15-29
V/Ni: 1.0	Pr/Ph: 0.7-1.1	DIASTERANE ⁷ INDEX: 50-60	18α(H)OLEANANE ¹² INDEX: 24-38	T ₈ /T _m : ¹⁷ 1.1-1.5
δ ¹³ C (‰): ¹ -24.4 to -25.1	I-C ₂₅ +I-C ₃₀ : ³ 160-330ppm	4-Me STERANE ⁸ INDEX: traces	HOPANE/STERANE ¹³ INDEX: 1.3-3.0	BISNORHOPANE ¹⁸ INDEX: undetected
δ ¹³ C (‰): ² -25.1 to -26.2	β-CAROTENE: ⁴ traces	C ₂₁ + C ₂₂ ⁹ STERANES: 30-42ppm	C ₃₄ /C ₃₅ ¹⁴ HOPANES: 0.6-0.7	C ₂₉ /C ₃₀ ¹⁸ HOPANES: 76-116

MEASUREMENT PROCEDURES

1. PDB (‰) Whole oil fraction.
2. PDB (‰) Saturates fraction.
3. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
4. Peak area (β) in RIC trace and normalised to added sterane standard.
5. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
6. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
7. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
8. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
10. Peak area of C₃₀17α(H),21β(H) hopane (35) measured in RIC and normalised to added sterane standard.
11. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
12. Peak area of 18α(H)-oleanane (X) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₃₀ 17α(H),21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
14. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).
15. Peak areas of C₁₉ to C₂₉ tricyclic terpanes (peaks 18+19+20+21+22+23+25+26) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
16. Peak area of C₂₄ tetracyclic terpene (24) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H) hopane (35) X100.
17. Peak area of C₂₇ 18α(H) trisnorhopane (T₈, peak 28) in m/z 191 chromatogram over peak area of C₂₇ 17α(H) trisnorhopane (T_m, peak 30).
18. Peak area of C₂₈ 28,30-bisnorhopane (32) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
19. Peak area of C₂₉ 17α(H),21β(H)-hopane (33) in m/z 191 chromatogram over peak area of C₃₀ 17α(H),21β(H)-hopane (35) X100.

* See Fig. 22 and Appendices.

The saturate fraction shows a maximum around (C_{18-22}), with a slight even/odd preference. In the less mature sample (PAS-9, Fig 22) significant abundances of high molecular weight n-alkanes occur. The pristane/phytane ratios are close to/or less than 1 (Table 9 and Fig. 22). Steranes occur in low to medium concentrations (up to 80 ppm; Table 10), considering the maturity of the oils, but 4-methylsteranes (not shown) are present only in trace abundance. Low molecular weight steranes are abundant relative to the C_{27} - C_{29} steranes (Table 10 and Fig. 22). One significant feature is the presence of diasteranes in higher relative abundances than in all the other oils (diasterane index up to 60; Table 8 and Fig. 22). The steranes show a dominance of C_{27} over the C_{29} components (Table 10 and Fig. 22). C_{30} steranes also are observed in these oils, although in low abundances, perhaps due to the advanced maturation stage (42-44 °API; Fig. 6).

The terpanes include the tricyclic series C_{20} to C_{31} and C_{27} to C_{35} hopanes, mainly $17\alpha(H)$, $21\beta(H)$, with a maximum at C_{30} (up to 230 ppm), and with hopane/sterane ratios in the range 1.3 to 3.0; Table 10). Interesting to note in both samples of this group is the dominance of C_{35} hopanes over their C_{34} counterparts (Table 10 and Fig. 22). Another significant feature of the m/z 191 chromatograms is the high relative abundance of biological markers diagnostic of higher plant inputs i.e. $18\alpha(H)$ -oleanane (peak X; Fig. 22) and Des-E C_{24} tetracyclic terpanes relative to tricyclics (peaks 24; Fig. 22). The T_s/T_m ratios show values > 1 (Table 10 and Fig. 22).

3.3 DISCUSSION

The application of biological marker compounds to the assessment of depositional environment using only oil samples should be made with caution. It is important to stress the need to understand and disentangle the effects of source, maturity, biodegradation, "contamination" in migration oil ("foreign biomarkers") and fractionation effects with expulsion on bulk,

Figure 22- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms of a sample, from group V oils, from Pará basin (PAS-9; for peak assignments see appendix I).

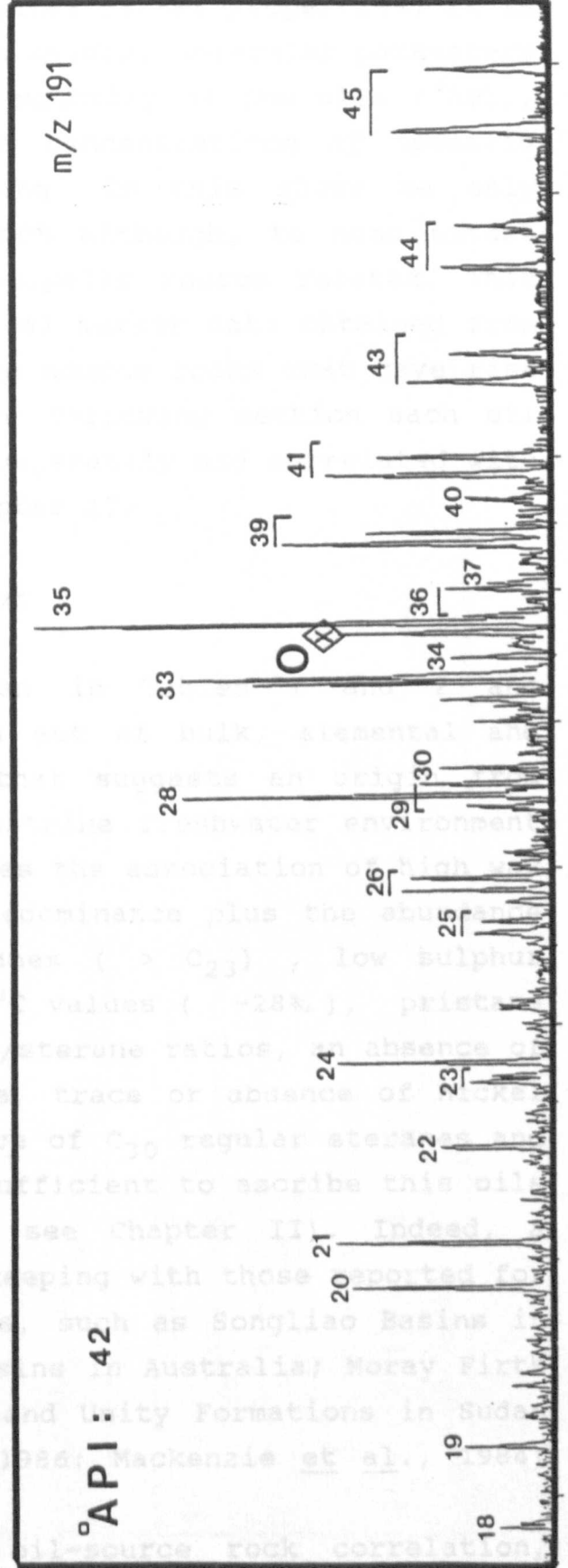
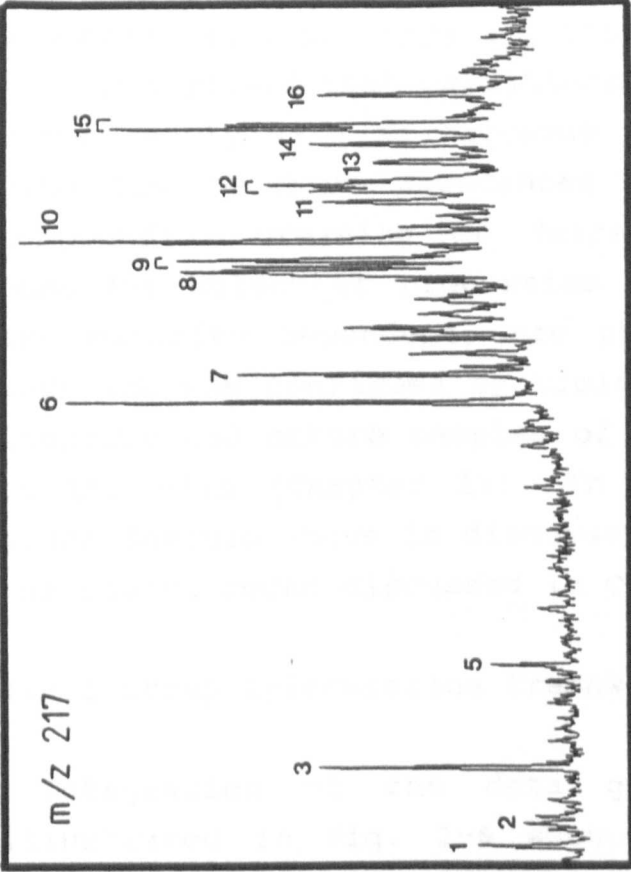
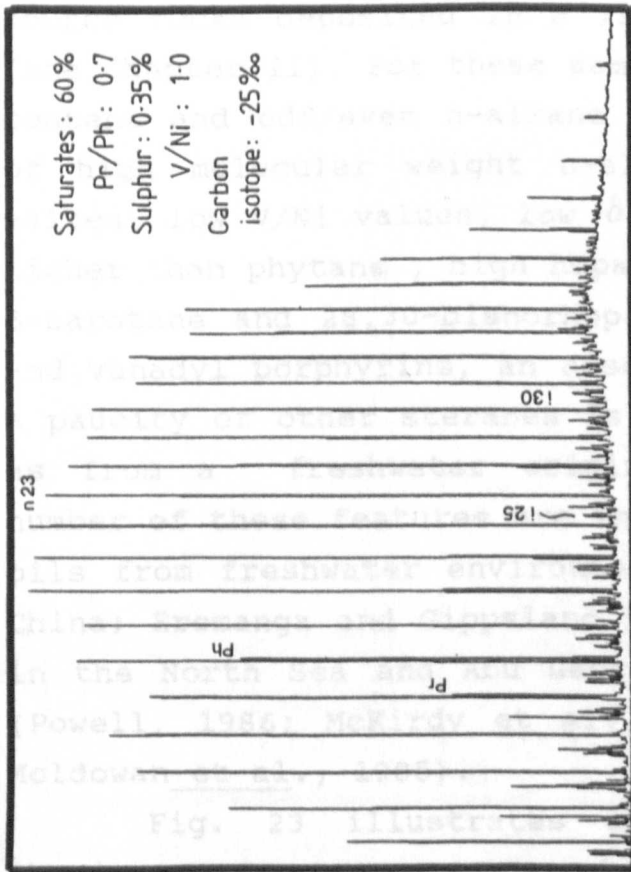


Fig. 2) Illustrates the correlation of source rock correlation using geochemical, isotopic, and elemental data, and m/z

elemental and, principally, biological marker properties. It is well recognised that variations in several molecular parameters occur mainly with an increase in maturity of the oils ($^{\circ}$ API), with the relative abundances and concentrations of specific compounds increasing or decreasing. In this study we only consider molecular properties which although, to some extent are maturity dependent, are principally source related. This approach was confirmed by biological marker data obtained from immature and mature samples of the source rocks that gave rise to the oils (Chapter II). In the following section each oil group defined above is discussed separately and correlated with the source rocks discussed in Chapter II.

3.3.1 Group I-lacustrine freshwater

Integration of the data given in Tables 1 and 2 and illustrated in Fig. 2-6 show, a set of bulk, elemental and molecular data for this group that suggests an origin from source rocks deposited in a lacustrine freshwater environment (see Chapter II). For these samples the association of high wax content and odd/even n-alkane predominance plus the abundance of high molecular weight n-alkanes ($> C_{23}$), low sulphur values, low V/Ni values, low $\delta^{13}C$ values (-28%), pristane higher than phytane, high hopane/sterane ratios, an absence of β -carotane and 28,30-bisnorhopane, trace or absence of nickel and vanadyl porphyrins, an absence of C_{30} regular steranes and a paucity of other steranes is sufficient to ascribe this oils as from a freshwater origin (see Chapter II). Indeed, a number of these features are in keeping with those reported for oils from freshwater environments, such as Songliao Basins in China; Eromanga and Gippsland Basins in Australia; Moray Firth in the North Sea and Abu Gabra and Unity Formations in Sudan (Powell, 1986; McKirdy et al., 1986; Mackenzie et al., 1984; Moldowan et al., 1985).

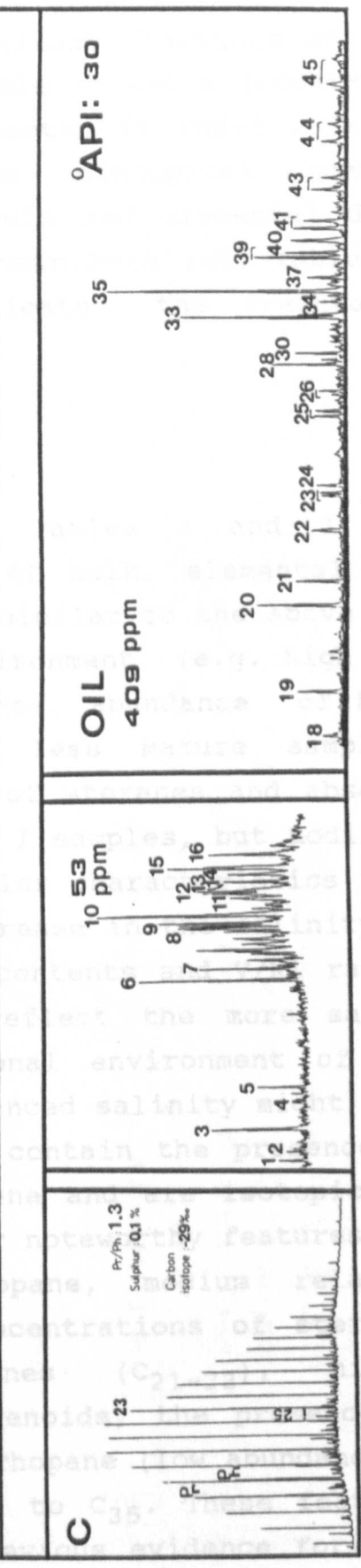
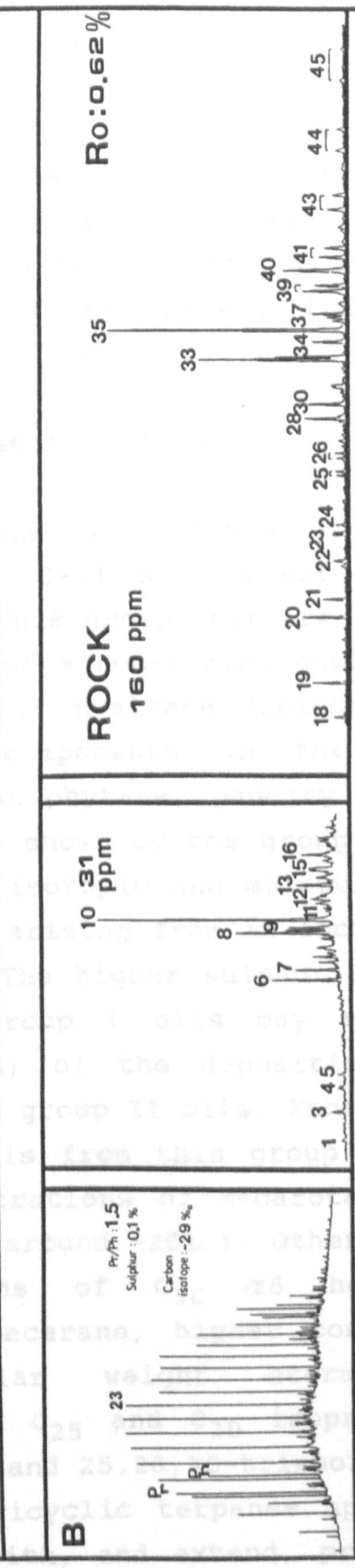
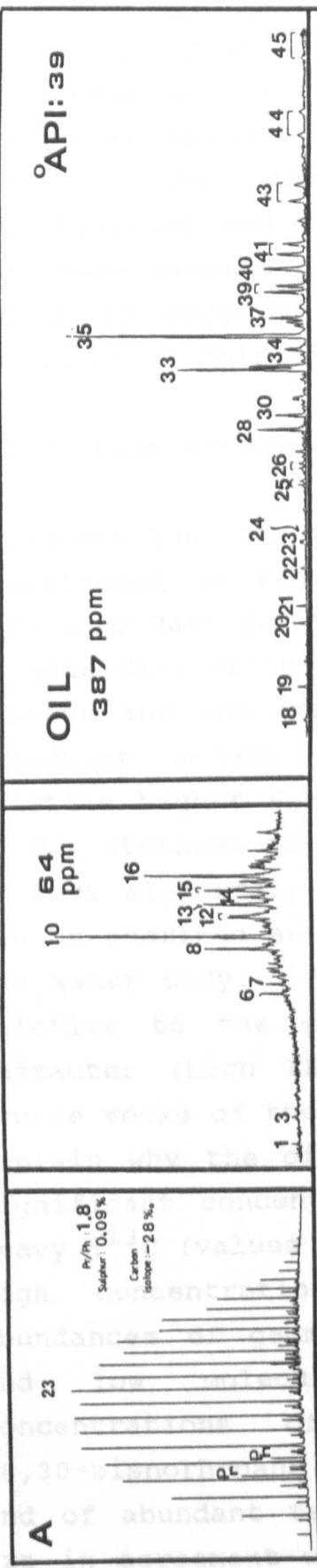
Fig. 23 illustrates an oil-source rock correlation, showing gas chromatograms, bulk and elemental data, and m/z

Figure 23- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for a lacustrine freshwater rock sample from Sergipe-Alagoas basin (sample B, CS-1) versus two typical samples, from group I oils from Ceará (sample A, CES-8) and Potiguar (sample C, RNS-53) basins (for peak assignments and quantitation see appendices I and II).

M/Z 191

M/Z 217

GC



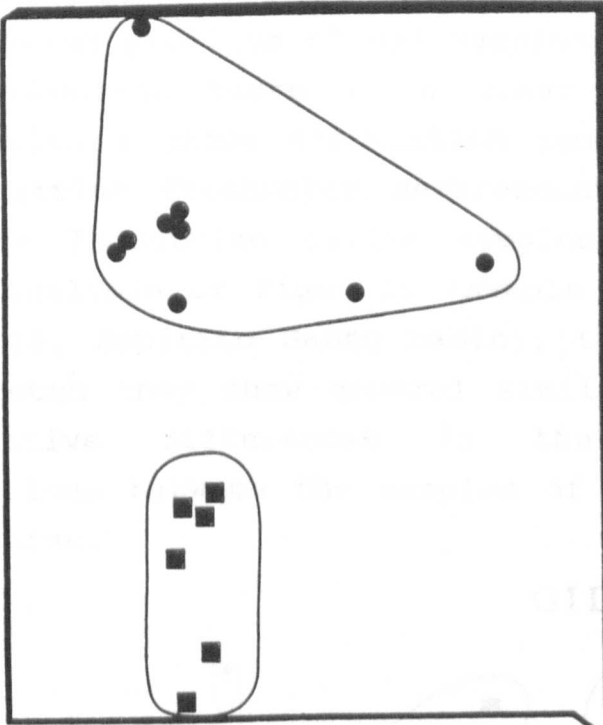
217 and 191 mass chromatograms of the alkane fractions of two oils (samples 1 and 5 in Fig. 1 and Table 1) and a lacustrine freshwater source rock discussed in Chapter II (CS-1). Taken overall, the similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and the others not shown here (cf. Tables 1 and 2 in Chapter II and here), indicate the freshwater character of this oil group.

3.3.2 Group II-Lacustrine saline.

Integration of the data given in Tables 2 and 3 and illustrated in Fig. 8-11 show a set of bulk, elemental and molecular data for this group that are similar to the above set of data diagnostic of a non-marine environment (e.g. high wax content and odd/even n-alkane dominance, abundance of high molecular weight components in the less mature samples, pristane higher than phytane, paucity of steranes and absence of C₃₀ steranes as shown by the group I samples, but modified by some elemental, isotopic and molecular characteristics that can be ascribed as arising from an increase in the salinity of the water body. The higher sulphur contents and V/Ni ratios relative to the group I oils may reflect the more saline character (high Eh) of the depositional environment of the source rocks of the group II oils. Enhanced salinity might also explain why the oils from this group contain the presence of significant concentrations of β -carotane and are isotopically heavy $\delta^{13}\text{C}$ (values around -25‰). Other noteworthy features are high concentrations of C₃₀ $\alpha\beta$ hopane, medium relative abundances of gammacerane, higher concentrations of steranes and low molecular weight steranes (C₂₁₋₂₂), higher concentrations of C₂₅ and C₃₀ isoprenoids, the presence of 28,30-bisnorhopane and 25,28,30-trisnorhopane (low abundances), and of abundant tricyclic terpanes up to C₃₅. These features are in agreement with, and extend, previous evidence for oils from lacustrine saline environments in China and the Green

Figure 24- Plot of principal component 1 versus principal component 2 for scores of biological markers elution profiles (metastable GC-MS) from oil samples derived from lacustrine freshwater and lacustrine saline water depositional environments on Brazilian marginal basins.

LACUSTRINE OILS



Component 1

FRESHWATER

SALINE WATER

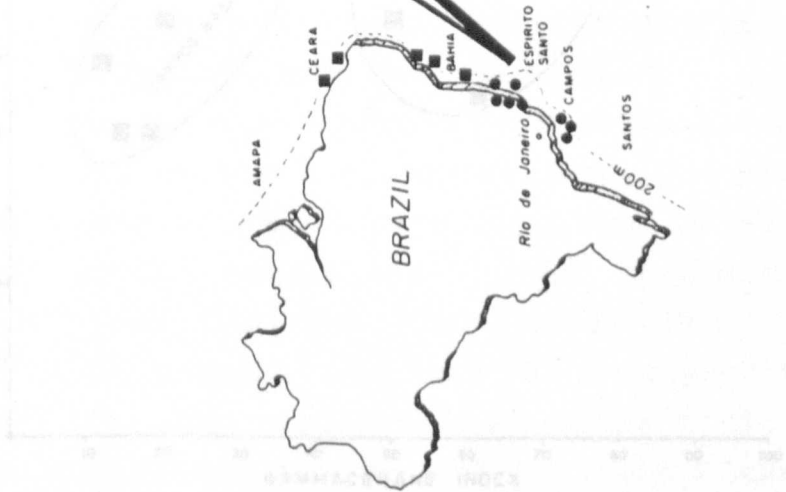


Figure 25- Plot of the differences between lacustrine saline oils from Campos and Espirito Santo basins, based on the variation in gammacerane index with pristane/phytane ratio (see appendix II).

River Formation (Reed, 1977; Powell, 1986; Shi Ji-Yang *et al.*, 1982; Jiang and Fowler, 1986). Hence, deposition of the source rocks that gave rise to the oils of this group is believed to have occurred in a saline lacustrine environment (see Chapter II). Fig. 24 illustrates a principal components plot modelled by comparing principal components obtained from the linked scan GC-MS elution profiles of oil samples from groups I and II. As can be observed there is a clear difference between both groups, with a close correlation among the oils derived from the lacustrine freshwater environment. The variance observed among the lacustrine saline samples can be explained by a careful analysis of Figs. 10 (sample 16, Campos basin) and 11 (sample 13, Espirito Santo basin), together with Figs. 25 to 27. Although they show general similarities, there are a few significant differences in the bulk and biological distributions between the samples of both Campos and Espirito Santo basins.

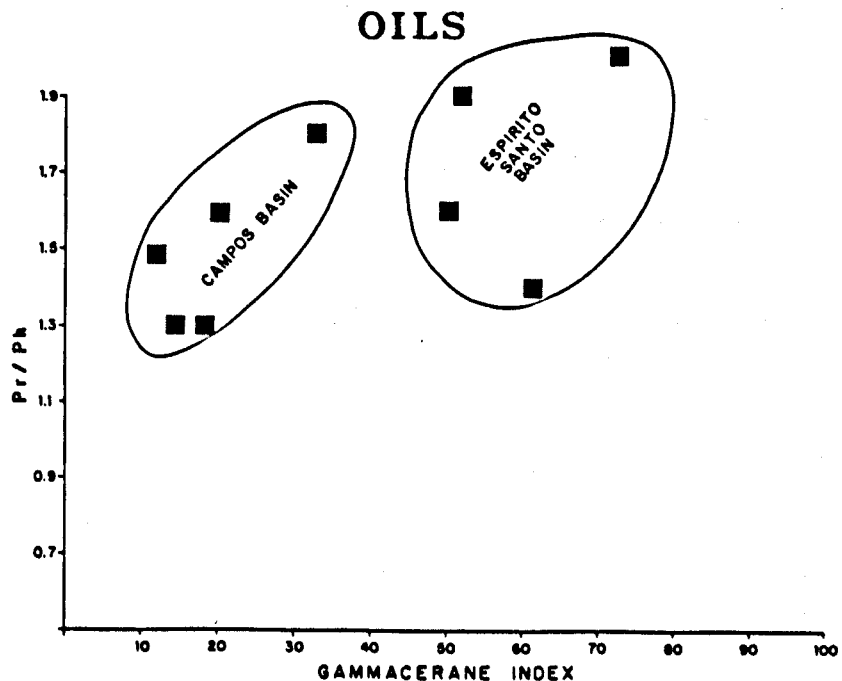


Figure 25- Plot of the differences between lacustrine saline oils from Campos and Espirito Santo basins, based on the variation in gammacerane index with pristane/ phytane ratio (see appendix II).

The most marked are the presence of higher concentrations of β -carotane, higher relative abundances of gammacerane (Fig. 25), lighter $\delta^{13}\text{C}$ values, and higher pristane/ phytane ratios (Figs. 25-27), and the presence of the Des-A C_{24} tetracyclic terpane in the oil samples from Espirito Santo basin. Indeed, similar results were observed among the organic-rich sediments from these basins discussed in Chapter II. This lends support to the idea put forward in Chapter II, that suggests an enhanced salinity together with a higher input of terrigenous organic matter in the environment of deposition of Espirito Santo source rocks.

Fig. 28 illustrates a principal components plot modelled by comparing principal components obtained from the linked scan GC-MS elution profiles of oil samples from group II. As can be observed there is also a clear difference between the samples from Campos and Espirito Santo basins, with a close correlation among the oils from the Campos basin. The variance observed among the samples from Espirito Santo basin (south and north) can be explained by an increase in higher plant input towards the north area of the basin (see Chapter II). The good correlation among the data from Figs. 24-27 with the results from Fig. 28 illustrates that principal component analysis can be useful in assess differences among oil families.

Figs. 29 and 30 shows an oil-source rock correlation, by way of gas chromatograms, bulk and elemental data, and m/z 217 and 191 mass chromatograms of the alkane fractions of samples from Campos (Fig. 29, A: oil sample 14; B: rock sample RJS-71 and C: oil sample 17) and Espirito Santo (Fig. 30, A: oil sample 13; B and C: rock samples IP-1 and RD-1 respectively) basins (see Chapter II). The similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and the others not shown here (cf. Tables 1 and 2 in Chapter II and this oil group), are clear, not only confirming the lacustrine saline character, but also showing the geochemical differences (e.g. see gammacerane (peak 40), $\delta^{13}\text{C}$, pristane/ phytane ratios and β -carotane)

between the samples from Campos and Espirito Santo basins (for more details see Chapters II and IV).

LACUSTRINE SALINE WATER
OILS FROM CAMPOS BASIN

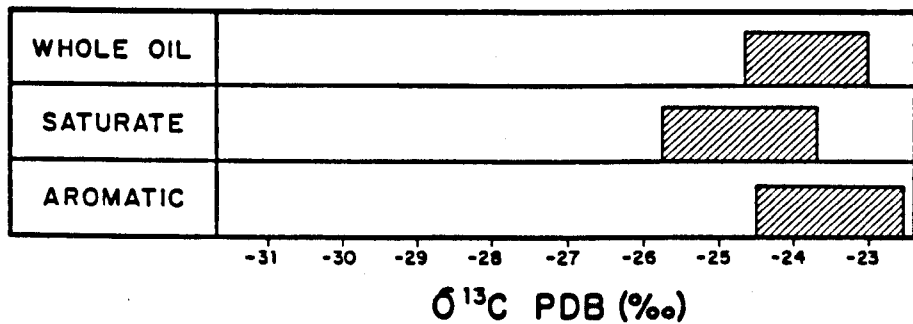


Figure 26- Variation of carbon isotopic data for whole oil and saturate and aromatic fractions for oils from the Campos basin.

LACUSTRINE SALINE LAKE
ESPIRITO SANTO BASIN

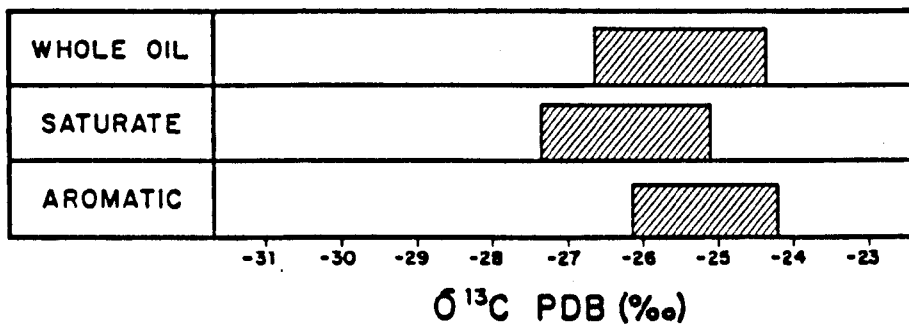


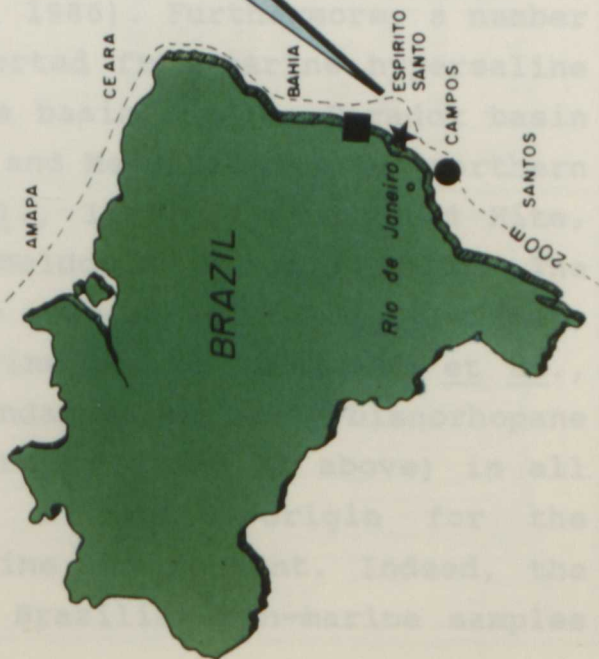
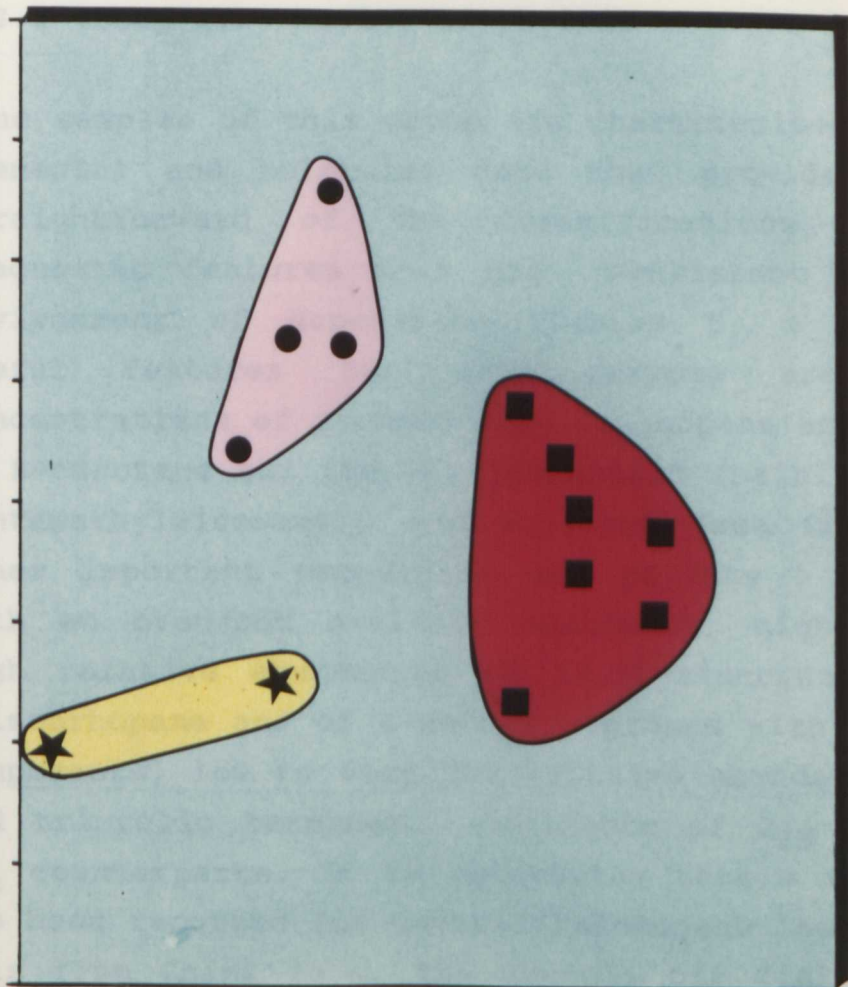
Figure 27- Variation of carbon isotopic data for whole oil and saturate and aromatic fractions for oils from the Espirito Santo basin.

Figure 28- Scores of biological marker data from oils derived from lacustrine saline water environment from Campos and Espirito Santo basins on principal component 1 versus scores on principal component 2 (for details see "Introduction in Chapter II).

LACUSTRINE SALINE WATER OILS

Component 2

Component 1



3.3.3 Group III- Marine Evaporitic

The samples of this group are characterised by a set of bulk, elemental and molecular data that provide perhaps the most straightforward of the classifications, since they have diagnostic features that are consistent with a hypersaline environment of deposition (Tables 5, 6 and Figs. 13-16). Useful features for this purpose are the very high concentrations of gammacerane, C₃₀ hopane and steranes, as well as β-carotane and the C₂₅ isoprenoid (mainly the 2.6.10.14.18-pentamethyleicosane), and squalane (see Chapter II and IV). Other important properties are phytane > pristane sometimes with an even/odd n-alkane dominance, high sulphur contents, high relative abundances of 28,30-bisnorhopane and 25,28,30-trisnorhopane and of 4-methyl steranes with a dominance of C₃₀ components, low to very low relative abundances of diasteranes and tricyclic terpanes, dominance of C₃₅ hopanes over their C₃₄ counterparts. It is noteworthy that a similar set of data has been reported for several Palaeogene lacustrine hypersaline oils from China (e.g. the Shengli oil field; Shi Ji-Yang *et al.*, 1982; the Jiangnan Basin; Fu Jiamo *et al.*, 1986 and Kelamayi oilfield; Jiang & Fowler, 1986). Furthermore, a number of similar results have been reported from marine hypersaline (evaporitic) oils in the Tarragona basin, Spain; Paradox basin (Utah), USA; Prinos basin, Greece and Messinian basin (northern Apennines), Italy (Albaiges *et al.*, 1986; Peterson and Hite, 1969; ten Haven *et al.*, 1987; Moldowan *et al.*, 1985). The presence, although in low relative abundances, of C₃₀ steranes, held to be an indicator of a marine source (Moldowan *et al.*, 1985), together with the high abundances of 28,30-bisnorhopane and 25,28,30-trisnorhopane (cf. groups I and II above) in all the Brazilian samples, suggest a marine origin for the establishment of such a hypersaline environment. Indeed, the C₃₀ steranes are absent from the Brazilian non-marine samples (groups I and II).

Figure 29- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for a lacustrine saline water source rock (sample B, RJS-71) versus two typical samples, from group II oils from Campos (sample A, RJS-305; sample C, RJS-139) basin (for peak assignments and quantitation see appendices I and II).

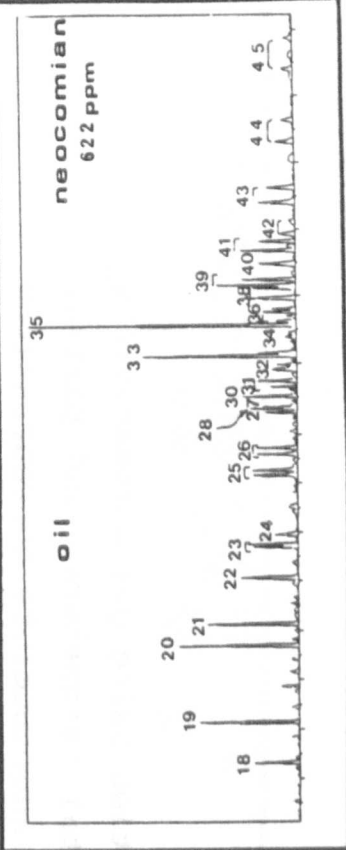
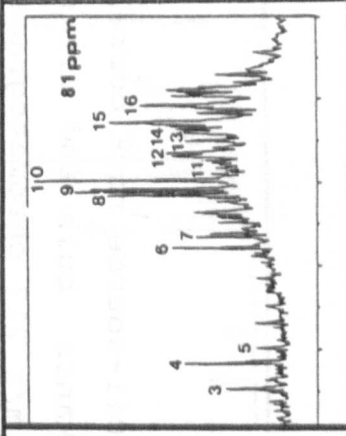
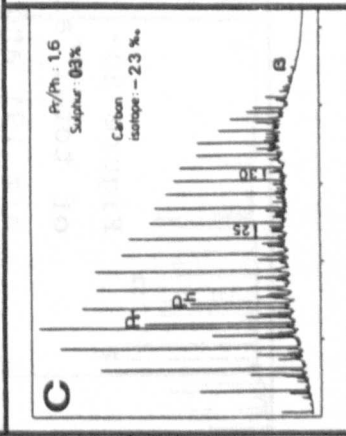
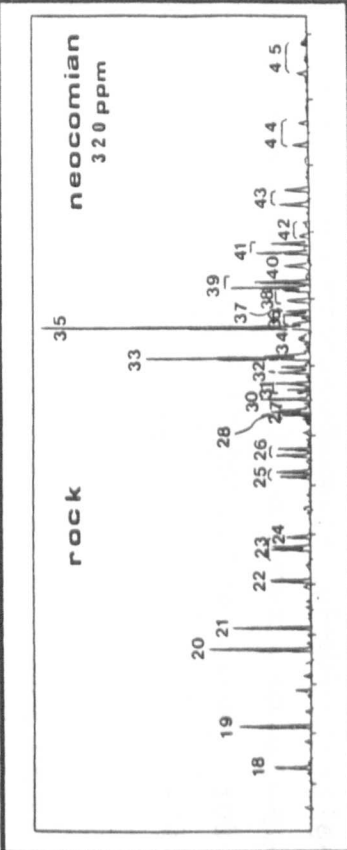
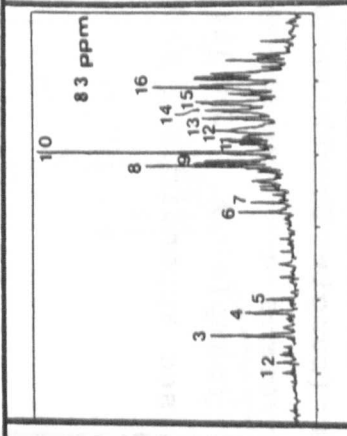
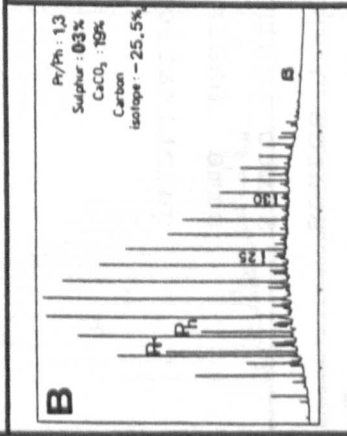
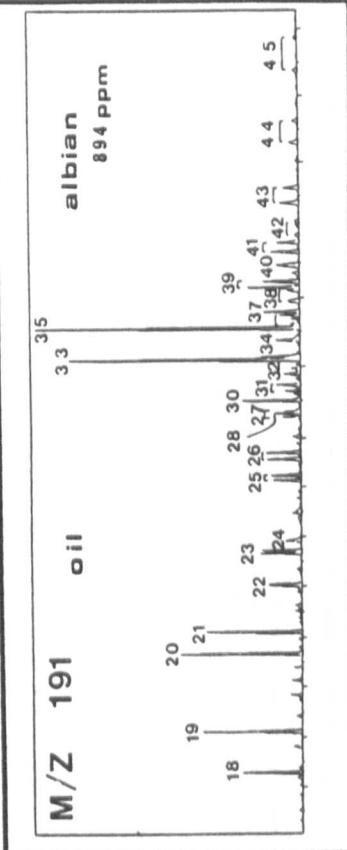
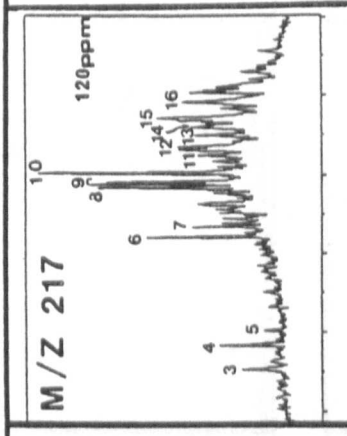
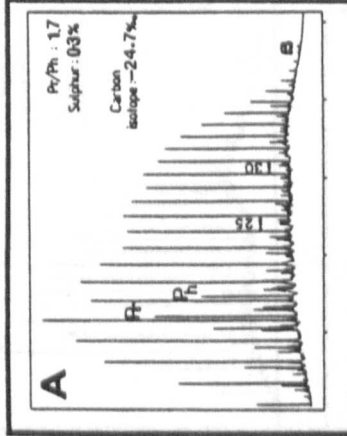
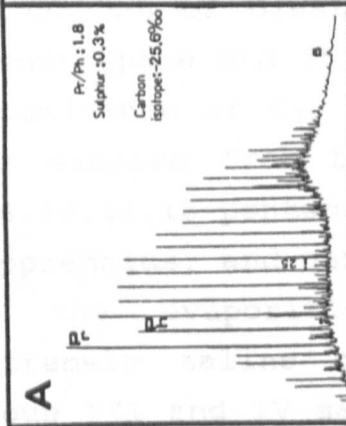


Figure 30- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for two typical lacustrine saline water source rocks (sample B, IP-1; sample C, RD-1) from Espirito Santo basin versus a typical group II oil sample from the same basin (sample A, SM-35; for peak assignments and quantitation see appendices I and II).

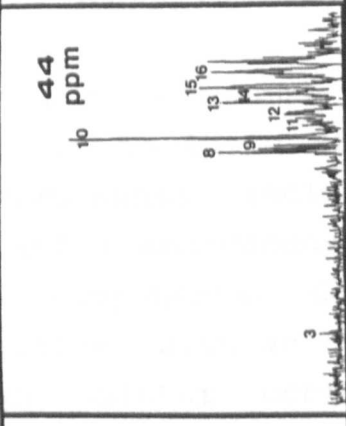
GC

M/Z 217

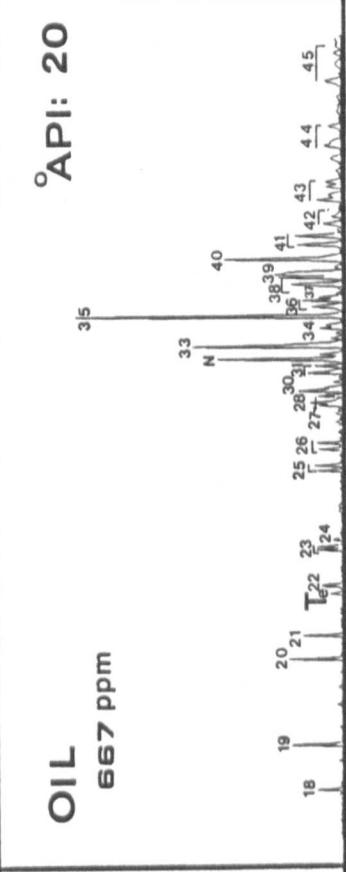
M/Z 191



Pr/Ph: 1.8
Sulphur: 0.3%
Carbon isotope: -25.6‰

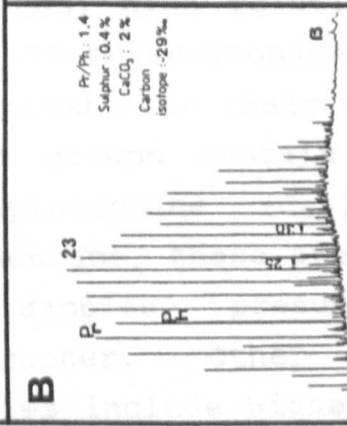


Pr/Ph: 1.4
Sulphur: 0.4%
CaCO₃: 2%
Carbon isotope: -29‰



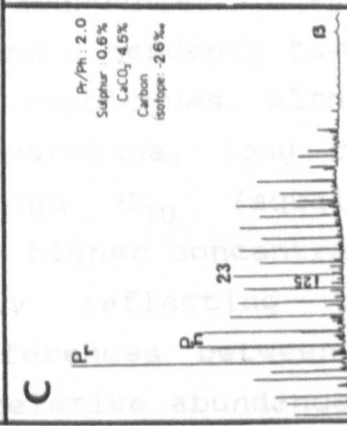
OIL
667 ppm

°API: 20

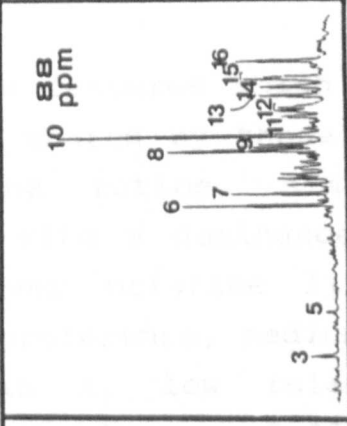


ROCK
1466 ppm

Ro: 0.63%



Pr/Ph: 2.0
Sulphur: 0.6%
CaCO₃: 4.5%
Carbon isotope: -2.6‰



ROCK
445 ppm

R: 0.66%

Fig. 31 illustrates an oil-source rock correlation, showing gas chromatograms, bulk and elemental data, and m/z 217 and 191 mass chromatograms of the alkane fractions of two oils (samples 22 and 23 in fig. 1 and Table 1) and a marine evaporitic source rock discussed in Chapter II (CES-41). The similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and the others not shown here (cf. Tables 1 and 2 in Chapter II and this oil group), are clear, thus confirming the marine evaporitic character of this oil group. Fig. 32, illustrates the use of linked scan GC-MS elution profiles (used in the multivariate study in this work; see Chapter II), in oil-source rock correlation, for samples A and B of Fig. 31. As can be observed there is a good match of the pattern distribution and a reasonable match for the concentrations for the biological parameters arising from the m/z 191, 217 and 231 mass chromatograms for both samples.

3.3.4 Group IV - Marine Carbonate

In some respects the group IV oils show features which are similar to those of group III. Features shared by these two environments include; low hopane/sterane ratios, similar relative abundances of 4-methyl steranes with a dominance of C₃₀ components, dominance of phytane over pristane linked sometimes with an even over odd n-alkane preference, medium to high sulphur contents, Ts/Tm less than 1, low relative abundances of diasteranes, high relative abundances of 28,30-bisnorhopane and 25,28,30-trisnorhopane, and a tendency towards a dominance of C₃₅ hopanes over their C₃₄ homologues. Although the samples from both groups contain β-carotane, long chain 2.6.10.14.18-pentamethyleicosane (C₂₅) and C₃₀ (squalane) isoprenoids, and gammacerane, these are in higher concentration in the evaporitic samples, presumably reflecting their extremely saline character. Other differences between the group III and IV samples include higher relative abundances of C₃₀ regular steranes, and tricyclic terpanes up to C₃₅, but

Figure 31- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for a marine evaporitic source rock (sample B, CES-41) versus two typical samples, from group III oils from Cear basin (sample A, CES-41; sample C, CES-8; for peak assignments and quantitation see appendices I and II).

M/Z 191

M/Z 217

GC

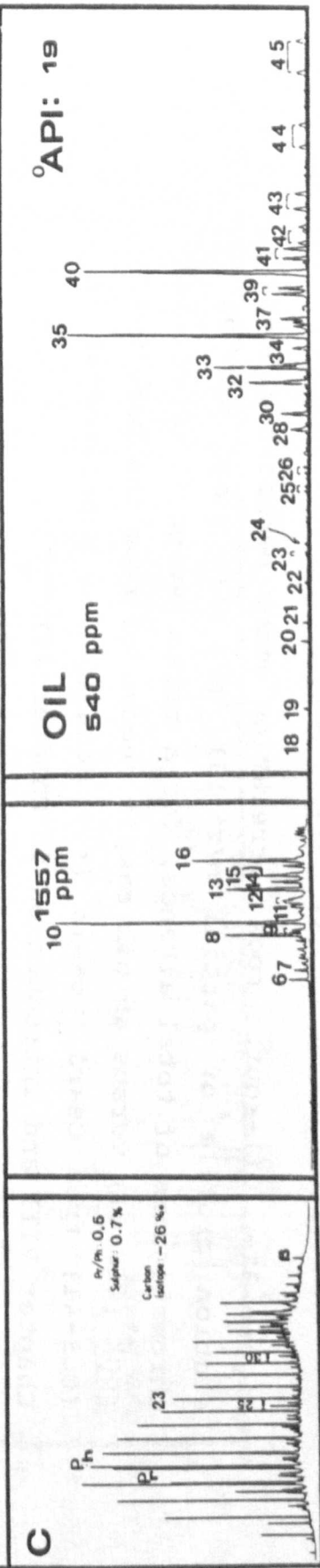
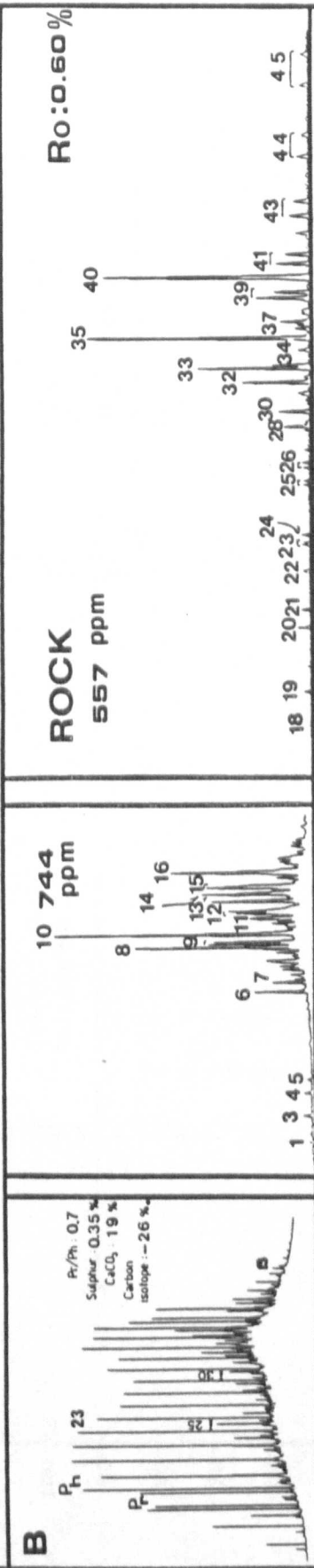
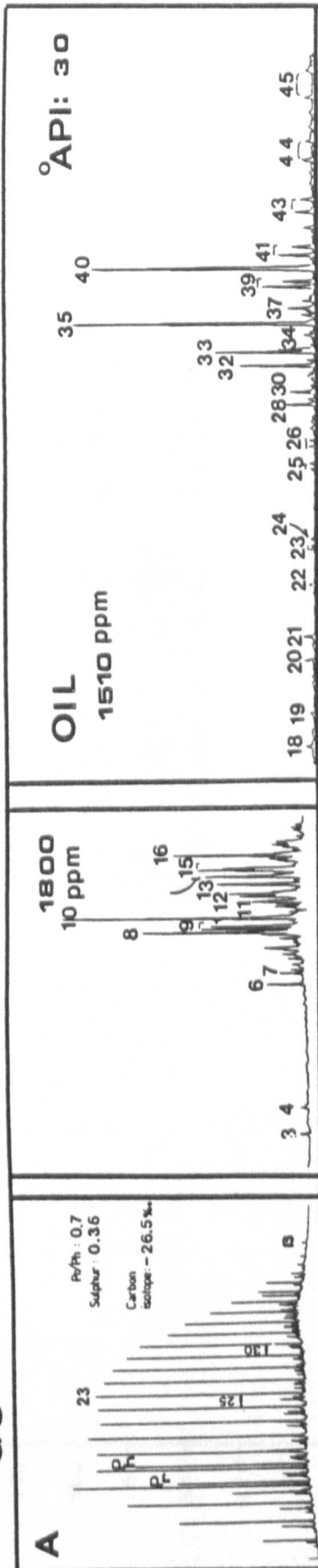
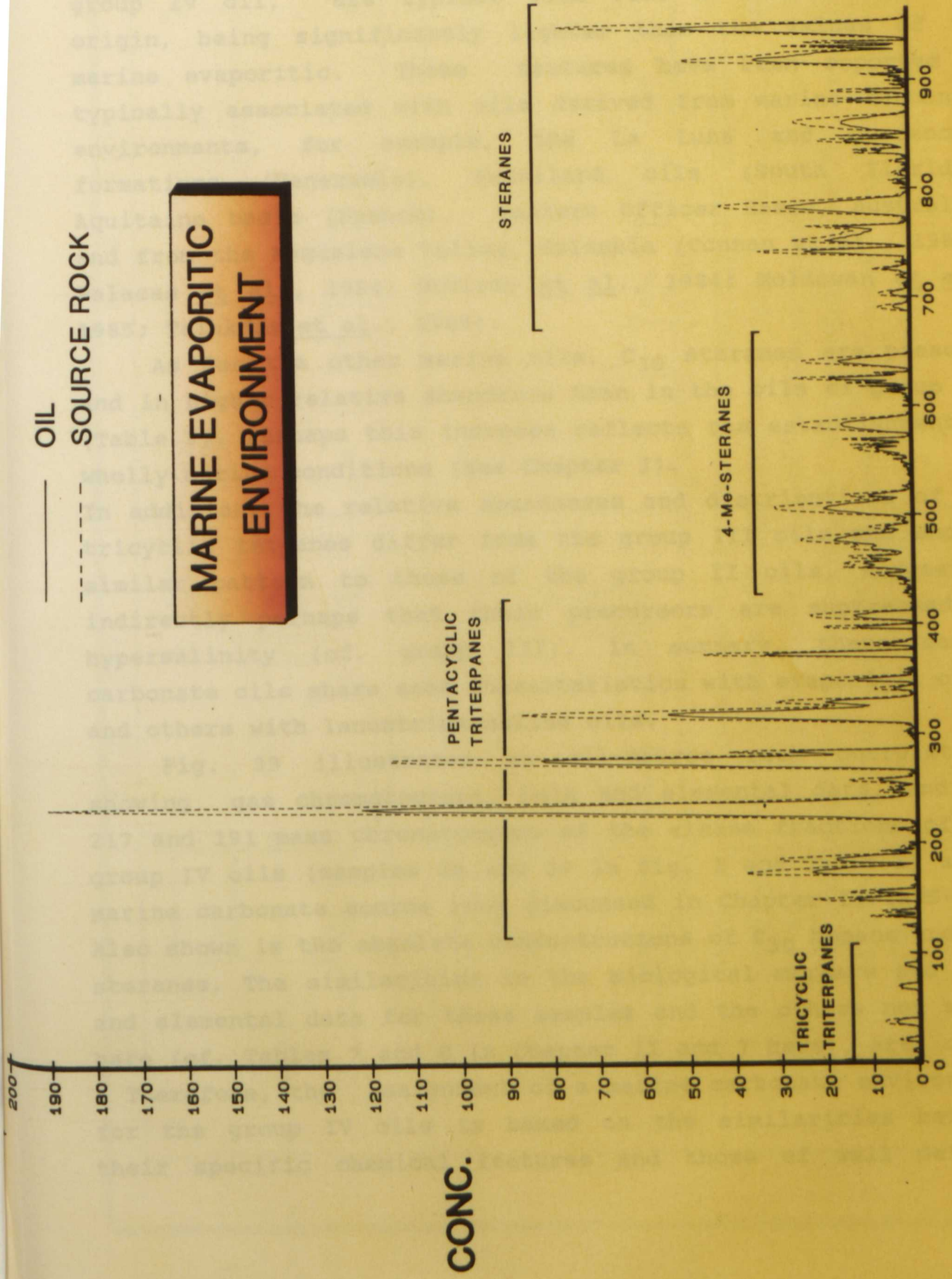


Figure 32- Oil-source rock correlation using metastable GC-MS elution profile of partial m/z 191, m/z 231 and m/z 217 chromatograms of total alkanes, for a marine evaporitic source rock (CES-41) versus an oil sample recovered from the same well (CES-41) from Ceará basin (for details see Experimental in Chapter VIII and Introduction in Chapter II).

— OIL
- - - SOURCE ROCK

MARINE EVAPORITIC ENVIRONMENT



VARIABLES

CONC.

lower C_{30} $\alpha\beta$ hopane and sterane concentrations (Tables 7 and 8 and Figs. 18 and 19) in the group IV. The $\delta^{13}C$ values for the group IV oil, are typical from oils of marine carbonate origin, being significantly lighter than the values of the marine evaporitic. These features have been reported as typically associated with oils derived from marine carbonate environments, for example, the La Luna and Querencual formations (Venezuela), Sunniland oils (South Florida), Aquitaine basin (France), Eastern Officer Basin, Australia, and from the Magdalena Valley, Colombia (Connan *et al.*, 1983; Palacas *et al.*, 1984; McKirdy *et al.*, 1984; Moldowan *et al.*, 1985; Talukdar *et al.*, 1986).

As for the other marine oils, C_{30} steranes are present, and in higher relative abundance than in the oils of group III (Table 3). Perhaps this increase reflects the establishment of wholly marine conditions (see Chapter I).

In addition, the relative abundances and distributions of the tricyclic terpanes differ from the group III oils and show a similar pattern to those of the group II oils, suggesting indirectly perhaps that their precursors are suppressed by hypersalinity (cf. group III). In summary, these marine carbonate oils share some characteristics with evaporitic oils, and others with lacustrine saline oils.

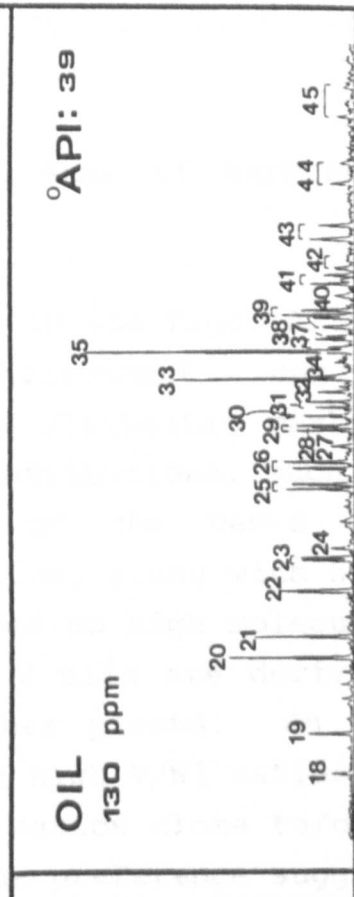
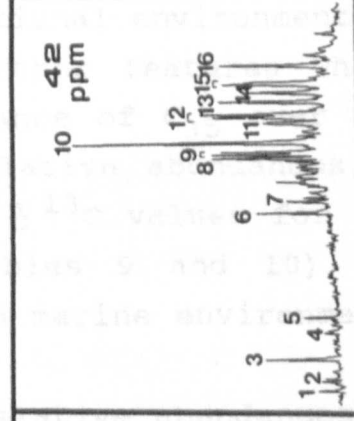
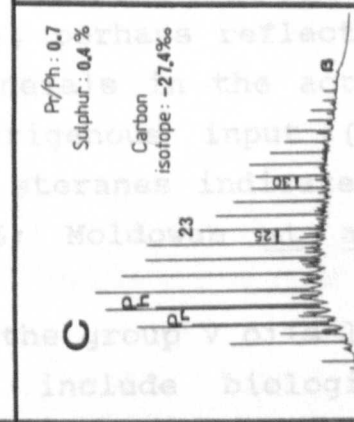
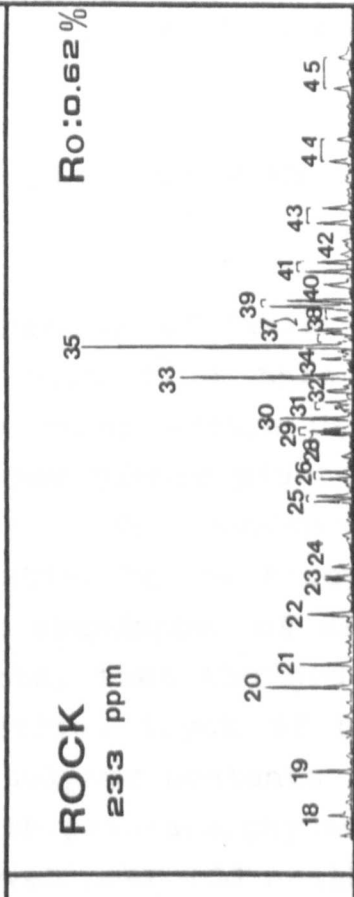
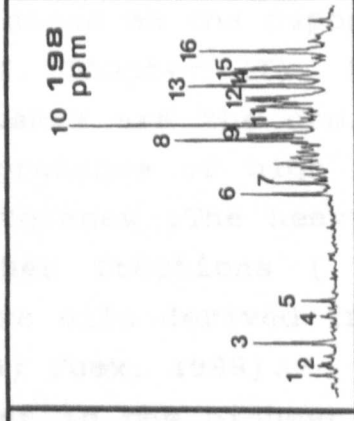
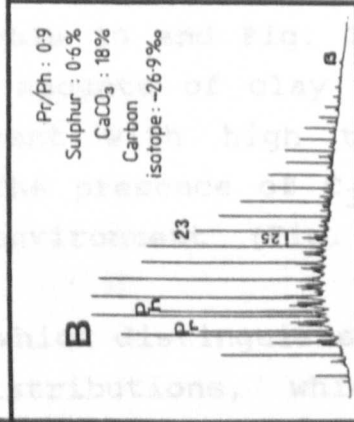
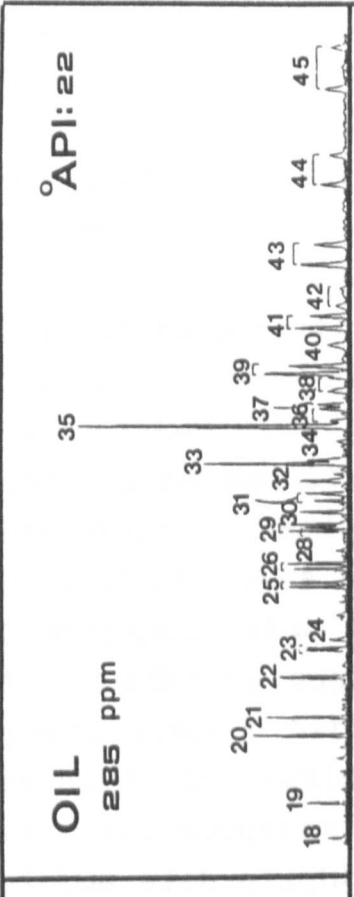
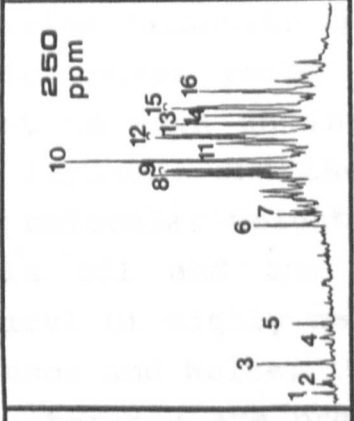
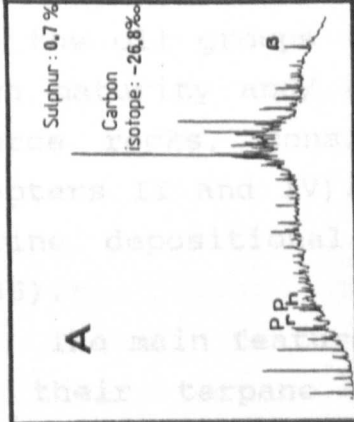
Fig. 33 illustrates an oil-source rock correlation, showing gas chromatograms, bulk and elemental data, and m/z 217 and 191 mass chromatograms of the alkane fractions of two group IV oils (samples 28 and 29 in Fig. 1 and Table 1) and a marine carbonate source rock discussed in Chapter II (APS-31). Also shown is the absolute concentrations of C_{30} hopane and C_{27} steranes. The similarities in the biological markers and bulk and elemental data for these samples and the others not shown here (cf. Tables 7 and 8 in Chapter II and 7 here), are clear. Therefore, the assignment of a marine carbonate environment for the group IV oils is based on the similarities between their specific chemical features and those of well defined

Figure 33- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for a marine carbonate source rock from Cassiporé basin (sample B, APS-31) versus two samples from group IV oils from Cassiporé (sample A, APS-27) and Maranhão (sample C, MAS-5) basins (for peak assignments and quantitation see appendices I and II).

M/Z 191

M/Z 217

GC



carbonate oils (see above), and confirmed by oil-source rock correlations.

3.3.5 Group V - Marine Deltaic with influence of carbonate lithology

The integration of the results of Tables 9, 10 and Figs. 21 and 22 indicate that the oils from this environment can be differentiated from the other groups using diagnostic markers thought to be specific for higher plant contributions, such as 18 α (H)-oleanane and of high abundances of the Des-E C₂₄ tetracyclic terpane relative to the tricyclics, along with high waxy contents. Also the abundance of medium to high molecular weight n-alkanes suggests, that the group V oils are derived, in part, from a terrestrial input of higher plants. On the other hand, the medium sulphur contents and high V/Ni ratios of these oils, together with pristane/phytane ratios close to/or < 1, linked with slight even over odd n-alkane preference suggest a marine carbonate influence on the depositional environment of their source rocks (cf. Chapter II). Further features which point to such an influence are the dominance of C₃₅ over the C₃₄ hopanes, and the presence of high relative abundances of low molecular weight steranes. The heavy $\delta^{13}\text{C}$ values for the whole oil and the other fractions (Tables 9 and 10) are typical of highly mature oils derived from marine environments (Tissot and Welte, 1984; Fuex, 1988).

Diasteranes are present in the highest relative abundances of all the oil groups (Table 10 and Fig. 22), perhaps reflecting high maturity and/or amounts of clay minerals in the actual source rocks, consistent with high terrigenous input (cf. Chapters II and IV). The presence of C₃₀ steranes indicates a marine depositional environment (Fig. 6; Moldowan *et al.*, 1985).

The main feature which distinguishes the group V oils lies in their terpane distributions, which include biological markers diagnostic of higher plant inputs, notably high

abundances of $18\alpha(H)$ -oleanane and the occurrence of high abundances of the C_{24} -tetracyclic terpane relative to the tricyclic terpane. These compounds have been reported in high relative abundances in oils derived from deltaic environments such as, the Tertiary Niger delta (Hills and Whitehead, 1966; Ekweozor *et al.*, 1979a), the Mahakam delta in Indonesia (Schoell *et al.*, 1983; Grantham *et al.*, 1983; Hoffmann *et al.*, 1984; the Beaufort-Mackenzie delta in Canada (Brooks, 1986), and Congo delta, Angola basin (Connan *et al.*, 1988). Hence, the presence of high abundances of $18\alpha(H)$ -oleanane and the C_{24} tetracyclic terpane in the group V oils, with an abundance of high molecular weight n-alkanes indicates their deltaic origin. In addition, these oils possess other geochemical characteristics consistent with an origin from source rocks deposited during the development of a marine deltaic system over a carbonate platform. Fig. 34 illustrates an oil-source rock correlation, showing gas chromatograms, bulk and elemental data, and m/z 217 and 191 mass chromatograms of the alkane fractions of two group V oils (samples 30 and 31 in Fig. 1 and Table 1) and a marine deltaic with carbonate influence source rock discussed in Chapter II (APS-36). Also shown is the absolute concentrations of C_{30} hopane and C_{27} steranes. The similarities in the biological marker distributions and concentrations and bulk and elemental data for these samples and the other not shown here (see MAS-10 in Chapter II), are clear and lend support to the assignment of a marine deltaic environment with carbonate influence for the depositional environment of the source rocks given the group V oils.

3.4 CONCLUSIONS

This investigation shows the potential value of a combined geochemical, statistical and biological marker approach (pattern distribution and concentration), using only oil samples, in the assessment and differentiation of the palaeoenvironment of deposition of their source rocks. The

Figure 34- Oil-source rock correlation using gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 and m/z 217 chromatograms, and absolute concentrations of steranes and hopane for a marine deltaic with carbonate influence source rock from Cassiporé basin (sample B, APS-36) versus two samples from group V oils from Pará basin (sample A, PAS-11; sample C, PAS-9; for peak assignments and quantitation see appendices I and II).

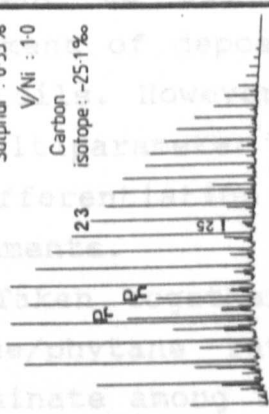
M/Z 191

M/Z 217

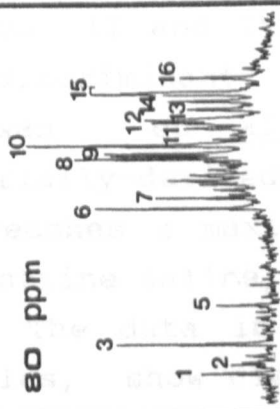
GC

A

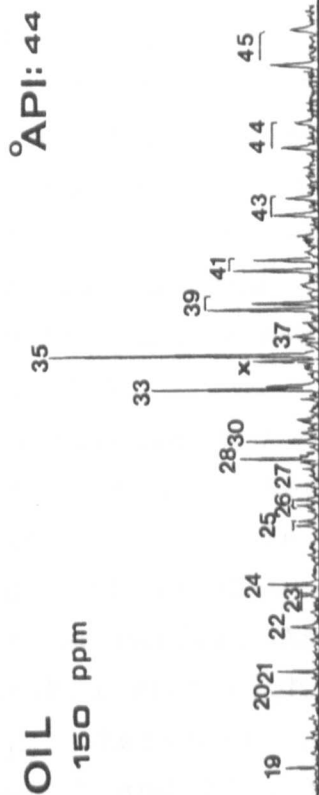
Pr/Ph : 1.1
Sulphur : 0.35%
V/Ni : 1.0
Carbon
isotope : -25.1‰



80 ppm



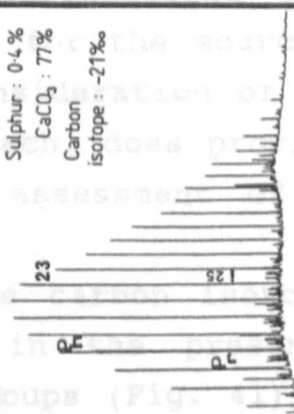
OIL
150 ppm



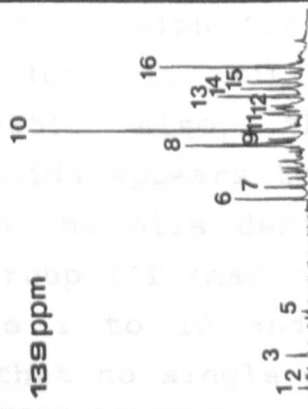
°API: 44

B

Pr/Ph : 0.7
Sulphur : 0.4%
CaCO₃ : 77%
Carbon
isotope : -21‰

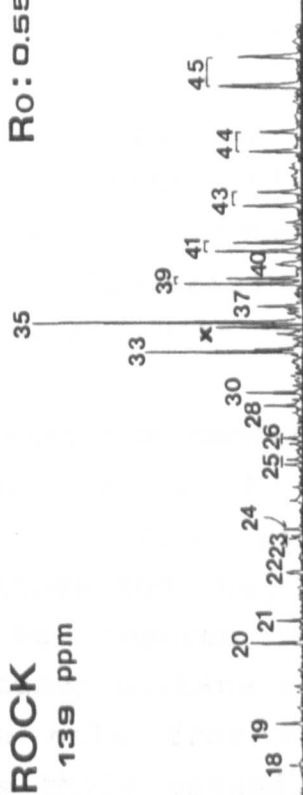


139 ppm



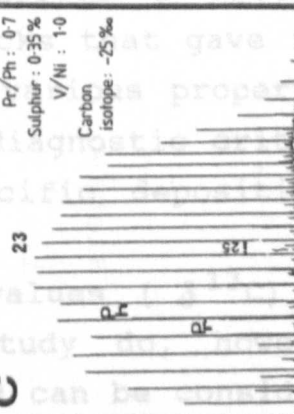
ROCK
139 ppm

Ro: 0.55%

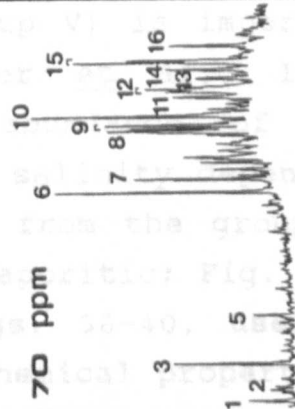


C

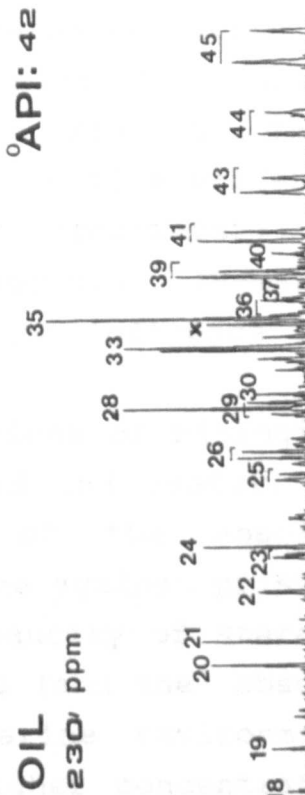
Saturates : 60%
Pr/Ph : 0.7
Sulphur : 0.35%
V/Ni : 1.0
Carbon
isotope : -25‰



70 ppm



OIL
230 ppm



°API: 42

results (Tables 1-10; Figs. 1-34) reveal differences within the oil samples investigated from Brazilian marginal basins enabling their classification into five groups (Fig. 35). These groups correlate with source rocks laid down in five different depositional regimes; namely, I-lacustrine freshwater; II-lacustrine saline water; III-marine evaporitic; IV-marine carbonate, and V-marine deltaic with carbonate influence (see Chapter II).

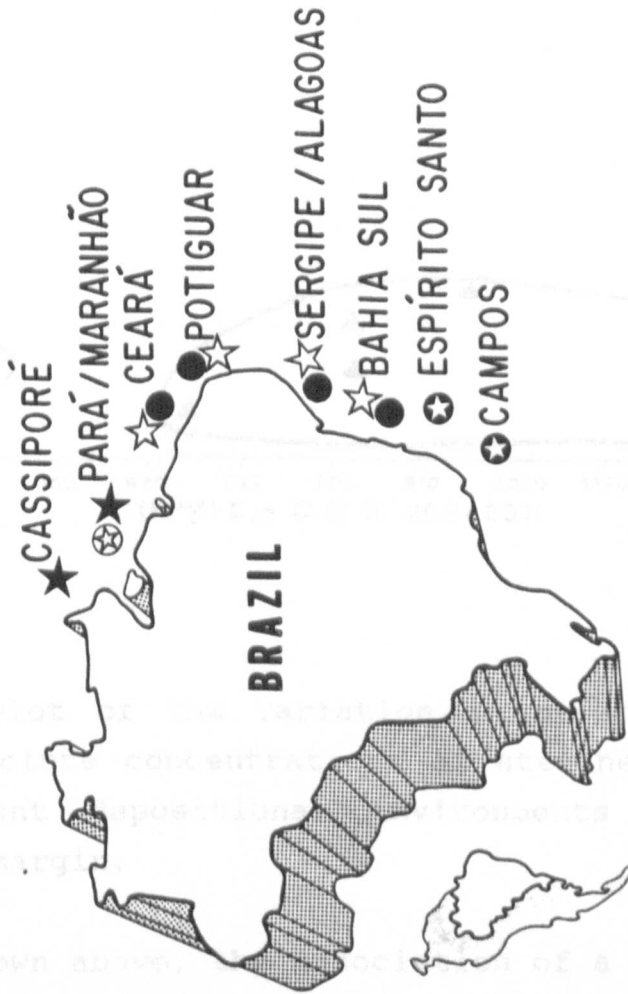
A quantitative approach using the concentrations of biological marker compounds has been shown to be valid and useful. For example, Figs. 36 and 37 show plots of the absolute concentrations of C_{27} steranes and C_{30} hopane against pristane / phytane ratios. As can be observed, the paucity of steranes associated with high pristane/ phytane ratios (and the absence of C_{30} steranes) in the oils from non-marine environments (groups I and II), versus their markedly higher concentration and lower pristane / phytane ratios in the marine-related ones (groups III and IV; see discussion for group V) is important and discriminant (Fig. 36; cf. Rullkötter et al., 1984; Moldowan et al., 1985). Also, the abundance of the bacterially-derived hopanoids appears to be salinity dependent and reaches a maximum in the oils derived from the group II (lacustrine saline) and group III (marine evaporitic; Fig. 37).

The data in Tables 1 to 10 and Figs. 38-40, used as examples, show clearly that no single geochemical property is sufficient to suitably characterise and assess a specific environment of deposition for the source rocks that gave rise to the oils. However, consideration of the various properties in a multiparameter approach, does provide diagnostic criteria for differentiation and assessment of specific depositional environments.

Taken together, the carbon isotope values ($\delta^{13}C$) and pristane/phytane ratios in the present study do, however, discriminate among the groups (Fig. 41), and can be considered a useful geochemical measure for the differentiation of non-

Figure 35- Location map of the Brazilian marginal basins showing the distribution of the oil samples investigated in accordance with the proposed depositional environment of the source rocks.

OIL TYPES



ENVIRONMENTS

- MARINE DELTAIC
- ★ MARINE CARBONATE
- ☆ EVAPORITIC
- ⊗ SALINE LAKE
- LACUST. FRESH WATER

marine and marine related oils found in the Brazilian marginal basins.

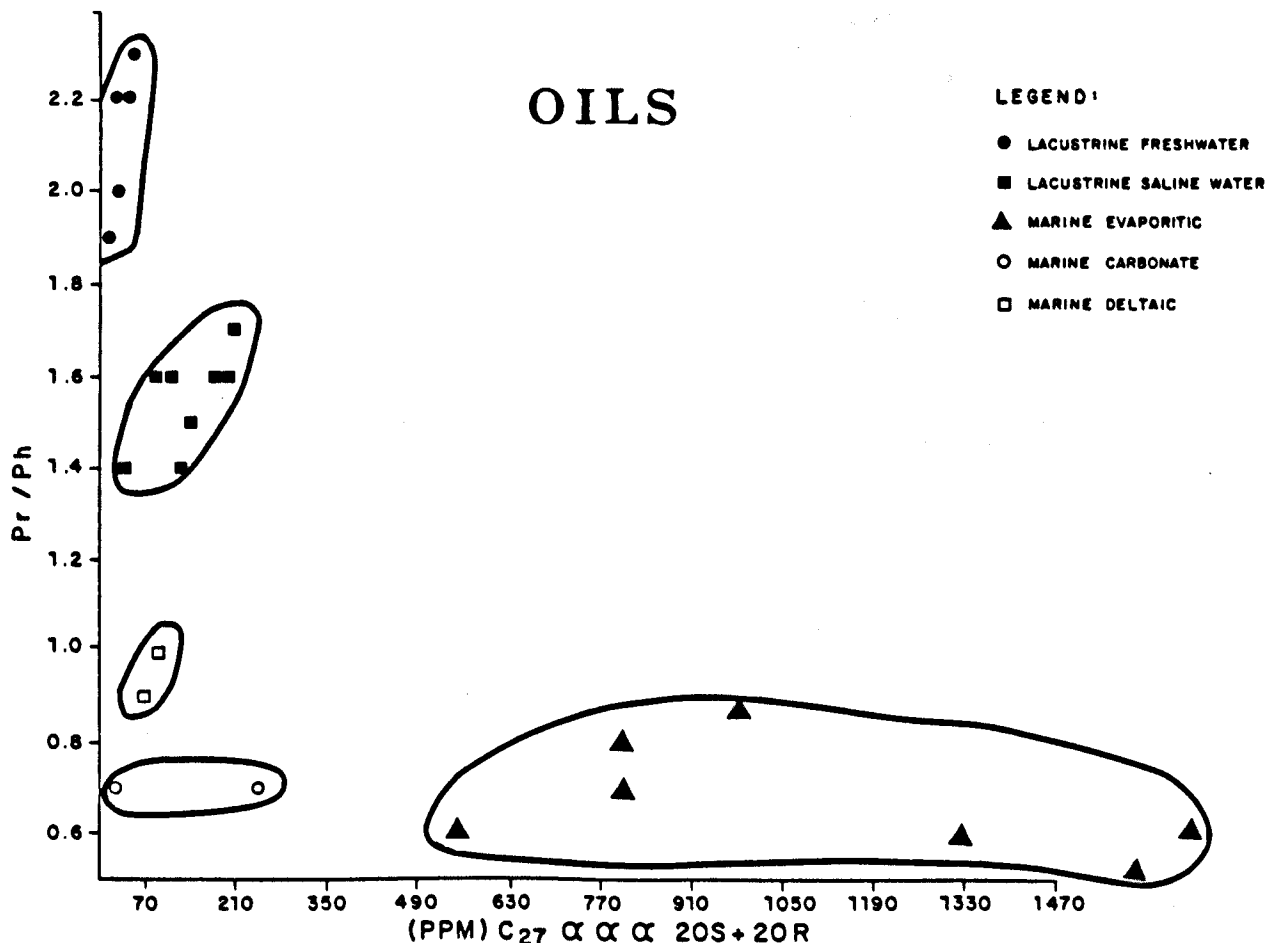


Figure 36- Plot of the variation in pristane/ phytane ratio with the absolute concentrations of steranes for oils derived from different depositional environments in the Brazilian continental margin.

As shown above, the association of a high wax content, a abundant high molecular weight n-alkanes, low sulphur and V/Ni values, light $\delta^{13}\text{C}$ values, high pristane/phytane ratios, an absence of C_{30} steranes and a paucity of the other steranes discriminates the lacustrine freshwater environment (group I).

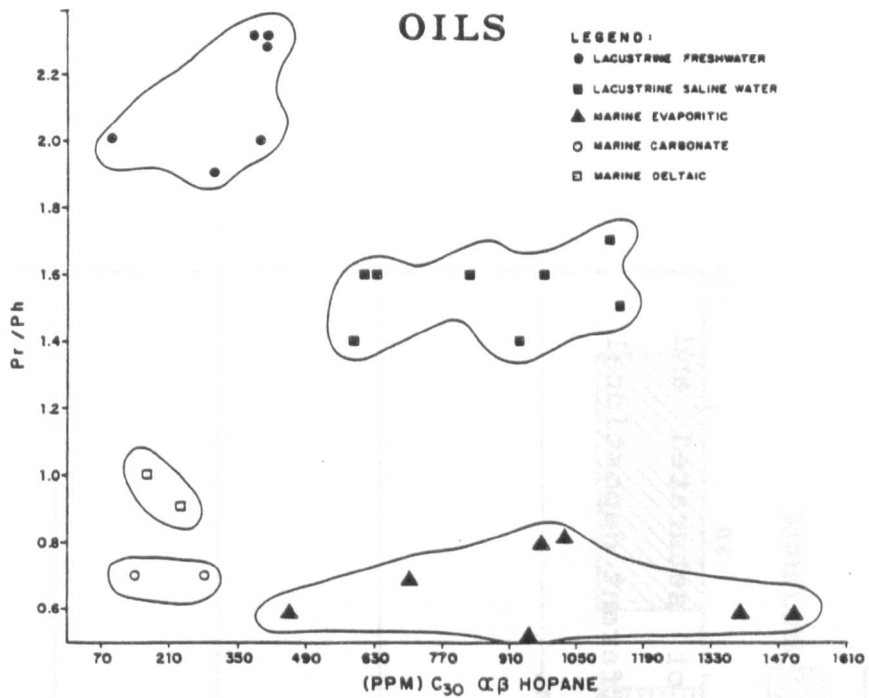


Figure 37 - Plot of the variation in pristane/ phytane ratio with the absolute concentrations of C₃₀ αβ hopane for oils derived from different depositional environments in the Brazilian continental margin.

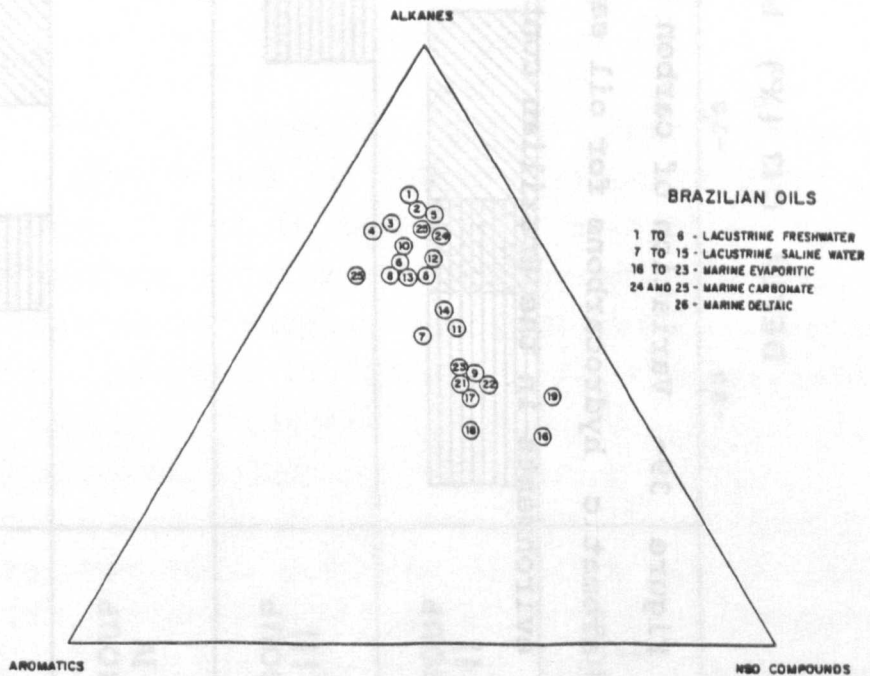
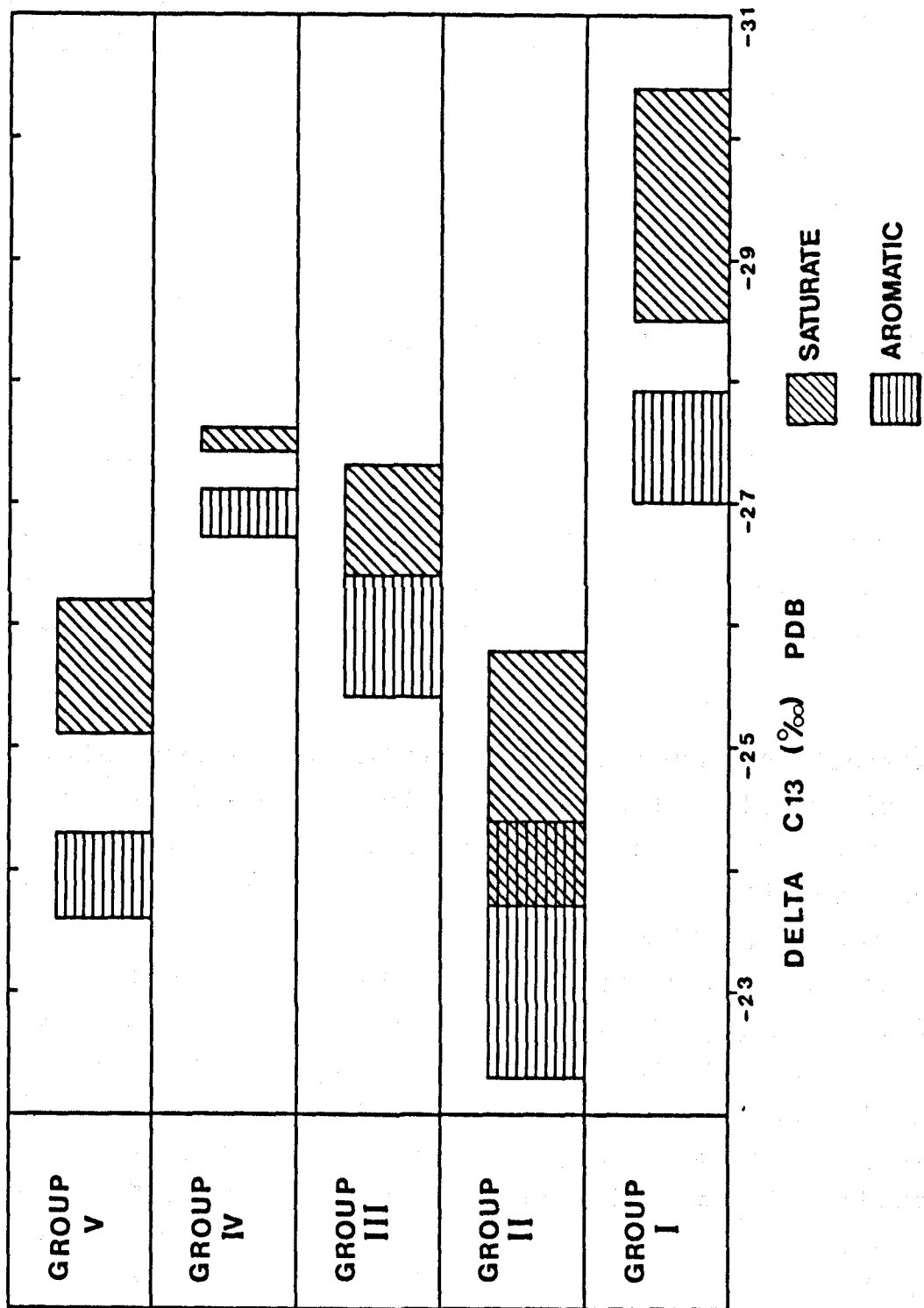


Figure 38- Relative abundance of alkanes, aromatics and NSO compounds in oil samples derived from different depositional environments in the Brazilian continental margin.

Figure 39- Variation of carbon isotopic data of saturated and aromatic hydrocarbons for oil samples from different depositional environments in the Brazilian continental margin.



BRAZILIAN OILS

- 1 TO 6 - LACUSTRINE FRESH WATER
 7 TO 15 - LACUSTRINE SALINE WATER
 16 TO 22 - MARINE EVAPORITIC
 23 AND 24 - MARINE CARBONATE
 25 - MARINE DELTAIC

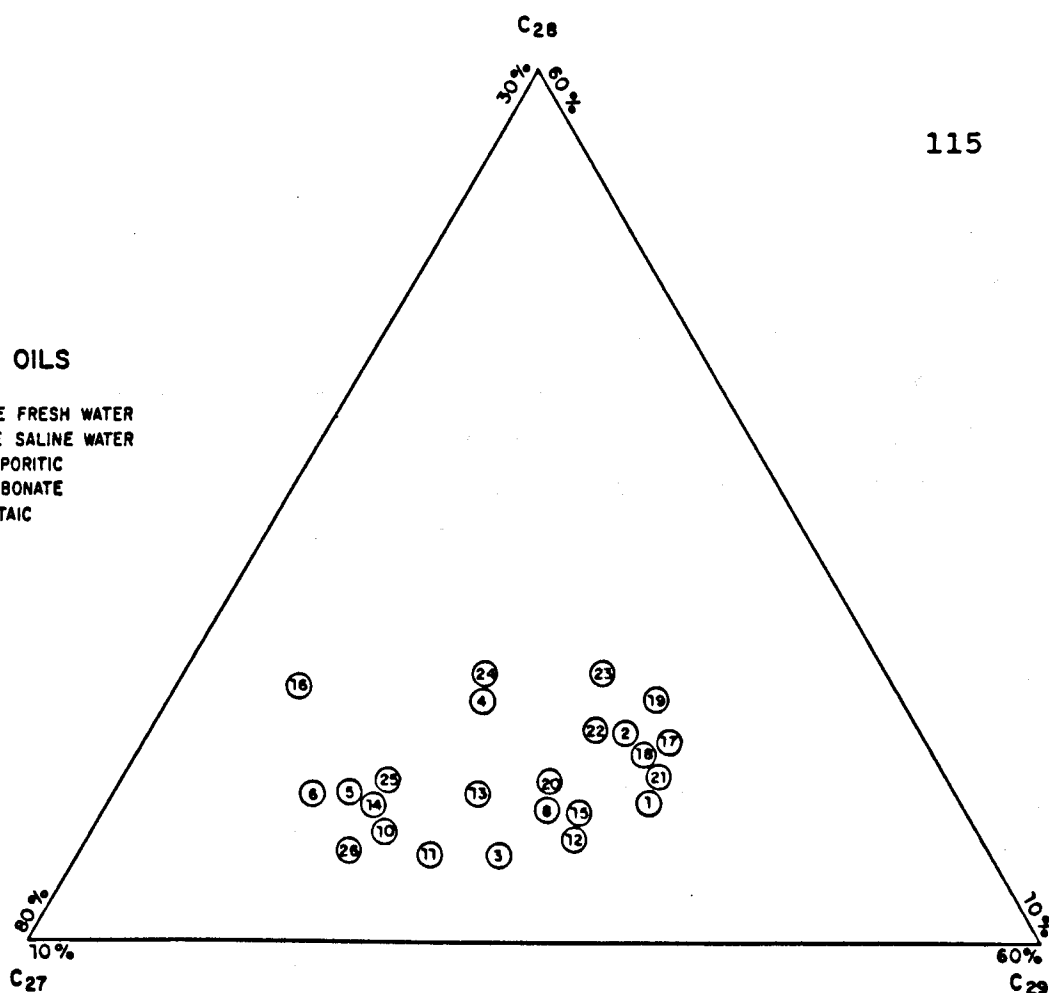


Figure 40- Carbon number (C_{27} , C_{28} , C_{29}) distributions of $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20R steranes for a number of oil samples from different depositional environments in the Brazilian continental margin.

The oils from a lacustrine saline water environment (group II) show a similar set of characteristics diagnostic of non-marine oils, but differ in respect of elemental, isotopic and molecular features arising from enhanced salinity, for example, higher values of sulphur and V/Ni ratios, heavier $\delta^{13}C$ values, and the presence of the C_{25} regular isoprenoid, β -carotane, low molecular weight steranes (C_{21-22}), 28,30-bisnorhopane and abundant tricyclic terpanes up to C_{35} .

The distinction between the non-marine oils (groups I and II) and those related to a dominant input of marine organic matter (groups III, IV), is based on a variety of parameters. The most useful are the high wax content and the abundance of high molecular weight n-alkanes in the non-marine oils and the presence of C_{30} steranes, and the abundance of steranes, 28,30-bisnorhopane and 25,28,30-trisnorhopane in the marine oils.

Distinction between the marine evaporitic (group III) and marine carbonate (group IV) oils is made using compounds such as gammacerane, β -carotane, low molecular weight steranes and tricyclic terpanes. In the evaporitic oils, gammacerane (Fig. 42) and β -carotane occur in very high abundance. In the carbonate oils, there is a high relative abundance of tricyclic terpanes up to C_{35} and of C_{21} and C_{22} steranes.

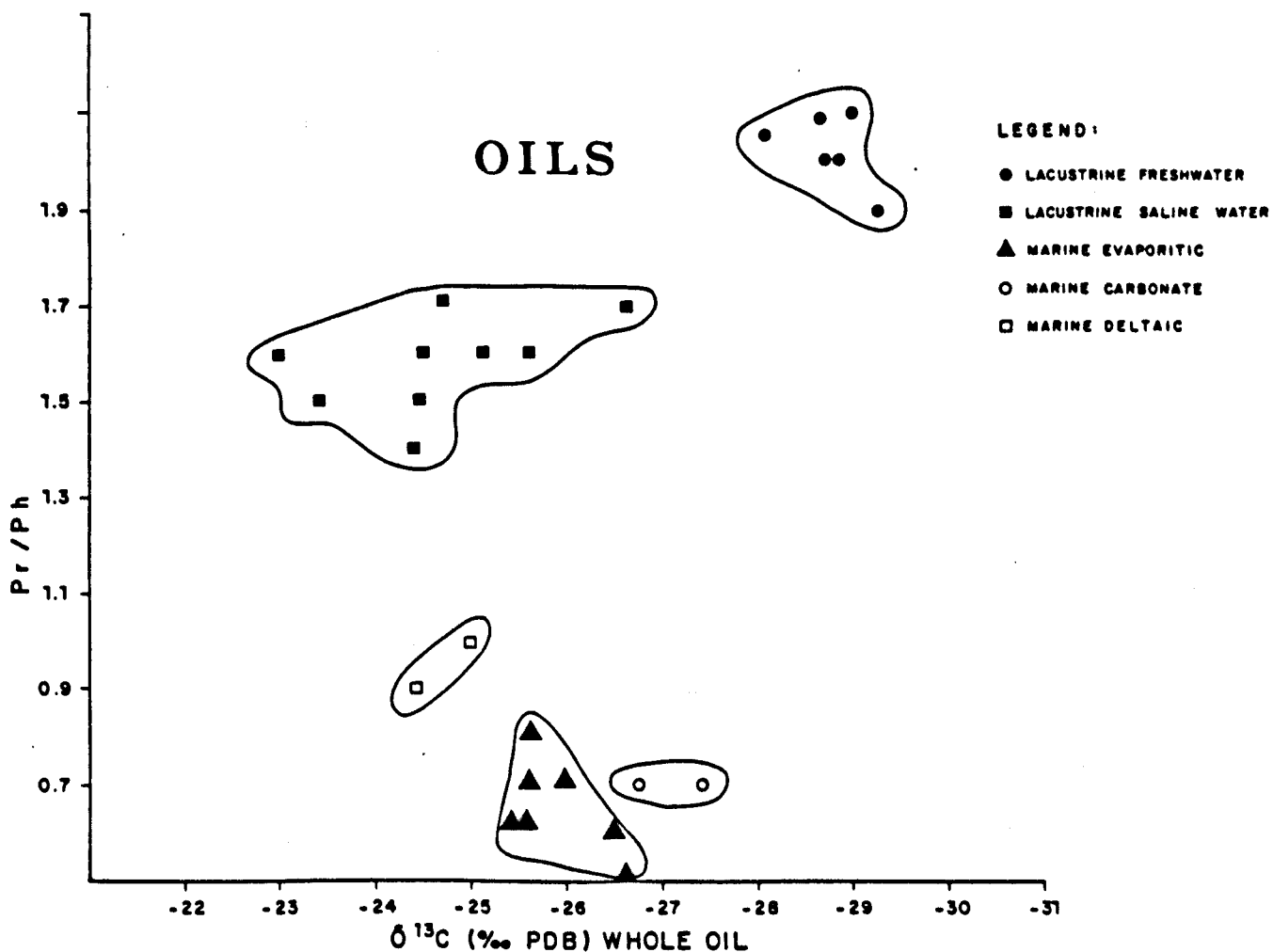


Figure 41 - Plot of the variation in pristane/ phytane ratio with carbon isotope whole oil data for oils derived from different depositional environments in the Brazilian continental margin (for quantitation approach see appendix II).

Several features shared by these two environments distinguish them from all the others, namely a dominance of phytane over pristane linked with an even over odd n-alkane preference, high sulphur contents, high sterane concentrations, low relative abundance of diasteranes, a dominance of C₃₅ hopanes over their C₃₄ homologues, and high amounts of long chain regular C₂₅ and C₃₀(squalane)isoprenoids.

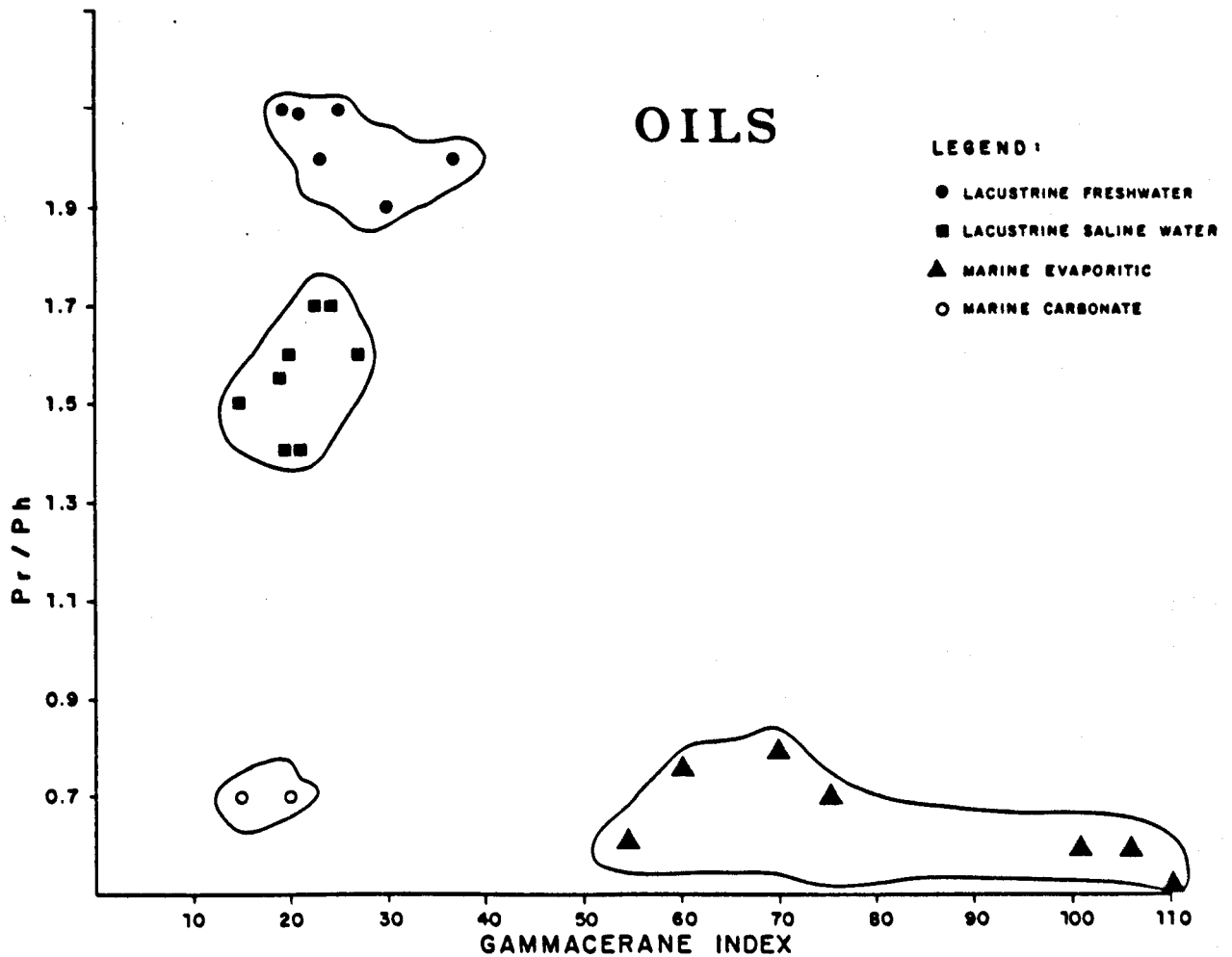



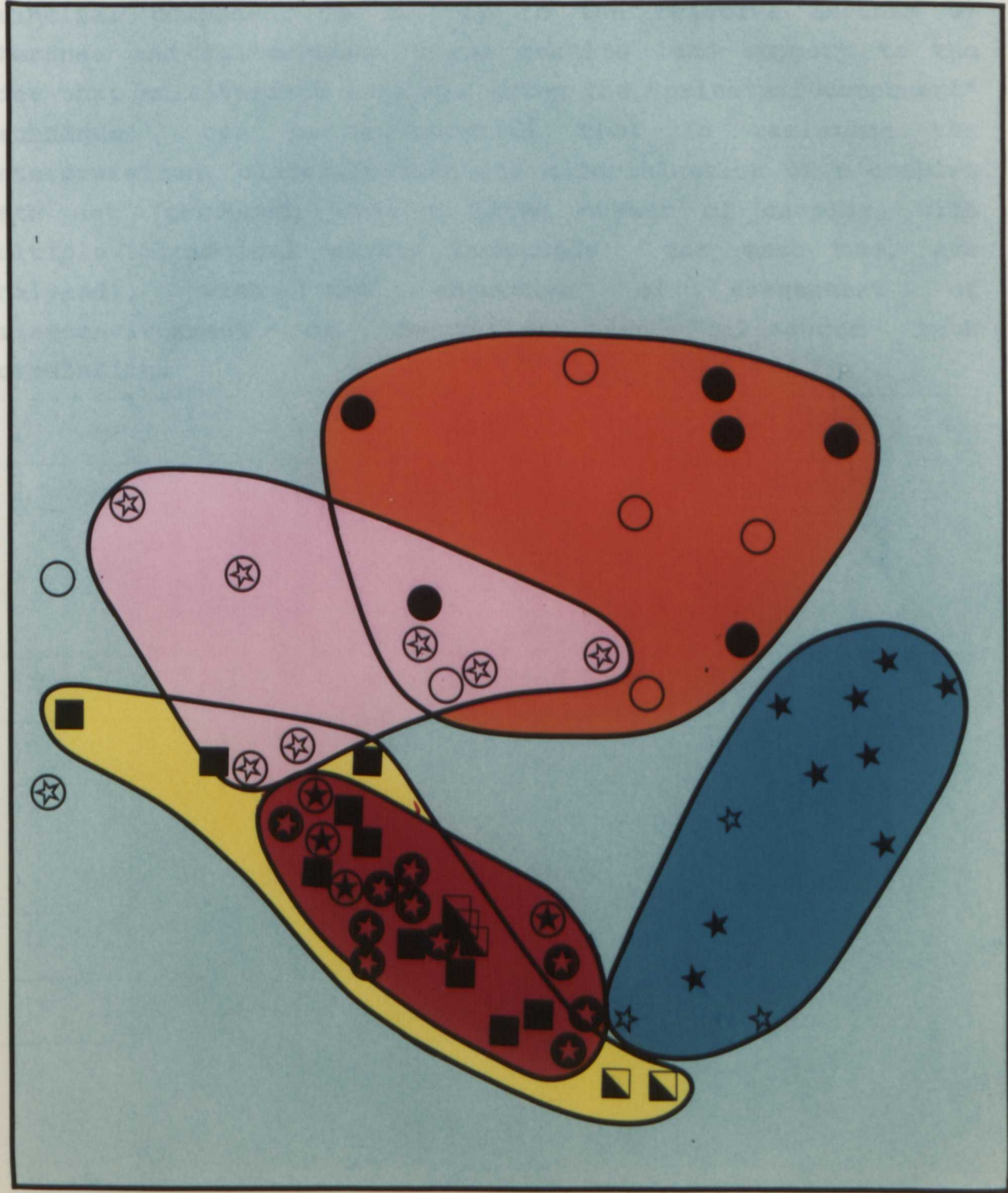
Figure 42 - Plot of the variation in pristane/ phytane ratio with gammacerane index (IG) for oils derived from different depositional environments in the Brazilian continental margin (for significance of IG see appendix II).

The marine deltaic oils (group V) can be differentiated from all the other groups of oils using diagnostic markers for specific higher plant contributions, namely $18\alpha(H)$ -oleanane and high relative abundance of the C_{24} tetracyclic terpane. They also show some of the features of the carbonate-derived oils, such as low pristane/phytane ratios, even/odd n-alkane dominance, high V/Ni ratios, dominance of C_{35} hopanes over their C_{34} counterparts, and high relative abundances of low molecular weight steranes. These features demonstrate the value of biological markers in the assessment of depositional environments using oils. From the results of this work we propose, as an extension of previous studies (Waples *et al.*, 1974; Hall and Douglas, 1983; Brassell and Eglinton, 1986), that low pristane/phytane ratios, even/odd n-alkane preference, and high abundances of specific acyclic isoprenoids (2,6,10,14,18-pentamethyleicosane and squalane), β -carotane and gammacerane may be considered useful salinity indicators related to the water column in the depositional environment of source rocks.

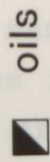
The large amount of data arising from Chapters II and III, make difficult their ready interpretation by traditional methods. The application of computational methods, as shown previously using principal component analysis (see above and Chapter II), can be of value. Fig. 43 summarises the oil-source rock correlation by the principal component analysis method using linked scan GC-MS elution profiles for oil and rock samples derived from lacustrine freshwater, lacustrine saline water, marine evaporitic and marine carbonate depositional environments. The resulting scores on the first principal component are plotted versus the scores on the second principal component. As can be observed the lacustrine samples are clearly separated from the marine samples. When only the lacustrine freshwater and saline water samples are plotted together they can be readily discriminate (Fig. 24). In general, oils tend to be closely associated with the source rocks of the same depositional environment. Also the

Figure 43- Scores of rock extracts and oils from Brazilian marginal basins on principal component 1 versus scores on principal component 2;  represents source rocks from lacustrine hypersaline facies.

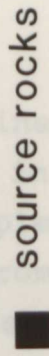
BRAZILIAN OILS AND SOURCE ROCKS



Lacustrine freshwater



oils



source rocks

Lacustrine saline water



oils



source rocks



source rocks

Marine evaporitic



oils



source rocks

Marine carbonate



oils



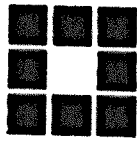
source rocks

Component 2

Component 1

lacustrine saline water rock samples from Espirito Santo basin, as considered in Chapter II, tend to be associated with the evaporitic samples, suggesting enhanced salinity, when compared with samples from Campos basin.

The effect of the variables on the principal components (loadings) show that the first principal component is related to the absolute concentration of biomarkers, while the second principal component is related to the relative amounts of steranes and triterpanes. These results lend support to the idea that multivariate analyses using the "principal component" technique can be a powerful tool in assisting the interpretation, classification and discrimination of a complex data set (produced, when a large number of samples, with multiple biological marker compounds for each one, are analysed), with the objective of assessment of palaeoenvironment of deposition and oil-source rock correlation.



CHAPTER IV

CHAPTER IV

**BIOLOGICAL MARKER COMPOUNDS IN THE ASSESSMENT OF
PALAEOENVIRONMENT OF DEPOSITION IN RELATION TO ORGANIC-RICH
SEDIMENTS AND PETROLEUMS; A GENERAL OVERVIEW.**

This chapter provides a review of current knowledge about biological marker features used to assist in assigning the depositional palaeoenvironments of ancient organic-rich sedimentary rocks and petroleum by drawing on the literature and on the findings in Chapters II and III. Only features appropriate to Brazilian marginal basins are discussed.

4.1 INTRODUCTION

Sedimentary organic matter contains complex assemblages of biological markers, which are compounds that have preserved in whole or in part their basic skeleton during and after diagenesis, being therefore a reflection of the precursor compounds in the organisms which contributed organic matter at the time of sediment deposition (cf. Eglinton, 1973). Therefore, a knowledge of the structures of individual components and their significance can provide valuable information about the prevailing environmental conditions. In addition, biological markers for use in palaeoenvironmental assessment should ideally be diagnostic of specific types of organisms with wide-ranging occurrences documented in recent and ancient well-described depositional environments (Brassell and Eglinton, 1986).

Several reviews about the use of biological marker indicators in the assessment of the depositional environments have already been published (e.g. Philp, 1982; Moldowan et al., 1985; Brassell & Eglinton, 1986; Volkman, 1987). Recently, many authors have shown that biological marker distributions can provide diagnostic criteria for the distinction of organic extracts and oils derived from source rocks deposited in environments such as lacustrine freshwater, freshwater-brackish, saline and hypersaline (e.g. Brassell et al., 1987; Fu Jiamo et al., 1986; Wang Tieguan et al., 1987); McKirdy et al., 1986; Philp and Gilbert, 1986; Moldowan et al., 1985; Powell, 1986); evaporitic (e.g. Albaiges et al., 1986; ten Haven et al., 1987; Connan and Dessort, 1987); marine carbonate (Talukdar et al., 1986; McKirdy et al., 1984; Palacas et al., 1984) and marine deltaic (Hills and Whitehead, 1966; Grantham et al., 1983; Brooks, 1986).

The present review extends these studies by incorporating the findings in Chapters II and III in a discussion of the application of biological marker compounds in the assessment

and characterisation of depositional environments. Such applications should be made with caution, since maturity (e.g. Chapter V) and biodegradation can play an important role in altering the distributions and concentrations.

In the following sections, the significance as source indicators, and GC and GC-MS features of several important classes of biological markers in sediments and petroleums are also shown. The major compound classes are acyclic (n-alkanes, short and long chain isoprenoids) and cyclic (β -carotane, terpenoids and steroids) compounds.

4.2 ACYCLIC BIOLOGICAL MARKERS

Two major groups are discussed, n-alkanes and acyclic isoprenoids:

4.2.1 n-Alkanes

The n-alkane distributions (e.g. Fig. 1) can be important as an environmental parameter, since they can provide clues about their biological origin (Hunt, 1979; Tissot & Welte, 1984). They arise from terrestrial higher plants and pelagic and benthic organisms such as phytoplankton and bacteria (Brassell *et al.*, 1978; Tissot & Welte, 1984). Generally, they show a variable distribution ranging from low to high molecular weight components, often with a specific carbon number preference (odd or even). It is established that the odd-numbered n-alkanes tend to predominate in the geosphere over their even-numbered counterparts (Hunt, 1979; Tissot & Welte, 1984). This is supported by the noted prevalence of odd-numbered components in a great number of terrestrial and aquatic plants. Often, sediment extracts and petroleums linked with lacustrine (freshwater, freshwater-brackish, saline and hypersaline) and marine deltaic depositional environments tend to have distributions with a predominance or relatively high abundance of long chain components (C_{22} - C_{35}), often linked with

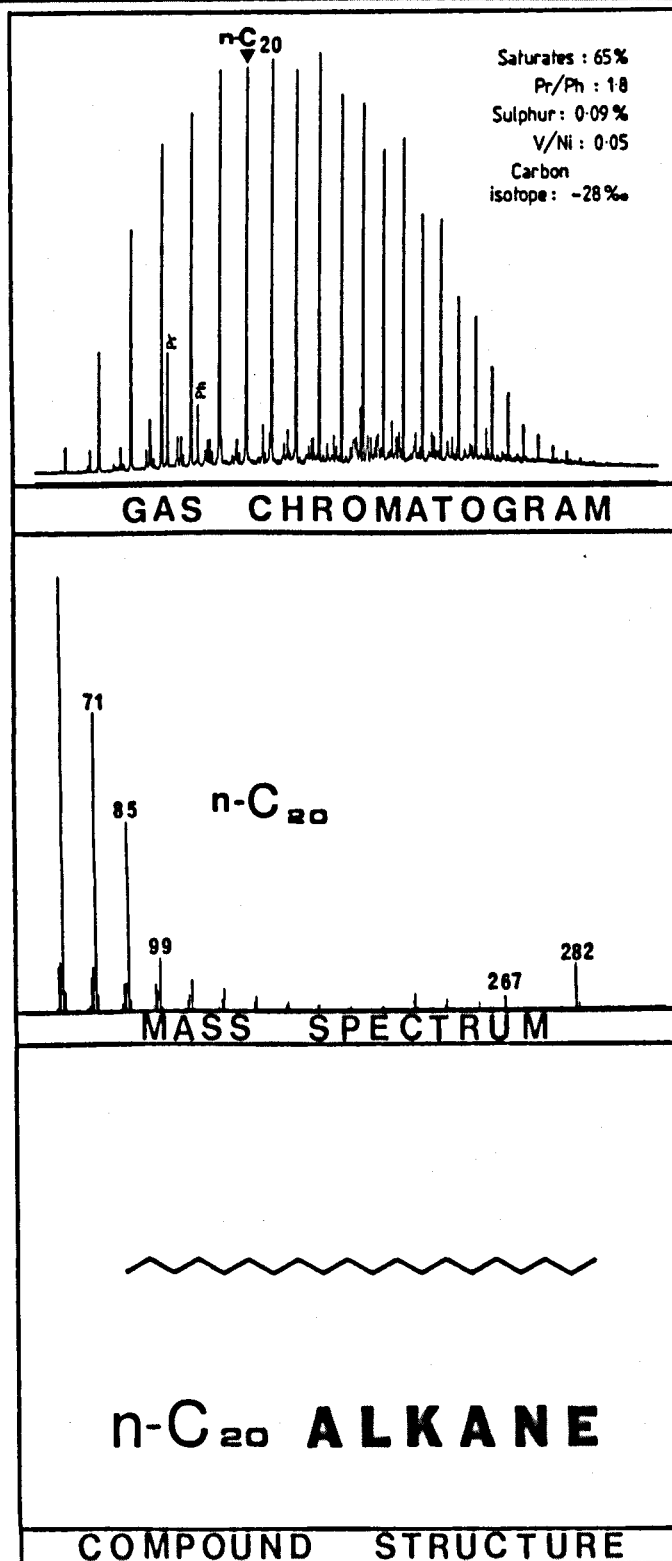
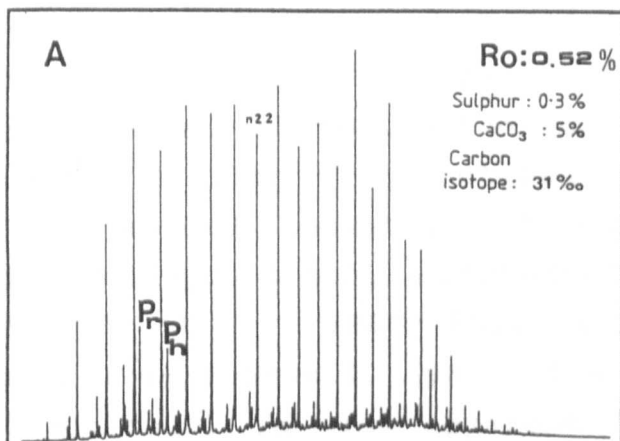


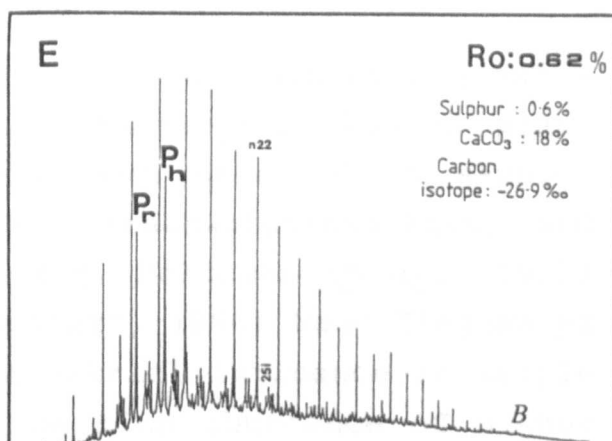
Figure 1- Gas chromatogram of total alkanes from an oil sample derived from a lacustrine freshwater environment (CES-8) with spectrum and structure of a C₂₀ n-alkane (for peak assignments see appendix I).

an odd-over-even preference (e.g. Fig. 1; Didyk et al., 1978; Brassell et al., 1978; Tissot & Welte, 1984), if the predominance has not been removed by maturation. These geochemical features indicate a major input of long chain lipids from higher plants (e.g. leaf waxes) and freshwater algae (e.g. *B. braunii*; Eglinton et al., 1962; Lijmbach, 1975; Tissot & Welte, 1984; McKirdy et al., 1986). It is also noteworthy that the n-alkane content is usually higher in continental than in marine sedimentary organic matter (Tissot & Welte, 1984). In contrast, a truly marine environment (e.g. open marine, marine hypersaline and marine carbonate), tends to result in sediment extracts and petroleums with odd and/or even-carbon-numbered distributions in the medium molecular weight range (C_{12} - C_{20} , with a frequent predominance of C_{15} - C_{17} components (Didyk et al., 1978; Brassell et al., 1978; Tissot & Welte, 1984). A preponderance of these low molecular weight n-alkanes reflects a marine phytoplankton input (e.g. et al., 1967; Brassell et al., 1978; Tissot & Welte, 1984). Bacterially derived n-alkane distributions, generally seem to peak in the n- C_{15} to n- C_{17} range, but may also occur as C_{24} - C_{35} components (Lijmbach, 1975; Tissot & Welte, 1984; McKirdy et al., 1986). It is interesting to note the predominance of even-carbon number n-alkanes often seem in samples from marine carbonate and hypersaline (evaporitic) sediments and petroleums (Tissot & Welte, 1984). The origin of this feature is not completely understood, although it has been suggested that it results from a reduction of marine algal precursors (fatty acids and alcohols), under anoxic conditions (Welte and Waples, 1973; Grimald et al., 1985; Connan et al., 1986). Whatever the explanation, there appears to exist a link between enhanced salinity in marine environments and even n-alkane predominance (e.g. Tissot & Welte, 1984; Fu Jiamo et al., 1986; ten Haven et al., 1985; Mello et al., 1988a, b). Fig. 2 shows a series of alkane gas chromatograms of rock extracts and oils from Brazilian marginal basins. Samples A to C (terrestrial influence) show a significant abundance of higher n-alkanes (

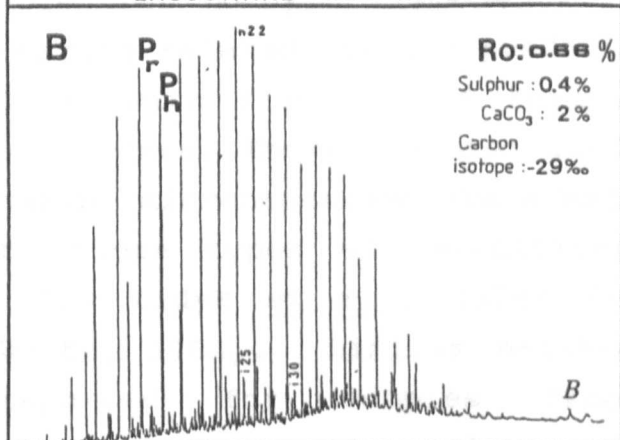
Figure 2- Gas chromatograms of total alkanes, bulk and elemental parameters from sediment extracts and oils from different depositional environments; A: lacustrine freshwater (PTA-1); B and C: lacustrine saline water (IP-1 and RJS-49); D: open marine with dominance of siliciclastic lithology (ESS-46); E: marine carbonate (APS-31); F: marine evaporitic (CES-7); G and H: marine deltaic with carbonate influence (PAS-9 and PAS-11; for peak assignments see appendix I).



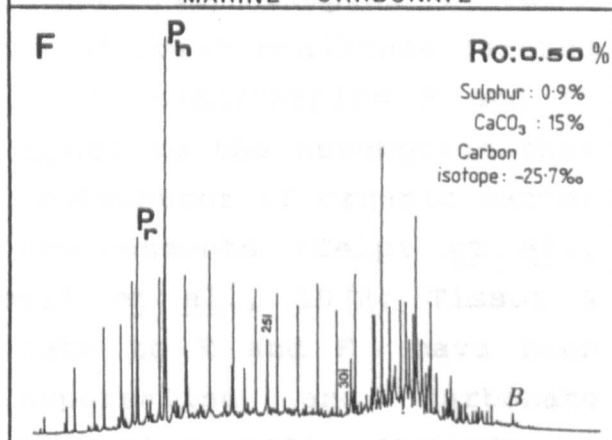
LACUSTRINE FRESHWATER



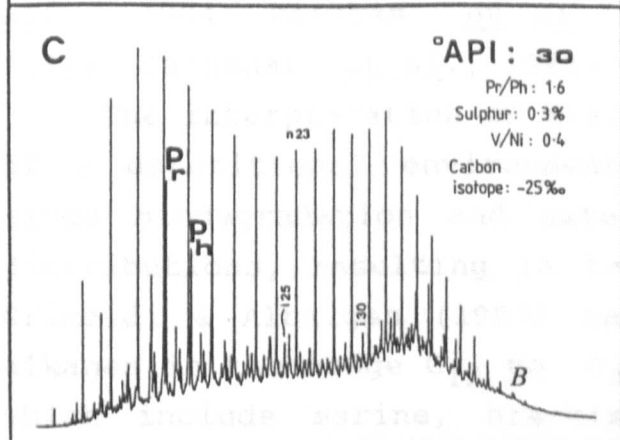
MARINE CARBONATE



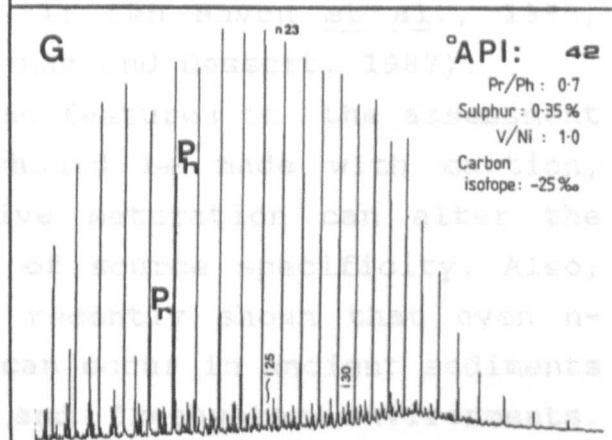
LACUSTRINE SALINE



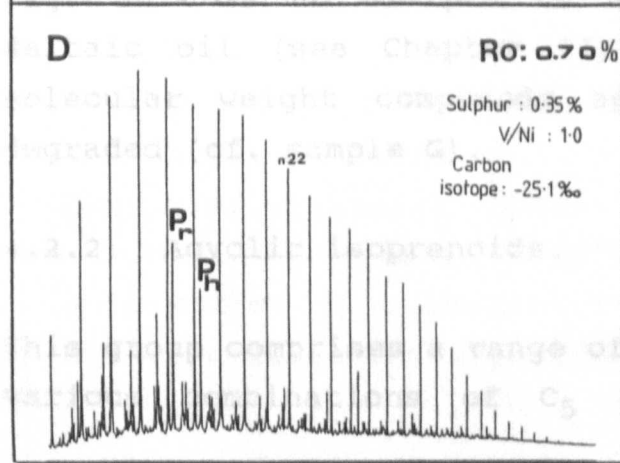
EVAPORITIC



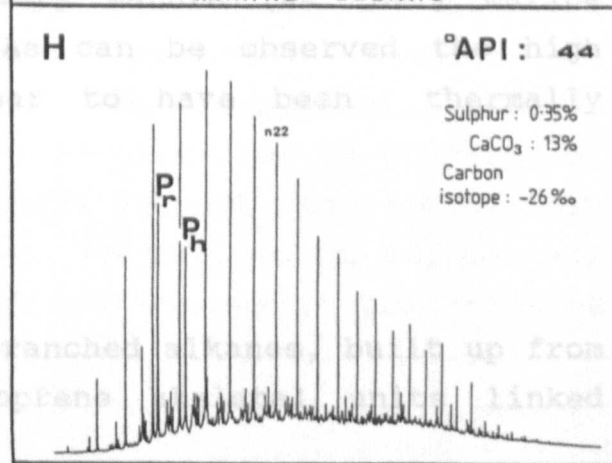
LACUSTRINE SALINE



MARINE DELTAIC



OPEN MARINE



MARINE DELTAIC

> C₂₃) and odd/ even predominance . These features suggest a lacustrine phytoplankton and/ or terrestrial higher plant input. Similar distributions have been observed in samples from several lacustrine freshwater, freshwater-brackish, and saline depositional environments (e.g. Moldowan et al., 1985; McKirdy et al., 1986; Philp and Gilbert, 1986; Wang Tieguan et al., 1988); Powell, 1986). The terrestrial influence in sample G (deltaic) is also apparent in the high abundance of higher molecular weight components. In contrast, samples D to F (marine related) show a predominance of lower n-alkanes (around C₁₇), with slight odd (sample D) or even (samples E and F) preference. These features lend support to the assumption that marine microorganisms are a major contributor of organic matter to these types of depositional environments (Gelpi et al., 1970; Didyk et al., 1978; Brassell et al., 1978; Tissot & Welte, 1984). Similar n-alkane data to E and F have been reported for samples from hypersaline and carbonate environments elsewhere (e.g. Welte & Waples, 1973; McKirdy et al., 1984; Palacas et al., 1984; ten Haven et al., 1985, 1987; Talukdar et al., 1986; Connan and Dessort, 1987).

The interpretation of n-alkane features in the assessment of a depositional environment should be made with caution, since biodegradation and extensive maturation can alter the distributions, resulting in loss of source specificity. Also, Grimaldi & Albaiges (1987) have recently shown that even n-alkanes in the range C₁₂ to C₂₂ can occur in ancient sediments which include marine, brackish and freshwater environments. Fig. 2H is an example of a very mature (44 °API) marine deltaic oil (see Chapter II). As can be observed the high molecular weight compounds appear to have been thermally degraded (cf. sample G).

4.2.2 Acyclic isoprenoids.

This group comprises a range of branched alkanes, built up from various combinations of C₅ isoprene skeletal units linked

together (Tissot & Welte, 1984; Volkman & Maxwell, 1986). The regular isoprenoids, especially C₁₉ (pristane), C₂₀ (phytane), C₂₅ (2,6,10,14,18 pentamethyleicosane), and C₃₀ (squalane), have for many years been used as palaeoenvironmental indicators (e.g. Maxwell et al., 1972; Waples et al., 1974; Didyk et al., 1978; Albaigés, 1980; Tissot & Welte, 1984; Volkman & Maxwell, 1986; ten Haven et al., 1987; Mello et al., 1988a, b). They are discussed separately in the following sections:

4.2.2.1 Short chain isoprenoids.

The best known and generally most abundant in organic-rich sediments and crude oils are the regular C₁₉ (pristane; e.g. Fig. 3) and C₂₀ (phytane; e.g. Fig. 4) compounds. Brooks et al. (1969) suggested that pristane is preferentially formed from the phytyl side chain of chlorophyll in an oxidizing environment, whereas phytane has its origin in the same precursor in a more reducing environment. As an extension, Didyk et al. (1978) proposed a direct relationship of the pristane / phytane ratio with the oxicity of the environment of deposition. Risatti et al. (1984) suggested, however, that in very immature sediments, differences in the ratio might arise from differences in the relative inputs of different organisms, with pristane arising from plankton and the phytane from archaeobacteria (e.g. methanogens). As an extension, Goossens et al. (1984) provided evidence that pristane could be generated from tocopherols in more mature sediments, with the phytane still arising mainly from archaeobacterial lipids (methanogens and halophiles). Recent hydrous pyrolysis studies of methanogens (Rowland et al. (1988) have suggested, however, that both pristane and phytane can be generated by cracking of archaeobacterial lipids. These studies suggest, therefore, that the relative abundance of pristane to phytane in sedimentary organic matter is a reflection of differences in the relative inputs from different organisms.

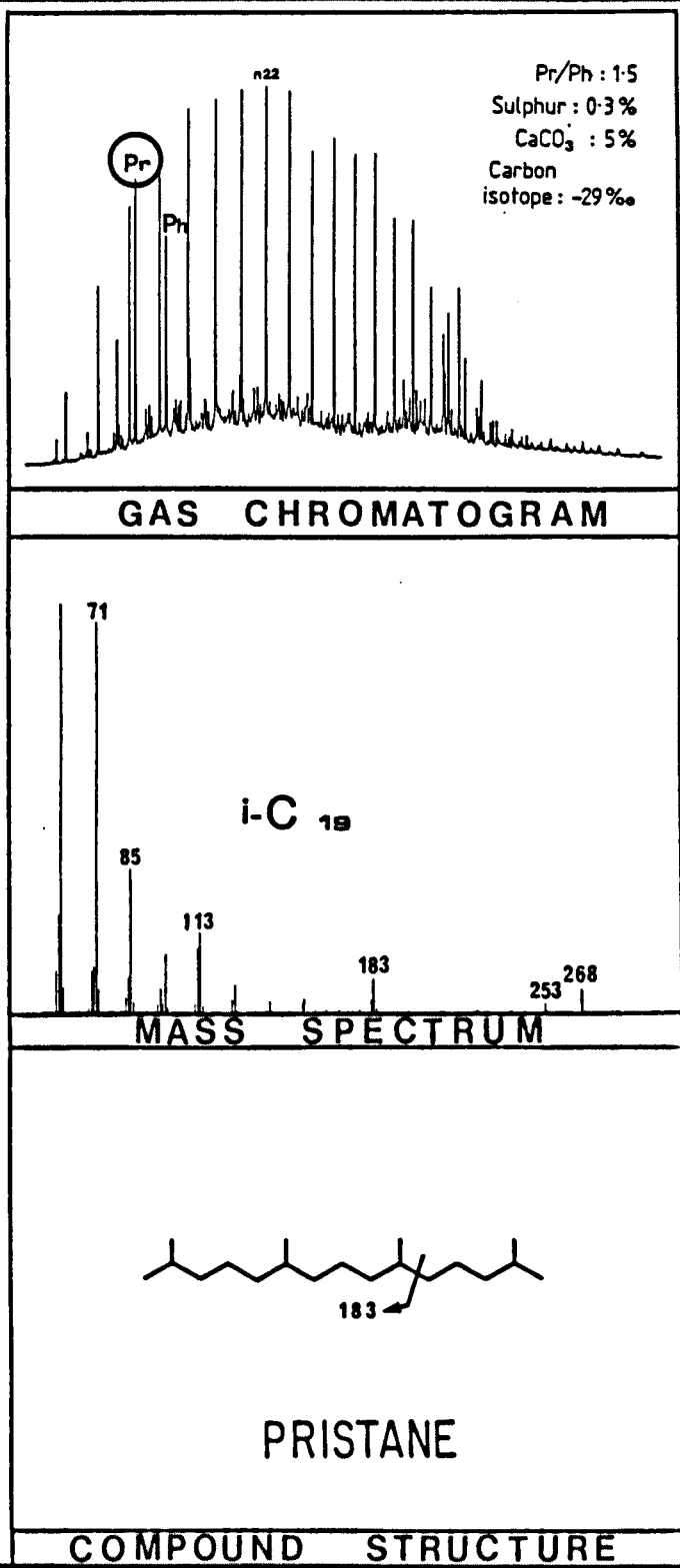
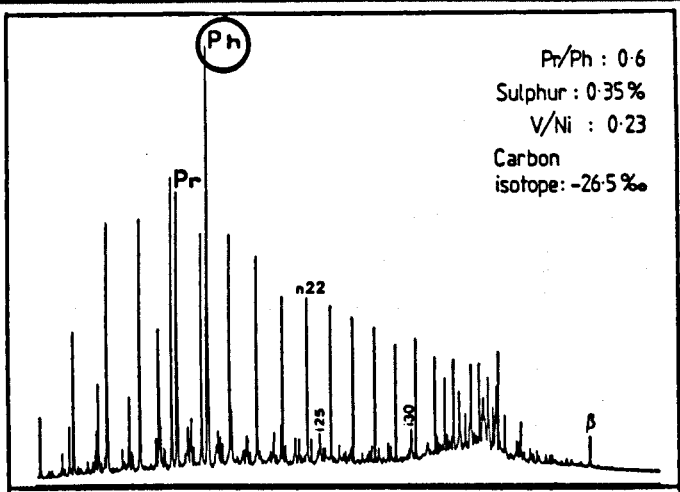
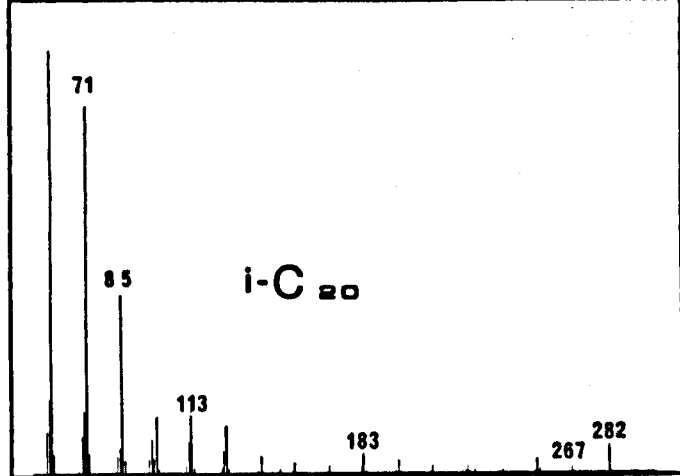


Figure 3- Gas chromatogram of total alkanes from a typical sediment extract from lacustrine freshwater environment (CS-1) with spectrum and structure of pristane (i-C₁₉; for peak assignments see appendix I).

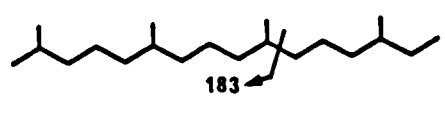


Pr/Ph : 0.6
 Sulphur : 0.35%
 V/Ni : 0.23
 Carbon
 isotope: -26.5‰

GAS CHROMATOGRAM



MASS SPECTRUM



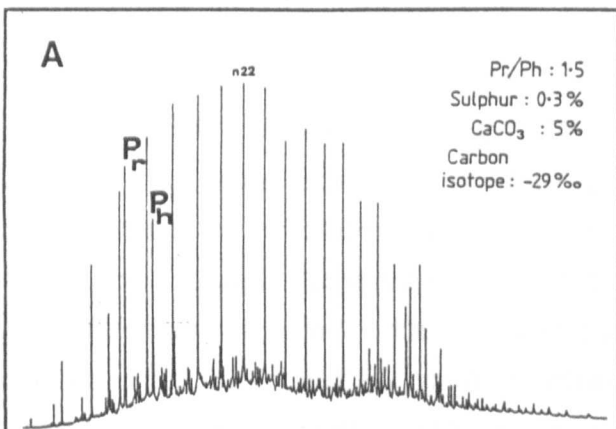
PHYTANE

COMPOUND STRUCTURE

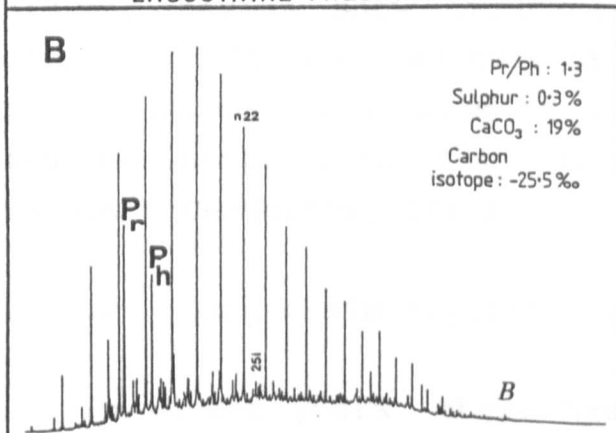
Figure 4- Gas chromatogram of total alkanes from an oil sample derived from an marine evaporitic environment (RNS-10) with spectrum and structure of phytane (i-C₂₀; for peak assignments see appendix I).

Recently, ten Haven et al. (1987) and Mello et al. (1988) have suggested that pristane/phytane ratios probably reflect the relationship between their precursors and the chemistry of the environment (e.g. water salinity and alkalinity), rather than simply the anoxic/oxic condition of sedimentation, as proposed by Brooks et al. (1969) and Didyk et al. (1978). It appears that pristane may originate from phytol (e.g. Didyk et al., 1978) and/ or tocopherols (Goossens et al., 1984) of photosynthetic organisms, and from methanogens (Rowland et al., 1988), whereas phytane may arise in part from phytol or alternatively from archaebacteria lipids in organisms such as methanogens and halophiles (Kaplan & Baedeker, 1970; Risatti et al., 1984; ten Haven et al., 1985, 1987; Volkman, 1986). In a freshwater environment, photosynthetic organisms containing phytol and tocopherols would be expected to be abundant. With an increase in salinity (higher Eh), however, the archaebacterial population (mainly halophilic), might be expected to increase in abundance. Thus, the more saline the environment, the greater the potential for an increase in the concentration of phytane precursors. This may help to explain the high predominance of pristane ($Pr/Ph > 1$) in freshwater and "normal" saline environments (lacustrine fresh and saline water and open marine) compared with the dominance of phytane ($Pr/Ph < 1$) in marine carbonate and hypersaline environments (e.g. Palacas et al., 1984; McKirdy et al., 1984; Fu Jiamo et al., 1986; Ten Have et al., 1985, 1987; Mello et al., 1988a, b). Fig. 5 shows a series of alkane gas-chromatograms from rock extracts and oils from different depositional environments. Samples A to D (lacustrine freshwater, lacustrine saline water and open marine environment, respectively), show pristane/phytane ratios > 1 (more than 90 oil and rock samples from the Brazilian marginal basins, unpublished results and also Chapters II and III). Conversely, samples E to H (marine carbonate, marine evaporitic and marine deltaic associated with carbonate platform environment, respectively) show a predominance of phytane over pristane (more than 50 oil and

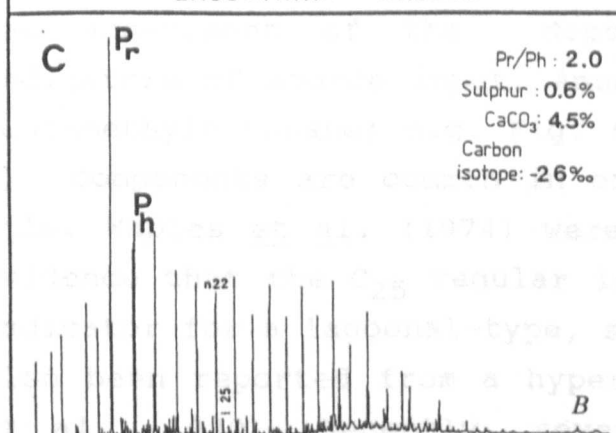
Figure 5- Gas chromatograms of total alkanes, bulk and elemental parameters from sediment extracts and oils from different depositional environments; A: lacustrine freshwater (CS-1); B and C: lacustrine saline (RJS-71 and RD-1); D: open marine with dominance siliciclastic lithology (ESS-46); E: marine carbonate (SES-14); F and G: marine evaporitic (CES-7 and CES-8); H: marine deltaic with carbonate influence (PAS-9; for peak assignments see appendix I).



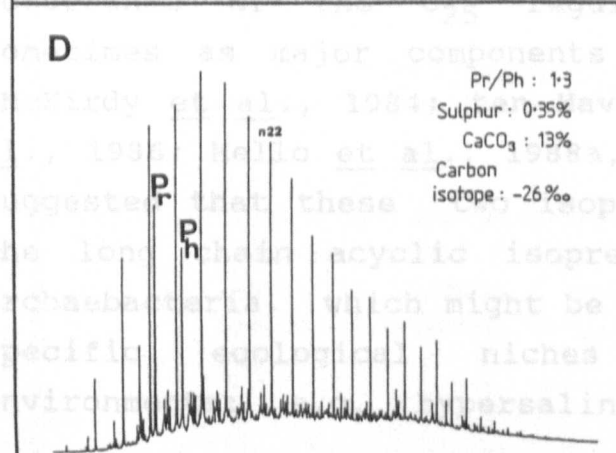
LACUSTRINE FRESHWATER



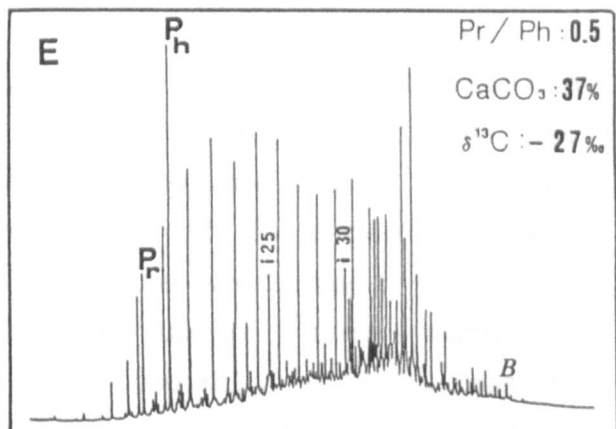
LACUSTRINE SALINE



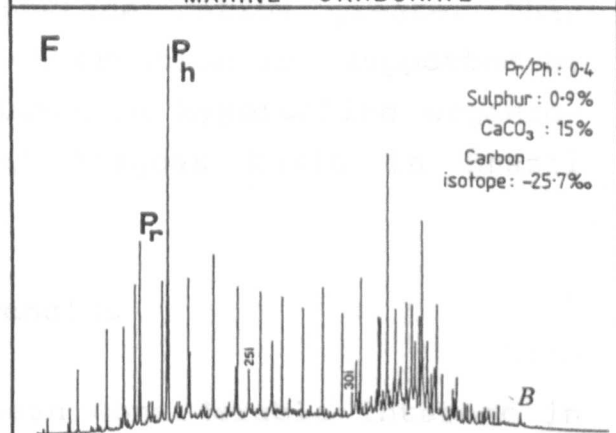
LACUSTRINE SALINE



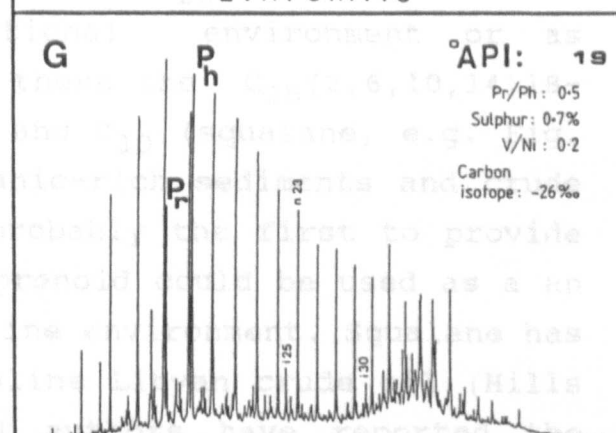
OPEN MARINE



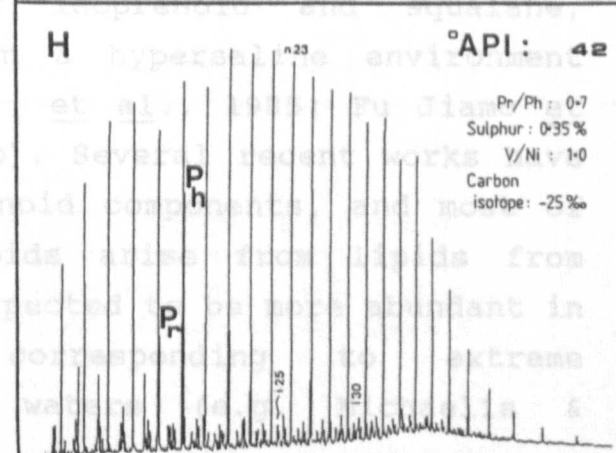
MARINE CARBONATE



EVAPORITIC



EVAPORITIC



MARINE DELTAIC

rock samples from the Brazilian marginal basins, unpublished results; cf. also Chapters II and III). These features lend support to the idea that the pristane/ phytane ratio might be considered a biological marker indicator of palaeoenvironment of deposition. However, caution must be exercised with the interpretation of this ratio, since under high maturity conditions the ratio could change considerably (highly mature evaporitic and carbonate source rocks and oils from Brazilian marginal basins show pristane/ phytane ratios greater than unity; unpublished results). This observation is supported by hydrous pyrolysis studies on an immature hypersaline organic-rich sediment, from the Sergipe/ Alagoas basin in Brazil (Soldan & Cerqueira, 1986).

4.2.2.2 Long chain acyclic isoprenoids

In recent years, there has been considerable interest in the longer chain acyclic isoprenoids ($> C_{20}$) and their use in the assessment of the depositional environment or as indicators of source input. Among these the C_{25} (2,6,10,14,18-pentamethyleicosane; e.g. Fig. 6) and C_{30} (squalane, e.g. Fig. 7) components are common in organic-rich sediments and crude oils. Waples et al. (1974) were probably the first to provide evidence that the C_{25} regular isoprenoid could be used as an indicator for a lagoonal-type, saline environment. Squalane has also been reported from a hypersaline Libyan crude oil (Hills et al., 1970). Recently, several authors have reported the occurrence of the C_{25} regular isoprenoid and squalane, sometimes as major components in a hypersaline environment (McKirdy et al., 1984; ten Haven et al., 1985; Fu Jiamo et al., 1986; Mello et al., 1988a, b). Several recent works have suggested that these two isoprenoid components, and most of the long chain acyclic isoprenoids arise from lipids from archaeobacteria, which might be expected to be more abundant in specific ecological niches corresponding to extreme environments: e.g. hypersaline waters (e.g. Michaelis &

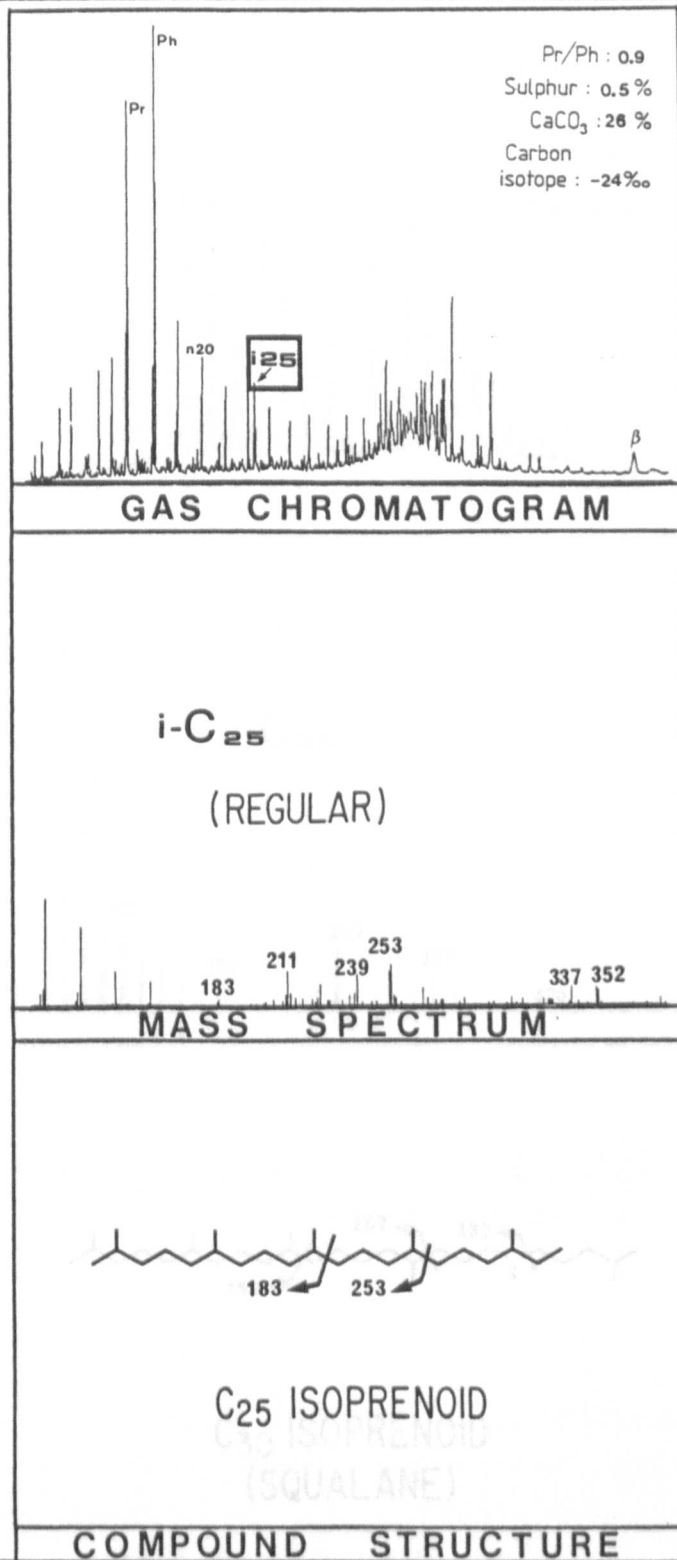
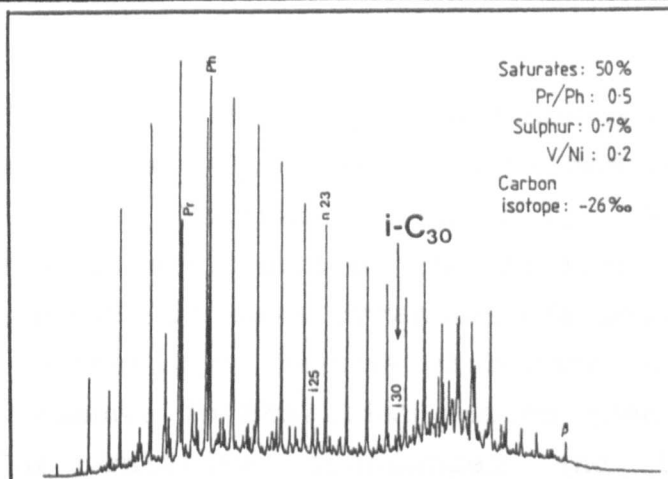
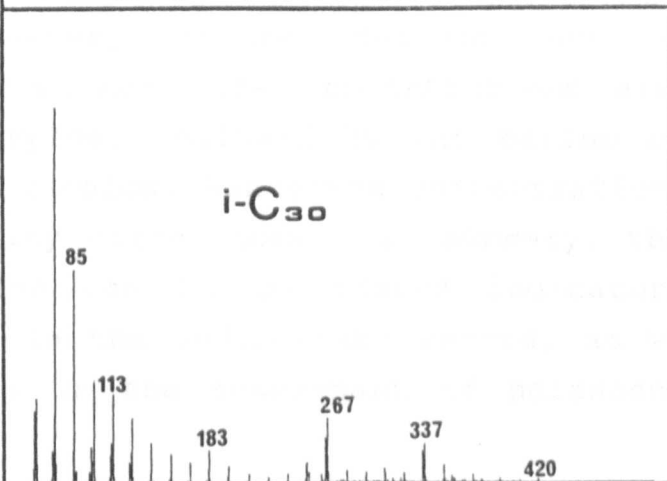


Figure 6- Gas chromatogram of total alkanes from a typical sediment extract from an evaporitic environment (FGT-1) with partial spectrum and structure of 2,6,10,14,18 pentamethyleicosane (i-C₂₅; for peak assignments see appendix I).

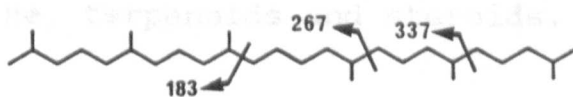


Saturates: 50%
 Pr/Ph: 0.5
 Sulphur: 0.7%
 V/Ni: 0.2
 Carbon
 isotope: -26‰

GAS CHROMATOGRAM



MASS SPECTRUM



**C₃₀ ISOPRENOID
 (SQUALANE)**

COMPOUND STRUCTURE

Figure 7- Gas chromatogram of total alkanes from a typical sediment extract from an evaporitic environment (CES-41) with spectrum and structure of C₃₀ acyclic isoprenoid (squalane; for peak assignments see appendix I).

The origin of biological marker compounds discussed in this paper are 8-carotene, terpenoids and steroids.

continental plants and lacustrine and marine algae, reaching sometimes more than 5% (dry weight; Tissot & Welte, 1984). Anders & Rosenblatt (1983) identified 8-carotene in sediment via reductive cleavage of 8-carotene. Although not proved, the reduction of 8-carotene appears to be a likely way to form 8-carotane (Tissot & Welte, 1984; Simonait, 1986).

Albrecht, 1979; Albaigés, 1980; Kaplan & Baedeker, 1970; Boon et al., 1983; Brassell et al., 1981; Albaiges et al., 1986; Tissot & Welte, 1984; Volkman & Maxwell, 1986). Fig. 8 illustrates presence in abundance of the regular i -C₂₅ and i -C₃₀(squalane) components in some organic-rich sediments and an oil sample from evaporitic, marine carbonate and lacustrine saline water environments in Brazilian basins (see also Chapter II and III). The relative abundances and the absolute concentrations are higher in these samples than in samples from lacustrine freshwater, marine deltaic and open marine environments. Furthermore, the concentrations are highest in the evaporitic samples, followed by the marine carbonate and lacustrine saline samples. Hence the concentrations appears to reflect the salinity differences. In summary, the long chain acyclic isoprenoids can be considered indicators of source input (bacterial) in the sedimentary record, as well as being diagnostic markers in the assessment of palaeoenvironment of deposition.

4.3 CYCLIC BIOLOGICAL MARKERS

The cyclic biological marker compounds discussed in this section are β -carotane, terpenoids and steroids.

4.3.1 β -Carotane

This compound(cf. Fig. 9) was first identified in lacustrine sediments from the Green River formation, deposited under saline conditions (Murphy et al., 1967). The corresponding unsaturated hydrocarbon β -carotene (C₄₀H₅₆), is abundant in continental plants and lacustrine and marine algae, reaching sometimes more than 5% (dry weight; Tissot & Welte, 1984). Anders & Robinson (1971) suggested the formation of β -carotane via reduction of β -carotene from plant pigments. Although not proved, the reduction of β -carotene appears to be a likely way to form β -carotane (Tissot & Welte, 1984; Simoneit, 1986)

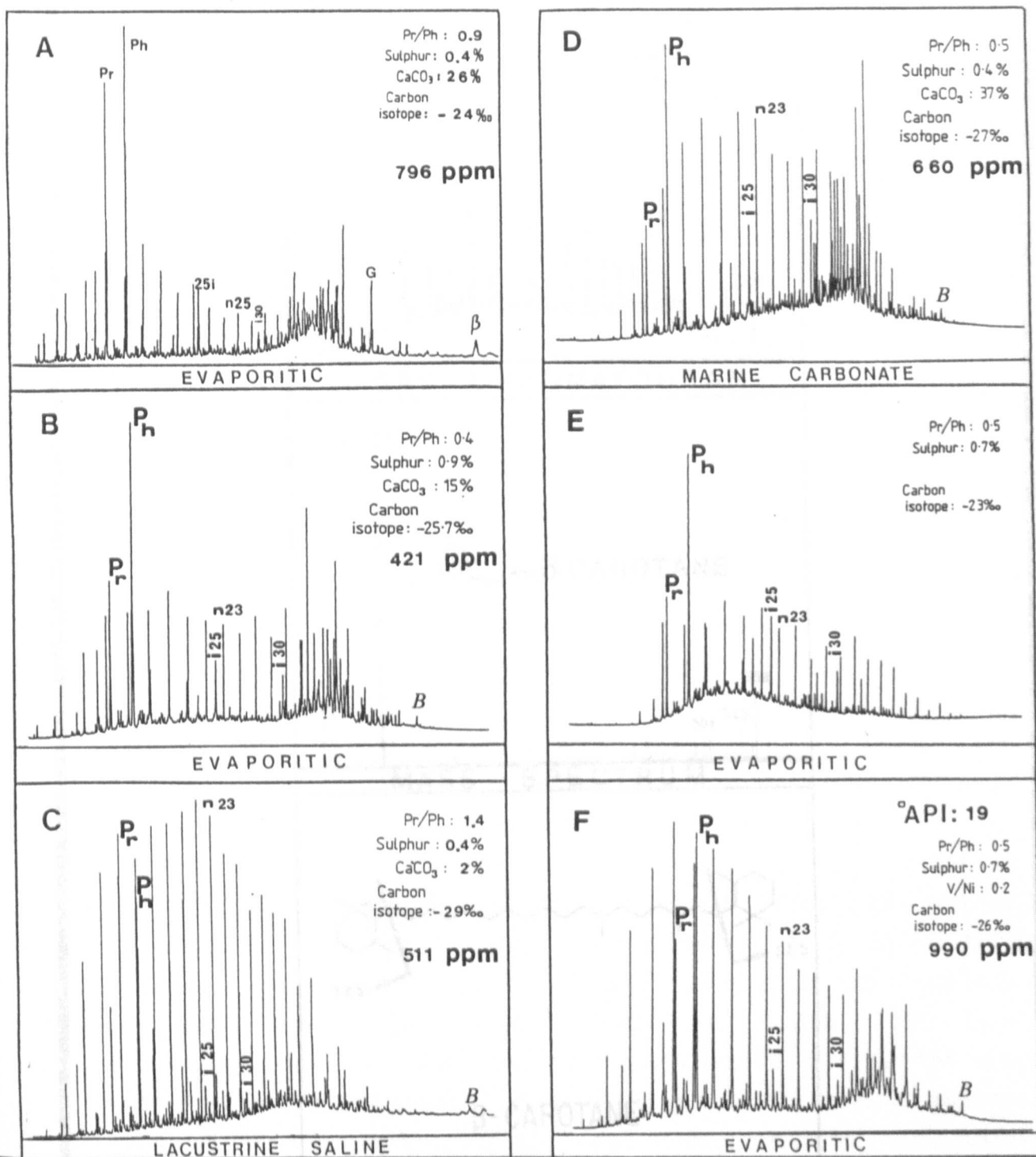
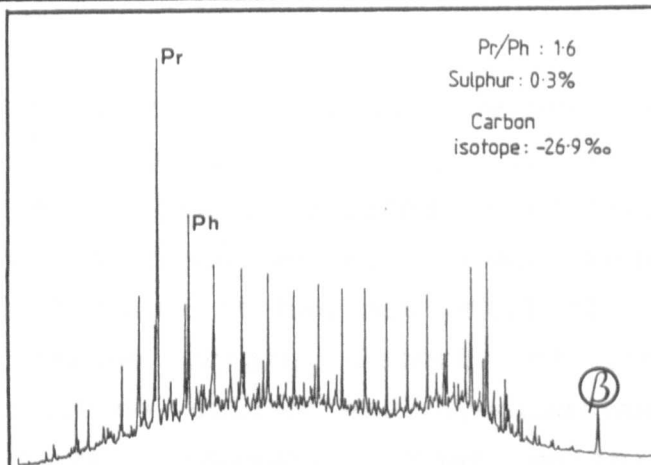
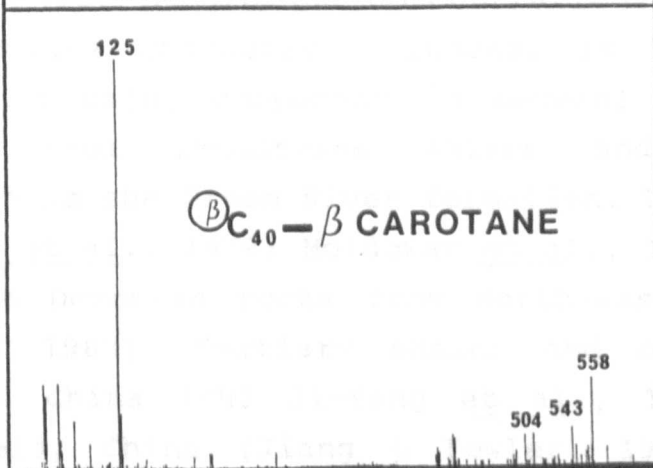


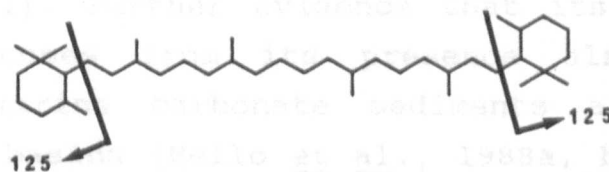
Figure 8- Gas chromatograms of total alkanes, bulk and elemental parameters from sediment extracts and an oil sample from different depositional environments, with ppm values of $i\text{-C}_{25} + i\text{-C}_{30}$ isoprenoids; A and B: marine evaporitic (FGT-1 and CES-7); C: lacustrine saline water (IP-1); D: marine carbonate (CAU-3); E and F: marine evaporitic (SM-1 and CES-8; for peak assignments and concentration procedures see appendices I and II).



GAS CHROMATOGRAM



MASS SPECTRUM



β -CAROTANE

COMPOUND STRUCTURE

Figure 9- Gas chromatogram of total alkanes from a typical lacustrine saline water environment (RJS-164) with spectrum and structure of β -carotane (for peak assignments see appendix I).

although a direct bacterial origin cannot be discounted. Recently, Hall and Douglas (1983) suggested that its sedimentary presence might be related to an anoxic lacustrine saline environment. Moldowan et al. (1985) regarded it as a terrestrial marker because it had not until then been reported from sources of marine origin. Reports of its presence in samples from lacustrine saline and hypersaline depositional environments suggests, however, that salinity may be a controlling factor for β -carotane concentrations, rather than simply the lacustrine character. Indeed, it has sometimes been reported as a major component in several oil and rock samples derived from lacustrine saline and hypersaline environments, such as the Green River formation, USA (Murphy et al., 1967; Tissot et al., 1978; Moldowan et al., 1985), Permian Autumn shales and Devonian rocks from North-eastern Scotland (Hall & Douglas, 1983), Tertiary shales and oils from the Shengli oilfield, China (Shi Ji-Yang et al., 1982) and the Kelamayi oil field, China (Jiang & Fowler, 1986) and from lacustrine saline and hypersaline sediments and derived oils from Brazilian marginal basins (Mello et al., 1988a, b and Chapters II and III). Further evidence that its abundance is salinity related comes from its presence also in marine evaporitic and marine carbonate sediments and oils from Brazilian marginal basins (Mello et al., 1988a, b and Chapters II and III), as also exemplified in Fig. 10 (see concentrations), and its absence from lacustrine freshwater and "normal" marine environments. Sample C is worthy of comment. This type of sample (Mello et al., 1988c and Chapter II), with a predominance of calcareous lithology, has been assigned as arising from an open marine highly anoxic environment and the presence of β -carotane in significant concentrations has been used as one piece of evidence for enhanced salinity at the time of deposition (Mello et al., 1988c, and Chapter VII). To summarize, β -carotane can be considered a specific biological marker indicator of enhanced salinity conditions in lacustrine and marine depositional environments.

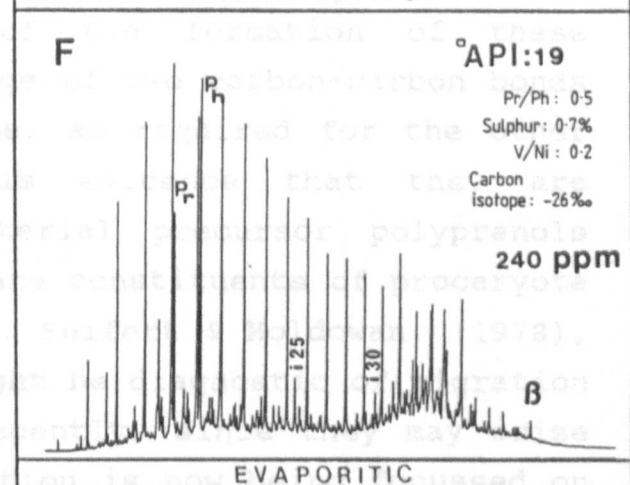
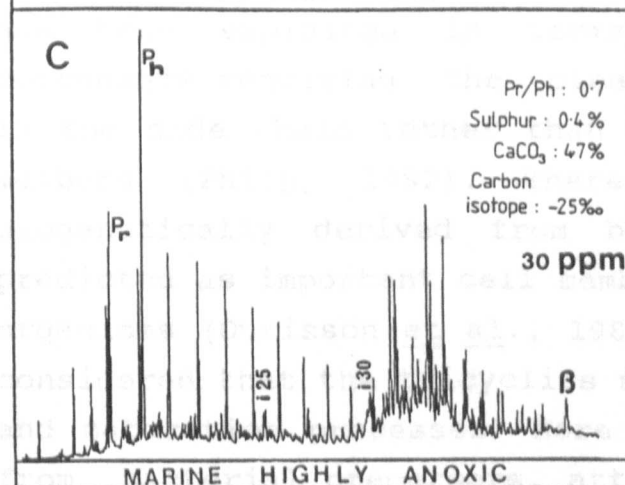
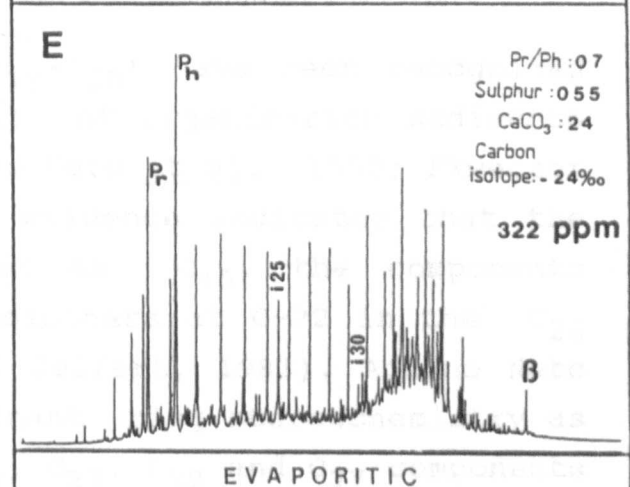
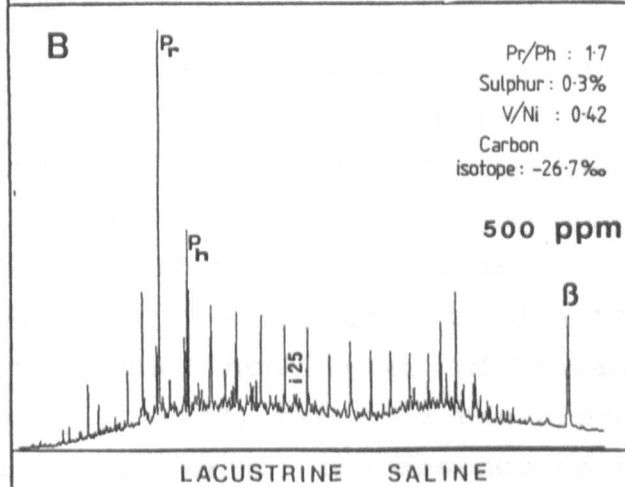
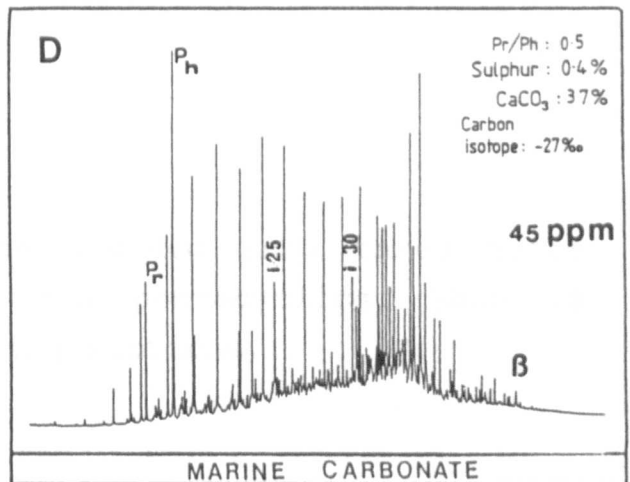
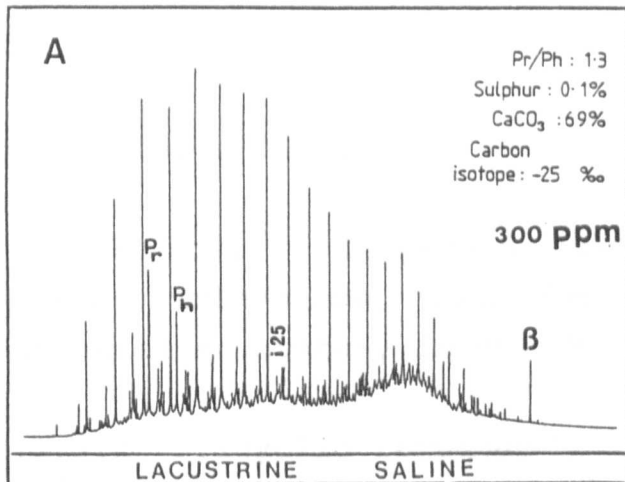


Figure 10- Gas chromatograms of total alkanes, bulk and elemental parameters and ppm values for β -carotene for sediment extracts and an oil sample from different depositional environments; A and B: lacustrine saline water (RJS-101 and RJS-164); C: marine highly anoxic with dominance of calcareous lithology (APS-29); D: marine carbonate (CAU-3); E and F: marine evaporitic (FGT-1 and F: CES-8; for peak assignments and concentration procedures see appendices I and II).

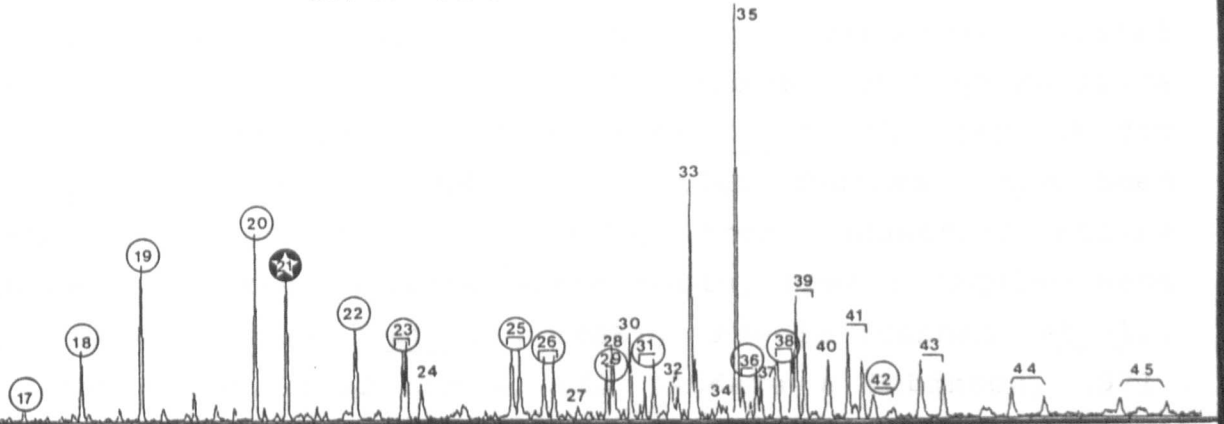
4.3.2 Terpenoids.

The cyclic terpenoids can be divided into three major groups; tricyclics, tetracyclics and pentacyclics. Each is discussed separately in the following sections.

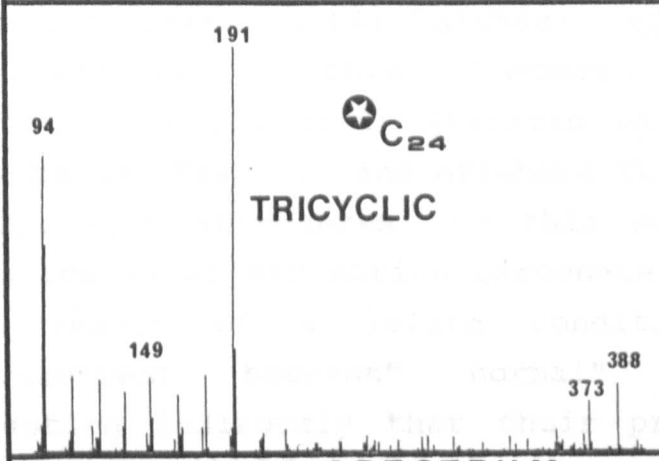
4.3.2.1 Tricyclic terpanes

The extended tricyclic terpanes (C_{19} - C_{30}) have been recognized as usual components (e.g. Fig. 11) of organic-rich sediments and oils of various origins (Aquino Neto et al., 1982; Ekweozor & Strausz, 1983). More recently, evidence indicates that the series extends at least as far as C_{45} , the components occurring as mixtures of diastereoisomers at C-22 in the C_{26} and higher homologues (Moldowan & Seifert, 1983). Aquino Neto et al. (1983) reported the predominant ring stereochemistry as $13\beta(H)$, $14\alpha(H)$. The absence of C_{22} , C_{27} , C_{32} and C_{37} components has been explained in terms of the formation of these components requiring the cleavage of two carbon-carbon bonds in the side chain rather than one, as required for the other members (Philp, 1982). There is evidence that they are biogenetically derived from bacterial precursor polyprenols predicted as important cell membrane constituents of procaryote organisms (Ourisson et al., 1982). Seifert & Moldowan, (1978), considered that the tricyclics might be diagnostic of migration and maturation processes. More recently, since they may arise from bacterial precursors, attention is now being focussed on their application as source input indicators. Indeed, the ratio of tricyclic terpanes/ C_{30} hopane has been proposed as a source correlation parameter (Seifert and Moldowan, 1981). Little has been reported, however, about the distribution of tricyclic components in terms of the environment of deposition. Mello et al. (1988a, b) suggested that their main significance lies in their abundance, rather than their distribution pattern (see also Chapter II and III). The investigation of a set of rock and oil samples from Brazilian basins indicated that samples

M/Z 191

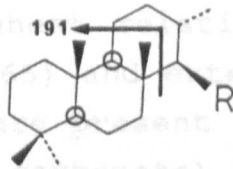


MASS FRAGMENTOGRAM



MASS SPECTRUM

TRICYCLIC TERPANES



R = H, CH₃, C₂H₅, i-C₃H₇....

COMPOUND STRUCTURE

A series of Des-E tetracyclic terpanes (e.g. Fig. 13).
Figure 11- Partial m/z 191 chromatogram of alkane fraction from an oil sample derived from lacustrine saline water environment (RJS-305) showing the distribution pattern of the tricyclic terpanes from C₁₈ to C₃₅, with the spectrum of the C₂₄ component and the tricyclic terpanes structure (for peak assignments see appendix I).
Anders & Robinson, 1983; Abdullah et al., 1988; Helle et al., 1989a, b). Little has been published about this

from lacustrine saline water and marine carbonate related environments are characterized by the presence of high relative abundances of components ranging from C₁₉ to C₃₅ (except for C₂₂, C₂₇ and C₃₂). Indeed, a similar feature has been reported for rock and oil samples from lacustrine saline environments in the Espirito Santo basin, Brazil (Aquino Neto et al., 1986; Rodrigues et al., 1988), Angola (Connan et al., 1988), the Green River shale, USA (Anders & Robinson, 1971; Reed, 1977); marine carbonate related environments from La Luna formation, Venezuela (Cassani, 1986; Talukdar et al., 1986), Middle Magdalena Valley, Colombia (Zumberge, 1984) and Sunniland formation, South Florida (Palacas et al., 1984), from the Aquitaine basin, France, and offshore Tunisia (Aquino Neto et al., 1983). High abundances of this series, linked with lacustrine saline water and marine carbonate environments appear to be a result of a saline condition for the depositional environment between "normal" marine and hypersaline, suggesting indirectly that their precursors are suppressed by hypersalinity conditions (Mello et al., 1988a, b; see also Chapters II and III). As examples, Fig. 12 shows m/z 191 mass chromatograms of the alkane fractions from a series of rock extracts from different depositional environments, possessing similar vitrinite reflectance values. As can be observed the highest relative abundance (tricyclic index (Ti) around 144 and 165) and extended series (up to C₃₅) of the tricyclic compounds are present in samples B (lacustrine saline water) and C (marine carbonate).

4.3.2.2 Tetracyclic terpanes.

A series of Des-E tetracyclic terpanes (e.g. Fig. 13), ranging from C₂₄-C₂₇, has been reported from rock and oil samples from a variety of depositional environments (e.g. Anders & Robinson, 1971; Trendel et al., 1982; Aquino Neto et al., 1983; Philp & Gilbert, 1986; Abdullah et al., 1988; Mello et al., 1988a, b). Little has been published about this

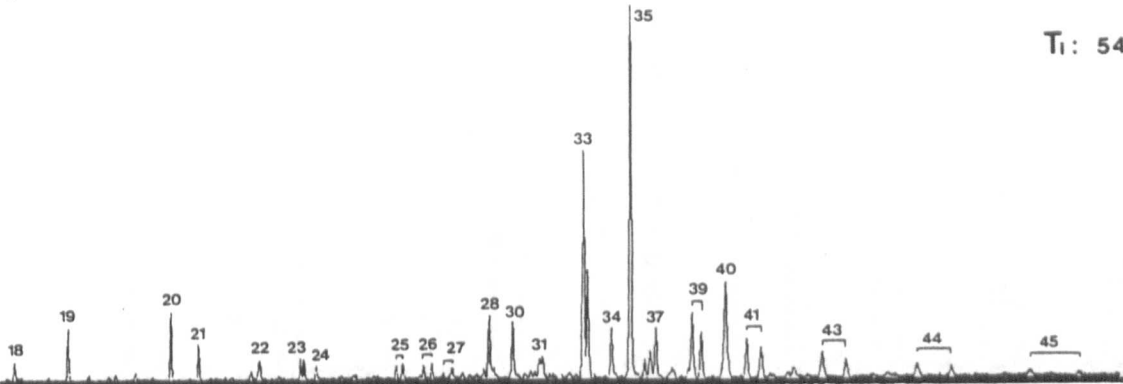
Figure 12- Partial m/z 191 chromatograms for alkane fraction from sediment extracts from different depositional environments, with vitrinite reflectance (Ro%) and tricyclic index(Ti) data; A: lacustrine freshwater (CS-1); B: lacustrine saline water (RJS-71); C: marine carbonate (APS-31); D: marine evaporitic (CES-41; for peak assignments and tricyclic index measurements see appendices I and II).

M/Z 191

A

Ro: 0.60 %

Ti: 54



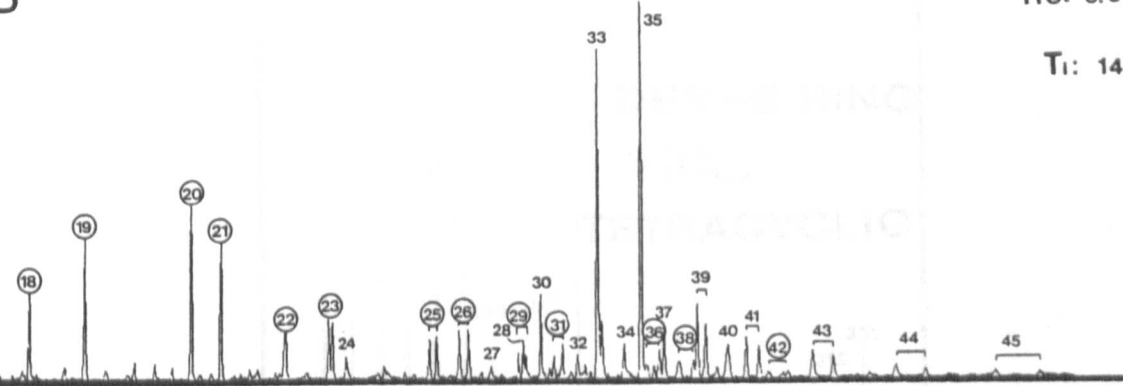
LACUSTRINE

FRESH WATER

B

Ro: 0.55 %

Ti: 144



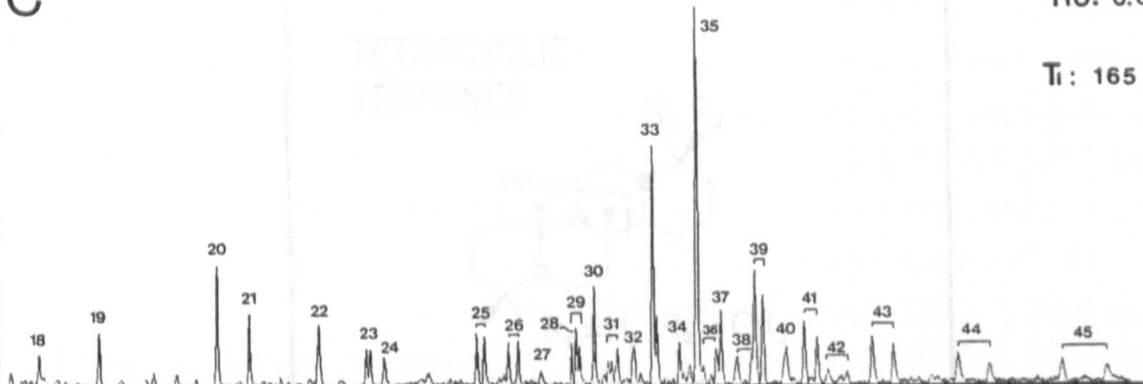
LACUSTRINE

SALINE WATER

C

Ro: 0.62 %

Ti: 165



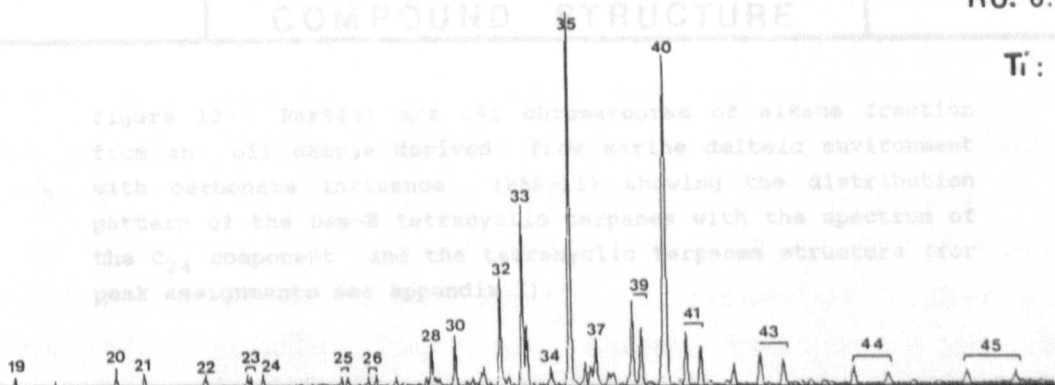
MARINE

CARBONATE

D

Ro: 0.60 %

Ti: 22

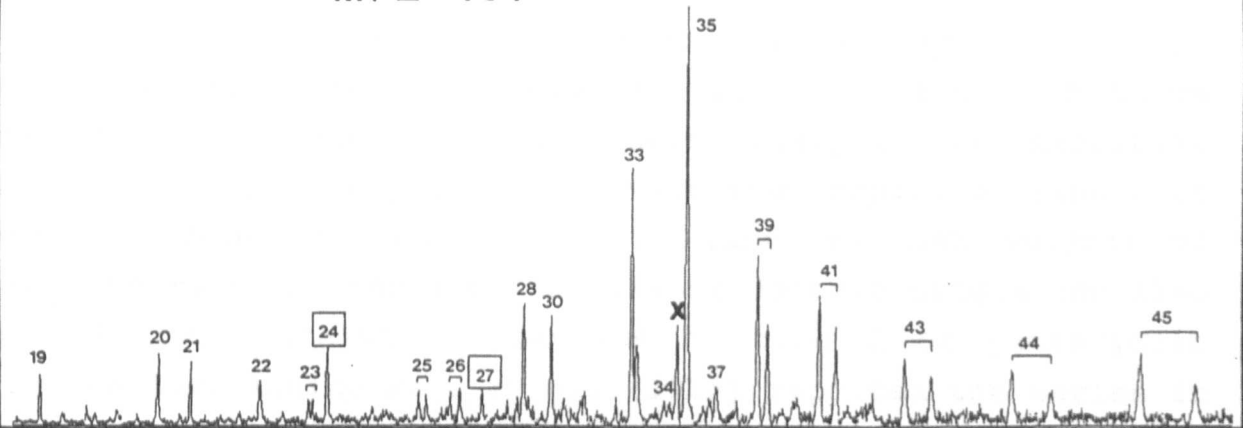


MARINE

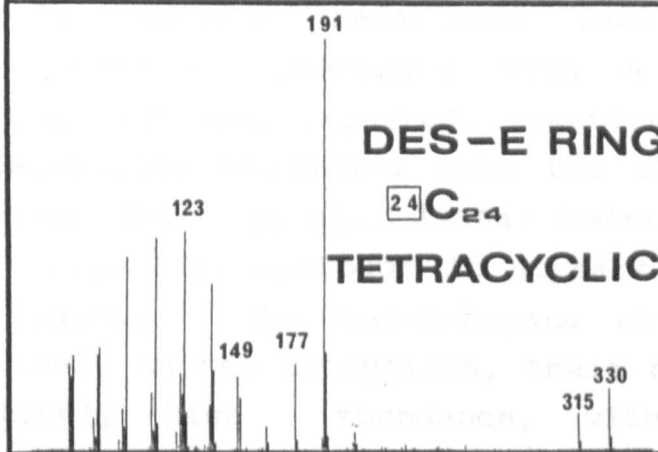
EVAPORITIC

Figure 13. Partial m/z 191 chromatograms of alkane fraction from an oil sample derived from marine diatomic environment with carbonate incidence (10%) showing the distribution pattern of the hex-5 tetra-cyclic terpenes with the spectrum of the C₂₄ component and the bicyclic terpenes structure (for peak assignments see appendix).

M/Z 191



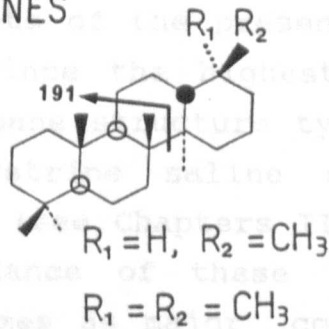
MASS FRAGMENTOGRAM



DES-E RING
 C_{24}
 TETRACYCLIC

MASS SPECTRUM

TETRACYCLIC TERPANES



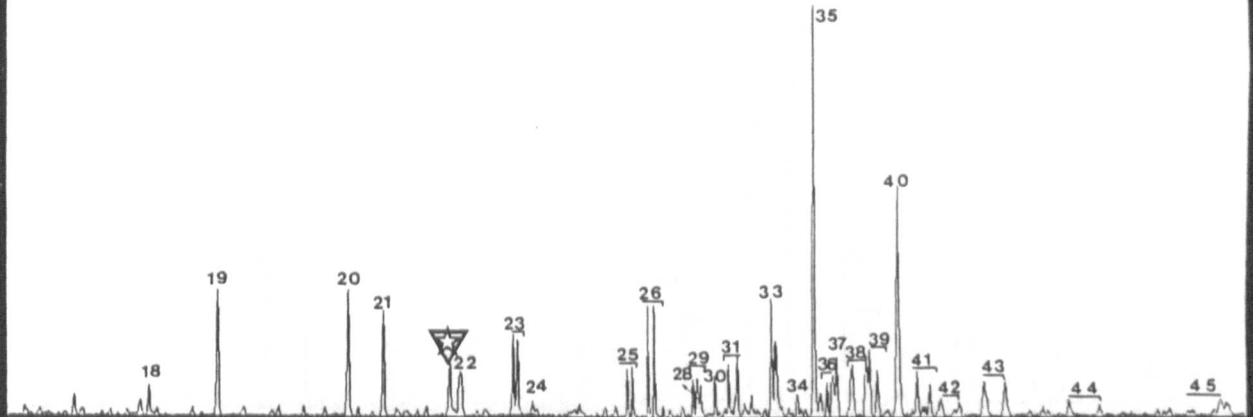
COMPOUND STRUCTURE

Figure 13- Partial m/z 191 chromatogram of alkane fraction from an oil sample derived from marine deltaic environment with carbonate influence (PAS-11) showing the distribution pattern of the Des-E tetracyclic terpanes with the spectrum of the C_{24} component and the tetracyclic terpanes structure (for peak assignments see appendix I).

As an example Fig. 14 shows the m/z 191 mass

relatively new class of biomarker. Trendel et al. (1982) proved the structures and proposed that the origin of these compounds came about through thermocatalytic or microbial degradation of hopane precursors, with the opening of ring E of hopanoids. Ekweozor et al. (1981) reported high amounts of C₂₄-C₂₇ tetracyclic terpanes in oils of deltaic origin and also proposed thermocatalytic cleavages of ring E of pentacyclic triterpenoids. Aquino Neto et al. (1983) reported the series in several marine carbonate oils and sediments, with the C₂₄ member being by far the most predominant. Recently, a novel C₂₄ tetracyclic compound, apparently with a Des-A-hopane structure (Fig. 13a) has been reported, sometimes as a major compound, from lacustrine sediments from the Espirito Santo basin, Brazil (Aquino Neto et al., 1986a; Rodrigues et al., 1988; this study; Fig. 14). Although it appears that some of these compounds (mainly C₂₄ Des-E-hopane structure type) occur almost as widely as the tricyclics, their co-occurrence, always in relatively high abundance, with non-marine/lacustrine depositional environments suggests that they may perhaps arise from precursors in terrestrial organisms, although a bacterial source cannot be discarded (see Brassell et al., 1983). The results of the present study support such an assumption in part, since the highest abundance of these compounds (mainly Des-E-hopane structure type) are found in the marine deltaic and lacustrine saline environments in the Brazilian marginal basins (see Chapters II and III). Indeed, a very high relative abundance of these compounds has been reported to occur, sometimes as major components of the m/z 191 mass chromatograms, in early Carboniferous coals (Spitsbergen, Norway) deposited in a flood plain/lacustrine environment (Abdullah et al., 1988), deltaic oils from Nigeria (Ekweozor et al., 1981), and Australian coals and oils derived from terrestrial sources (Philp & Gilbert, 1986). Hence in the absence of other evidence, the presence of high abundances of tetracyclic terpane compounds may be a marker of higher plant input. As an example Fig. 14 shows the m/z 191 mass

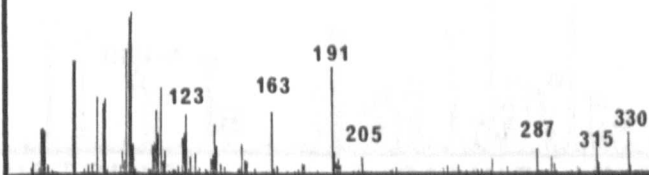
M/Z 191



MASS FRAGMENTOGRAM

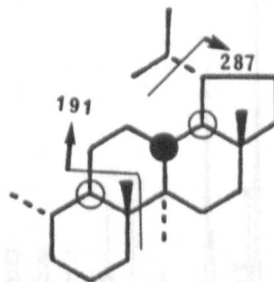
DES-A RING

 C₂₄ TETRACYCLIC



MASS SPECTRUM

Des A C₂₄ TETRACYCLIC



COMPOUND STRUCTURE

Figure 13a- Partial m/z 191 chromatogram of alkane fraction from a sediment extract derived from lacustrine saline water environment (RD-1) showing the distribution pattern of the Des-A tetracyclic terpene with the spectrum of the C₂₄ component and its structure (for peak assignments see appendix I).

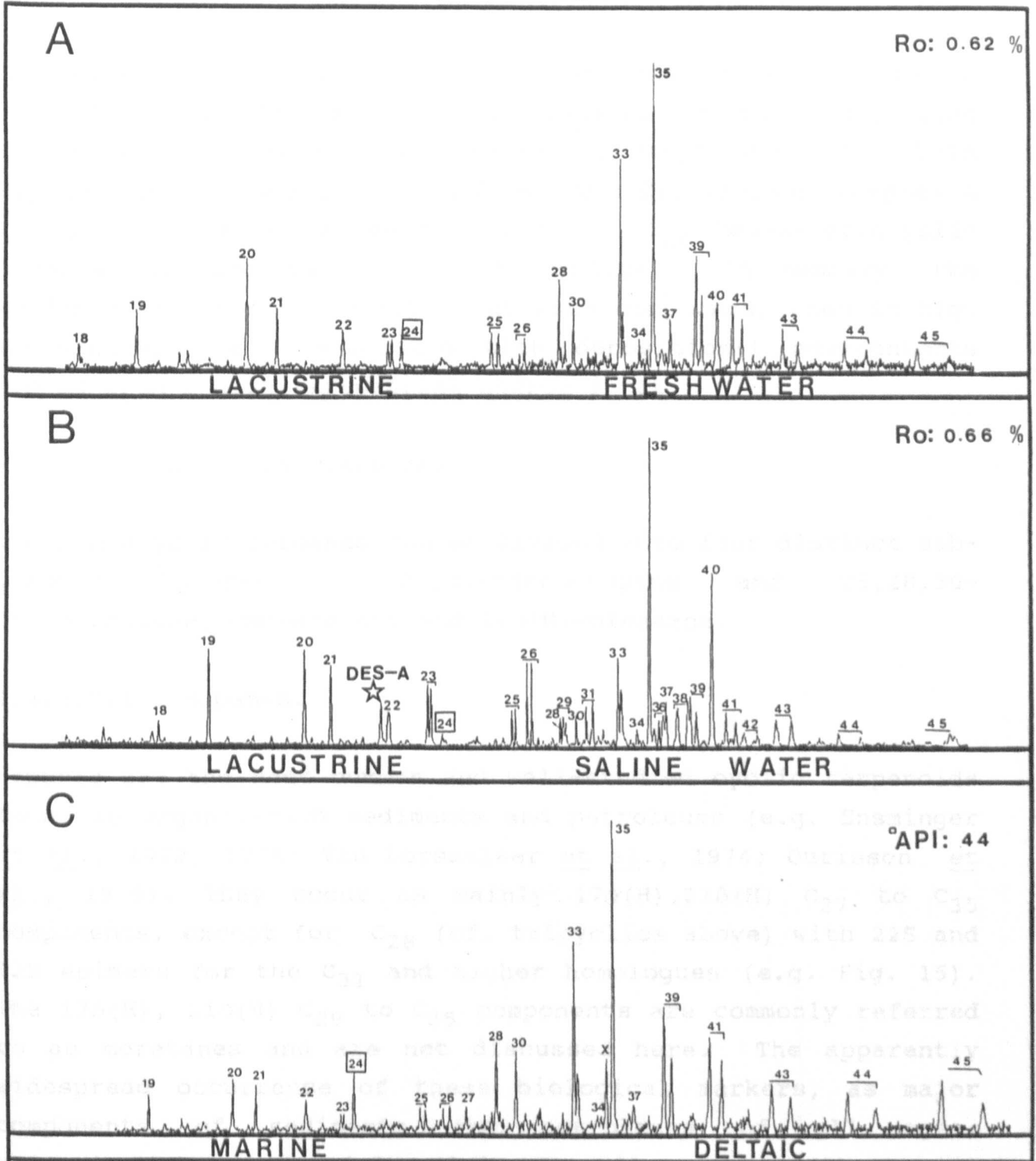


Figure 14- Partial m/z 191 chromatograms for alkane fraction from sediment extracts and an oil from different depositional environments and vitrinite reflectance (Ro) data; A: lacustrine freshwater (RNS-53); B: lacustrine saline water (RD-1); C: marine deltaic with carbonate influence (PAS-11; for peak assignments see appendix I).

chromatograms of a series of rock extracts and an oil sample from different depositional environments in the Brazilian continental margin. As can be observed, sample B contains both C₂₄ tetracyclic terpanes (Des-A and Des-E), whereas samples A and C, have high abundances of the C₂₄ Des-E-tetracyclic terpane relative to the C₂₆ tricyclics. In summary, the evidence at present suggests that such compounds, when in high abundances, are associated with depositional environments linked with a high terrestrial source input.

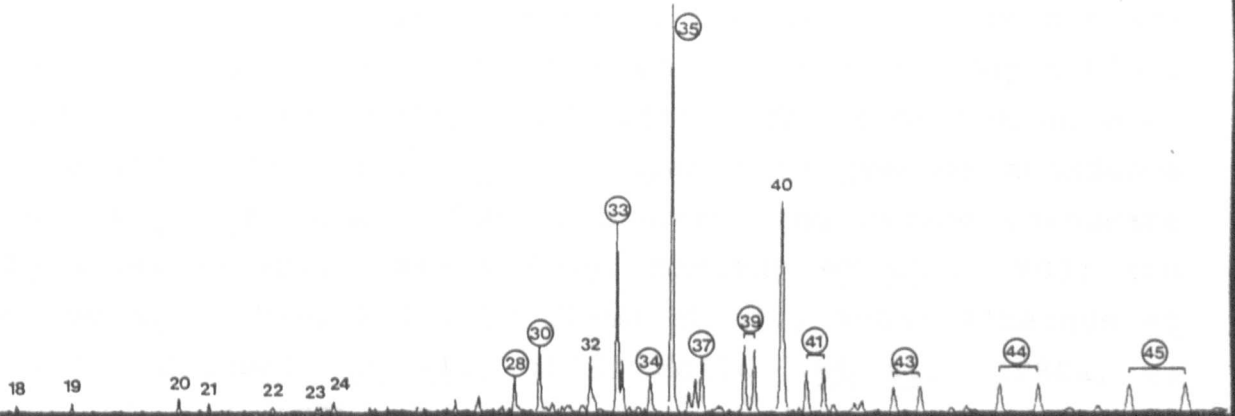
4.3.2.3 Pentacyclic terpanes.

The pentacyclic terpanes can be divided into four distinct subgroups; hopanes, 28,30-bisnorhopane and 25,28,30-trisnorhopane, gammacerane and 18 α (H)-oleanane.

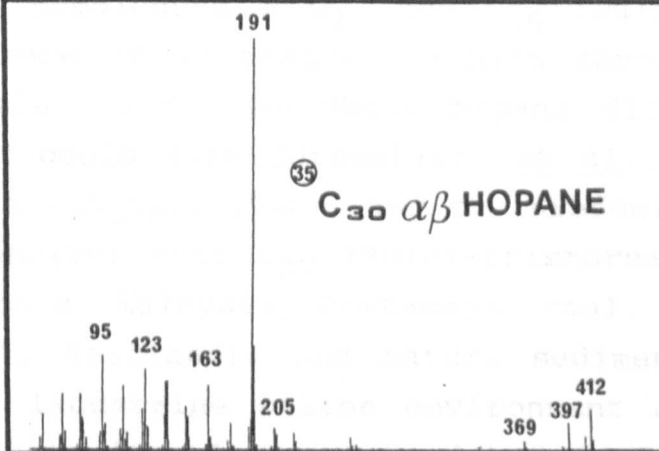
4.3.2.3.1 Hopanes.

Hopanes are the most common and well-studied cyclic terpenoids found in organic-rich sediments and petroleums (e.g. Ensminger et al., 1972, 1974; Van Dorsselaer et al., 1974; Ourisson et al., 1979). They occur as mainly 17 α (H), 21 β (H) C₂₇ to C₃₅ components, except for C₂₈ (cf. tricyclics above) with 22S and 22R epimers for the C₃₁ and higher homologues (e.g. Fig. 15). The 17 β (H), 21 α (H) C₂₉ to C₃₅ components are commonly referred to as moretanes and are not discussed here. The apparently widespread occurrence of these biological markers, as major components of sediments and petroleums of all ages, necessitated a bacterial origin for them. Indeed, bacterial precursors for the hopanes in the form of polyhydroxyhopanoids (important cell membrane constituents) are now well documented (Ourisson et al., 1979 and 1982). Generally, the hopane distributions in sediments and oils are usually very similar; thus the main significance of these biological markers in palaeoenvironmental assessment, as for the tricyclics, must lie in their abundance, rather than in their distribution pattern.

M/Z 191

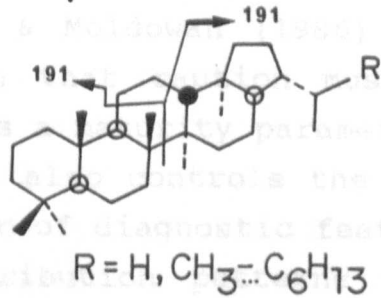


MASS FRAGMENTOGRAM



MASS SPECTRUM

$\alpha\beta$ HOPANES



COMPOUND STRUCTURE

Figure 15- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from marine evaporitic environment (CES-7) showing the distribution pattern of the hopanes with the spectrum of the C₃₀ component and the hopane structure (for peak assignments see appendix I).

In a limited number of cases the distribution pattern does seem to be related to the environment of deposition, although this is not fully understood. The most common are: hopane distributions with C_{35} $\alpha\beta$ hopanes in greater abundance than the C_{34} homologues often characterizing marine carbonate and hypersaline environments (e.g. McKirdy et al., 1983; ten Haven et al., 1985, 1988; Fu Jiamo et al., 1986; Albaigés et al., 1986; Brassell et al., 1988; Mello et al., 1988a, b; Chapter II and III). In some cases, there are carbonate examples with C_{34} homologues $> C_{33}$ and C_{35} (Palacas et al., 1984); the occurrence of an abnormally high abundance of the C_{31} $\alpha\beta$ hopanes relative to the whole hopane distribution in immature peats and coals (Van Dorsselaer et al., 1977; Quirk et al., 1982; Villar et al., 1988), and the predominance of C_{27} $17\alpha(H)$ -trisorhopane(Tm) over C_{27} $18\alpha(H)$ -trisorneopane(Ts) in coals (Tertiary coals, Malaysia, Cretaceous coal, New Zealand, Carboniferous coal, Scotland), and mature sediments and oils associated with a lacustrine saline environment and a marine carbonate environment with higher plant input (McKirdy et al., 1983; Abdullah et al., 1988; Fowler et al., 1988; Mello et al., 1988a, b,; see Chapter III). The Ts/ Tm ratio was established as a typical maturity parameter by Seifert and Moldowan (1980). More recently, Seifert & Moldowan (1986) showed awareness of the problem by stating that caution must be exercised when applying this feature as a maturity parameter since the source input or mineral matrix also controls the ratios. Hence, apart from this limited number of diagnostic features it is difficult to relate hopane distribution patterns to the depositional environment. However, consideration of absolute concentrations (Rullkötter et al., 1984) of hopanes was shown in Chapters II and III to be valid and useful in differing environments of deposition (see also Mello et al., 1988a, b). The lower concentrations of these compounds in freshwater environments relative to saline and hypersaline ones, indicates a lower bacterial input in the former. Perhaps, this observation relates to a salinity increase (Eh-pH) in an environment

stimulating the growth and activity of appropriate bacteria, thereby increasing the terpenoid concentrations. Alternatively, in saline and hypersaline environments, a selected number of adapted bacteria species thrive with little or no competition, producing therefore a tremendous input of lipids to the sedimentary organic matter.

Fig. 16 shows m/z 191 mass chromatograms of a series of rock extracts with similar vitrinite reflectance values from different depositional environments in the Brazilian marginal basins (see also Mello et al., 1988a, b and Chapters II and III). As can be observed in these illustrative examples (chosen deliberately not to represent the extremes of the concentration ranges, see Chapter II) the highest value for the C_{30} $\alpha\beta$ hopane concentration is seen in the evaporitic sample (D), and the C_{35} components are higher than the C_{34} ones. It is also interesting to note the high concentration in the sample derived from a lacustrine saline environment (sample B), and that T_s/T_m (peaks 28/30) is less than 1 in the marine carbonate and lacustrine saline water samples (B and C; see Chapter II and III).

4.3.2.3.1 28,30-Bisnorhopane and 25,28,30-Trisnorhopane

In recent years, there has been considerably more interest in the pentacyclic 28,30-bisnorhopane (e.g. Fig. 17) and the related C_{27} 25,28,30-trisnorhopane (e.g. Fig. 18) than in the other triterpanes. This is mainly due to their selective occurrence, as well as their preferential association with sulphur-rich, highly anoxic environments (e.g. Seifert et al., 1978; Grantham et al., 1980; Rullkötter et al., 1982a, b; Volkman et al., 1983). The 28,30-bisnorhopane was first identified by Petrov et al. (1976) in a petroleum from the Northern Volga, USSR. Seifert et al. (1978) isolated it from the marine Monterey formation, USA, and proved it had the $17\alpha(H), 21\beta(H)$ configuration. Recently, both compounds have been identified in coals (low amounts), sediment extracts and oils

Figure 16- Partial m/z 191 chromatograms for alkane fraction from sediment extracts from different depositional environments, C₃₀ αβ hopane concentration (ppm) and vitrinite reflectance (Ro%) data; A: lacustrine freshwater (CS-1); B: lacustrine saline water (RJS-71); C: marine carbonate (APS-31); D: marine evaporitic (CES-7; for peak assignments and concentration procedures see appendices I and II).

M/Z 191

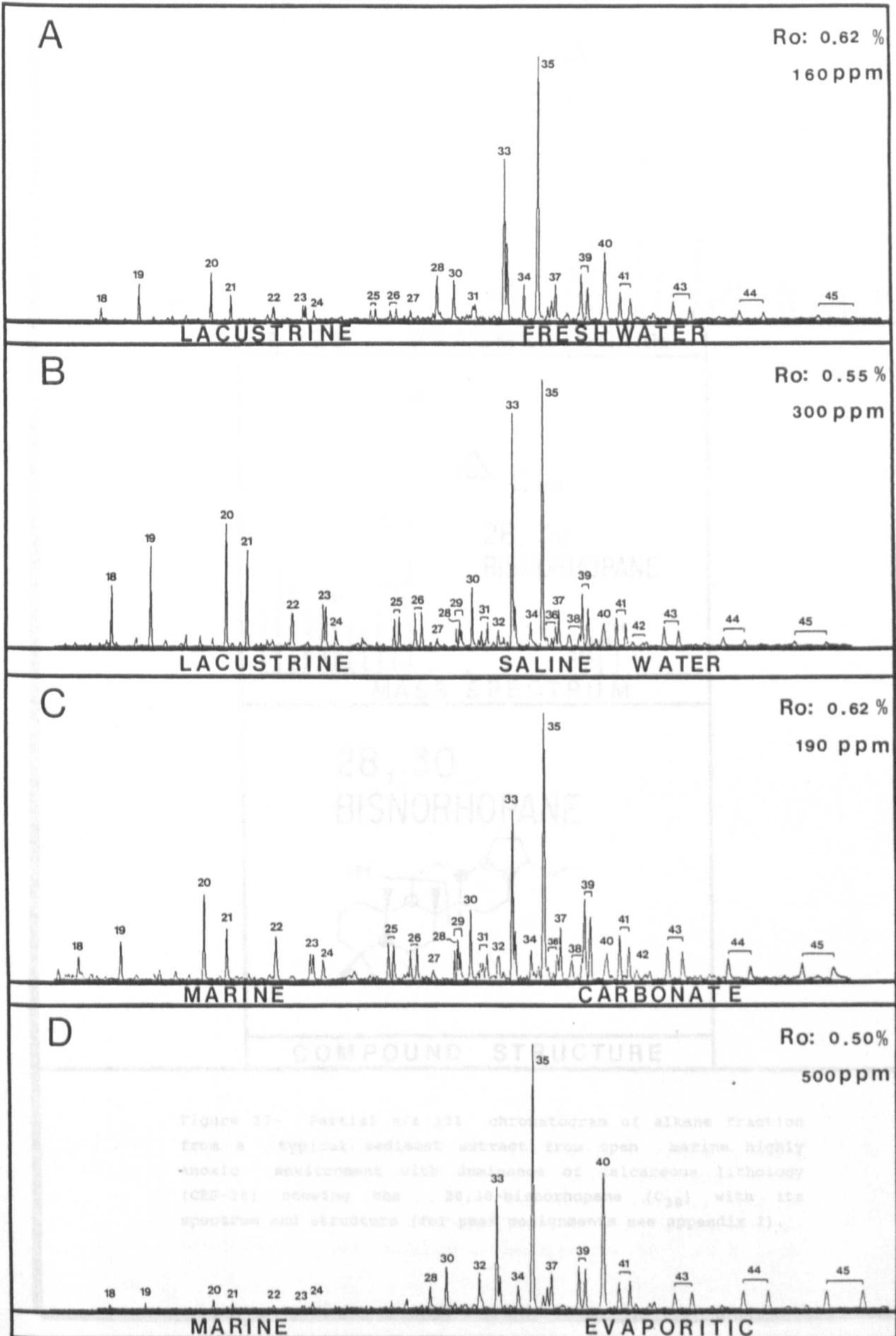
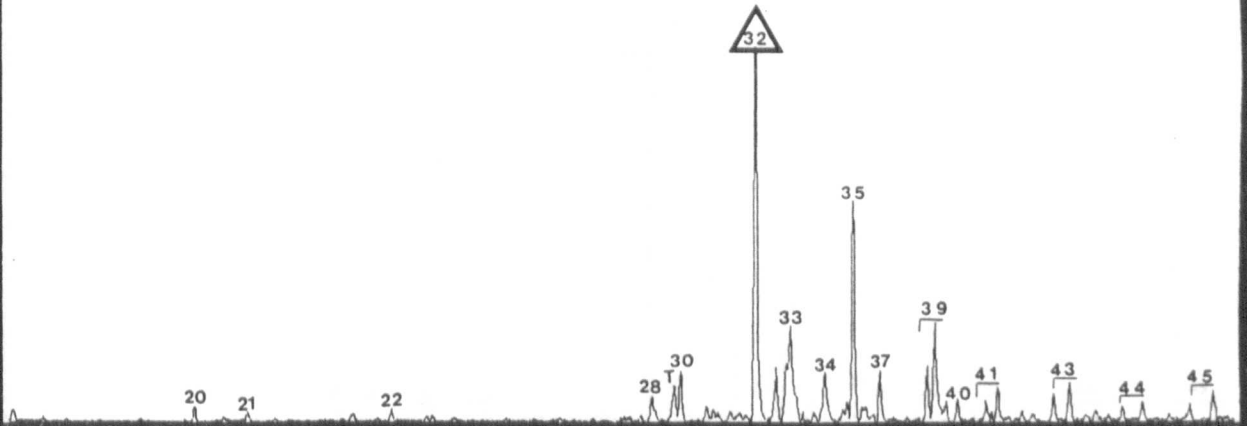
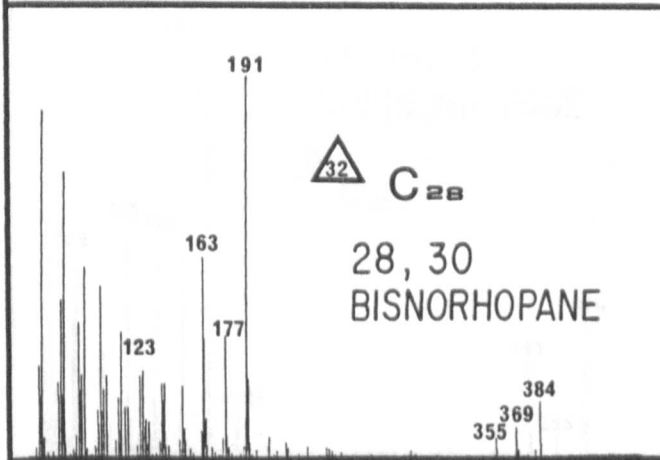


Figure 17- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from open marine, highly anoxic environment with dominance of siliceous lithology (CEP-36) showing the 28,30 bisnorhopane (C₃₁) with its structure and structure (for peak assignments see appendix 3).

M/Z 191

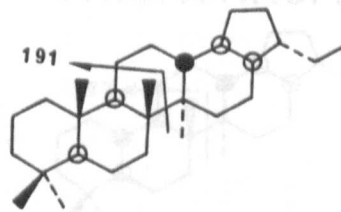


MASS FRAGMENTOGRAM



MASS SPECTRUM

28, 30
BISNORHOPANE

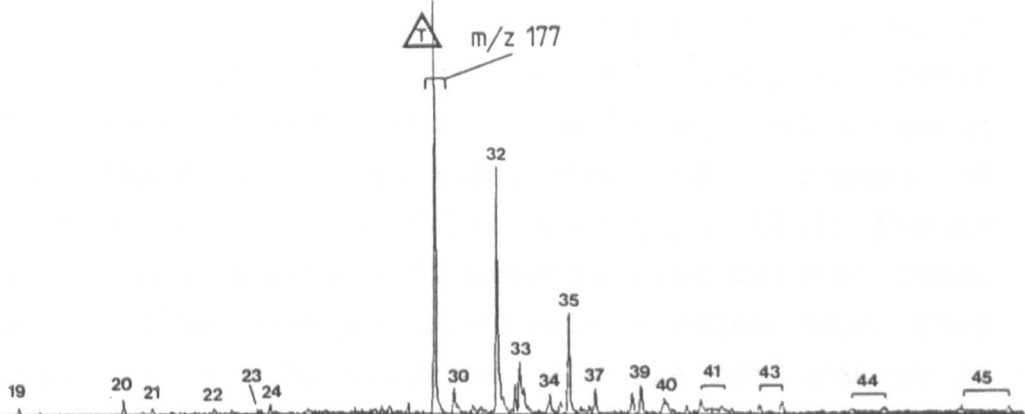


COMPOUND STRUCTURE

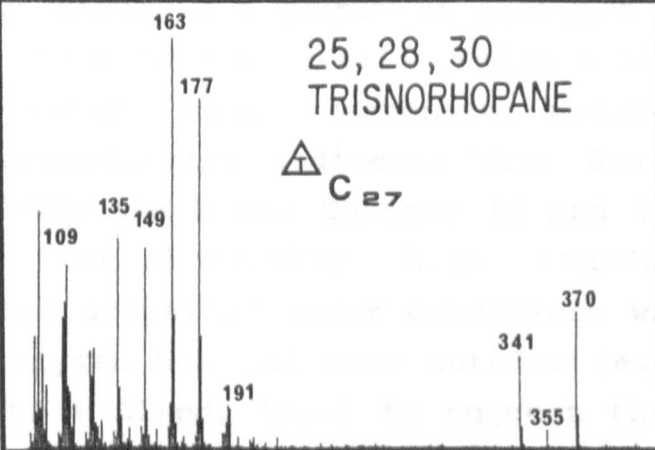
Figure 17- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from open marine highly anoxic environment with dominance of calcareous lithology (CES-28) showing the 28,30-bisnorhopane (C₂₈) with its spectrum and structure (for peak assignments see appendix I).

structure (for peak assignments see appendix I).

M/Z 191



MASS FRAGMENTOGRAM

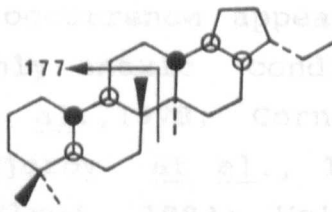


25, 28, 30
TRISNORHOPANE



MASS SPECTRUM

25, 28, 30
TRISNORHOPANE



COMPOUND STRUCTURE

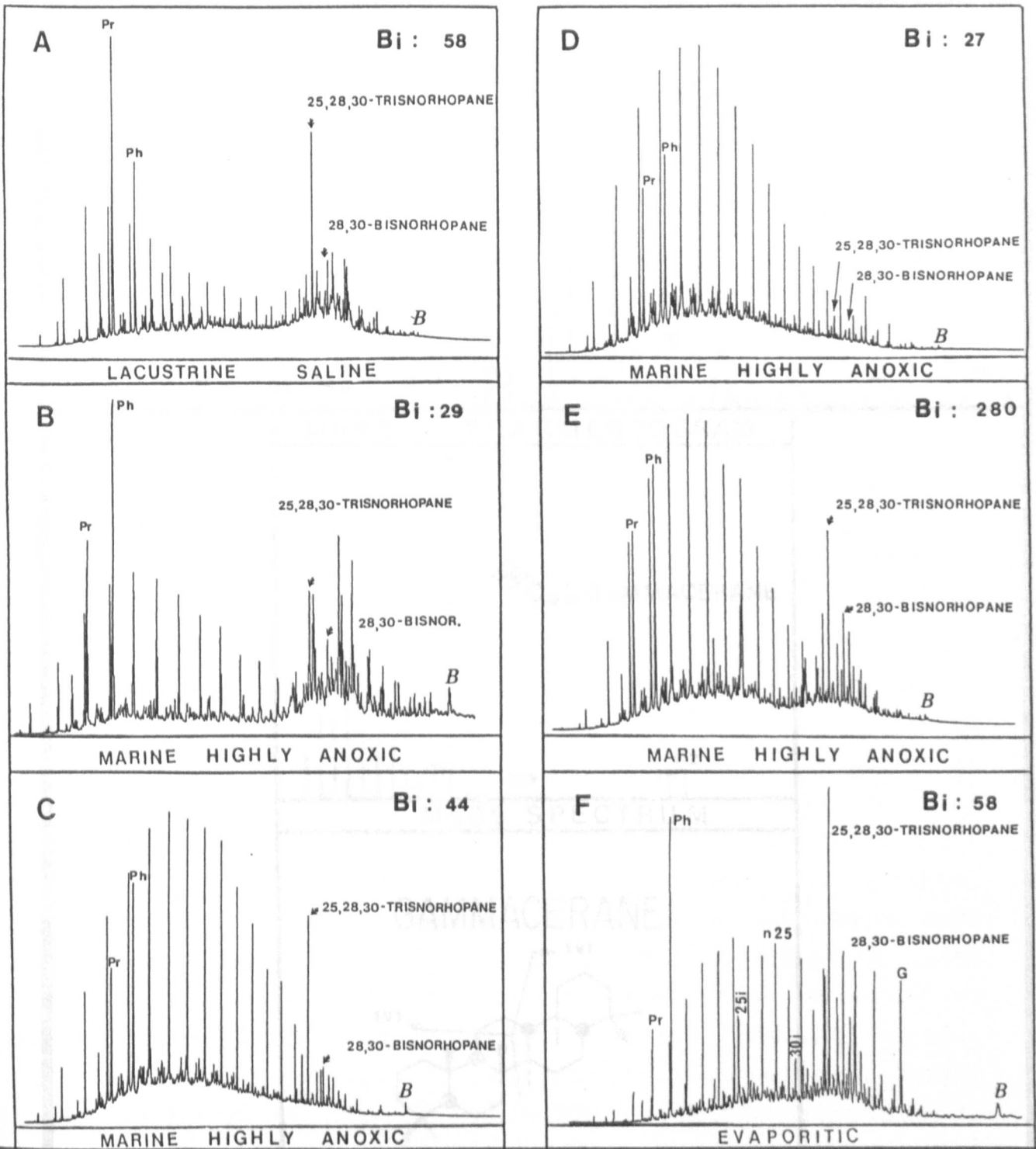
Figure 18- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from open marine highly anoxic environment with dominance of calcareous lithology (CES-19) showing the 25,28,30-trisnorhopane (C₂₇) with its spectrum and structure (for peak assignments see appendix I).

from many parts of the world, varying in age from Pliocene to pre-Devonian (Anders et al., 1978; Fowler & Douglas, 1984; Philp & Gilbert, 1986). The structural similarity and frequent co-occurrence of these two compounds, has led a number of authors (Grantham et al., 1980; Volkman et al., 1983; Fowler and Douglas, 1984) to suggest a diagenetic link between them. It has been shown from kerogen pyrolysis studies that they occur in sediments as free hydrocarbons and are not present as part of the kerogen (Noble et al., 1984). Recently, it has been reported that they occur in a number of distinct depositional environments, i.e. coals from Australia (Philp & Gilbert, 1986), lacustrine saline water, marine carbonate, marine hypersaline and open marine organic-rich sediments from Brazilian basins (Mello et al., 1988a and b and Chapter II and III). Although they occur widely, the abnormally high abundance of these compounds in samples deposited under conditions where there is a severe lack of oxygen has led some authors (e.g. Rullkötter et al., 1982a; Katz & Elrod, 1983) to suggest that they arise from a precursor or precursors in anaerobic bacteria living in strongly reducing conditions. This suggestion arose from the fact that anaerobic bacteria are known to form mat structures (up to 80% of the biomass) within anoxic zones (Gallardo, 1978). Certainly, where they occur in sediments in high relative abundance, this occurrence appears to be associated with deposition under highly anoxic conditions (e.g. Seifert et al., 1978; Anders et al., 1978; Cornford et al., 1980; Grantham et al., 1980; Bjoroy et al., 1980; Rullkötter et al., 1982a, b; Katz & Elrod, 1983; Volkman et al., 1983; Curiale et al., 1985; Mello et al., 1988a, c and Chapter VII). Furthermore, the high absolute concentrations of these compounds (occasionally with the C₂₇ component as the major hydrocarbon) associated with highly anoxic depositional environments in the Brazilian continental margin (Mello et al., 1988c and Chapters II and VII) gives some weight to the idea that the bacteria contributing to the precursors of these terpanes appear to be restricted to severely anoxic

environments (cf. Katz and Elrod, 1983). This allows these biological markers (when in high abundance) to be considered as independent evidence for the presence of extensive severely oxygen deficient conditions in the bottom waters during sediment deposition. For example, Fig 19 shows gas chromatograms of the alkane fractions for several organic-rich sediments deposited in extremely anoxic conditions in the Brazilian marginal basins (see also Chapter II and VII). As can be observed, the 28,30-bisnorhopane and the related C₂₇ 25,28,30-trisnorhopane occur in high concentrations (the former up to 1400 ppm of extract in sample F, and up to 130 ppm in sample E), with the bisnorhopane index (Bi) showing the highest values in the marine highly anoxic samples (B to E). Sample A also contains a high concentration and bisnorhopane index values, although this was not generally observed for the Brazilian samples from this environment (Mello et al., 1988a, b and Chapters II and III). In all of the samples in Fig. 19 the compounds are the major components of the m/z 191 and m/z 177 mass chromatograms, respectively. In contrast, in the lacustrine freshwater and marine deltaic samples from the Brazilian marginal basins these components are absent or present in trace quantities. Also they are in low abundance in the other lacustrine saline samples and open marine samples with a predominance of siliciclastic lithology (Mello et al., 1988a, b and Chapters II and III).

4.3.2.3.3 Gammacerane.

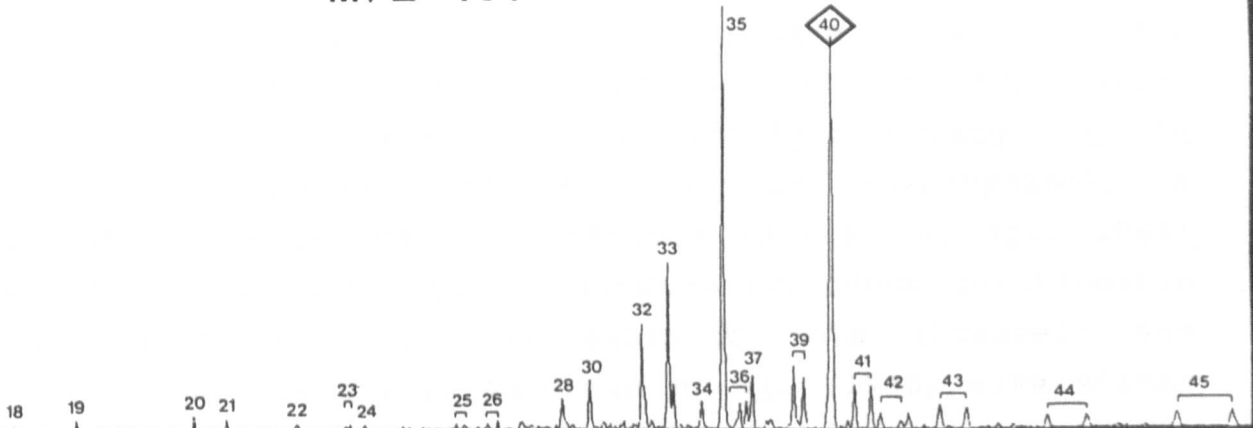
Gammacerane is a non-hopanoid pentacyclic terpane (e.g. Fig. 20), with a much less widespread distribution than the hopanes. This compound was first identified in lacustrine sediments of the Green River shale (Hills et al., 1966), and was initially considered a diagnostic marker of lacustrine environments (Seifert & Moldowan, 1981). Many authors (e.g. Rohrback, 1983; Rodrigues, 1983; Cerqueira et al., 1984; Albaigés et al., 1986; ten Haven et al., 1986; McKirdy et al., 1985; Moldowan



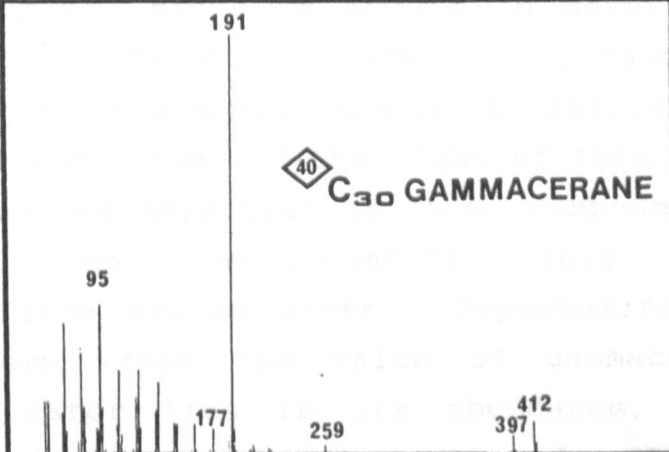
COMPOUND STRUCTURE

Figure 19- Gas chromatograms of total alkanes from sediment extracts from different depositional environments with values of bisnorhopane index; A: lacustrine saline water (ESS-34); B to E: open marine highly anoxic environment with dominance of calcareous lithology (APS-29, CES-56, RJS-225 and CES-28, respectively); F: marine evaporitic (FGT-1, 945m; for peak assignments and bisnorhopane index measurements see appendices I and II).

M/Z 191

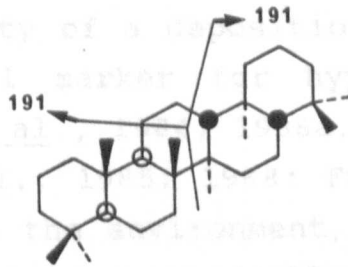


MASS FRAGMENTOGRAM



MASS SPECTRUM

GAMMACERANE



COMPOUND STRUCTURE

Figure 20- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from marine evaporitic environment (CES-41) showing gammacerane with its spectrum and structure (for peak assignments see appendix I).

chromatograms, have been reported for sediments and petroleums from hypersaline environments: e.g. the Green River, USA, Ameghino-Marin (Shi Ji-Yang et al., 1982), Messina (Shi Ji-Yang et al., 1982; Shangli et al., 1982; Fu Jianso et al., 1986), Ceara basin, Brazil

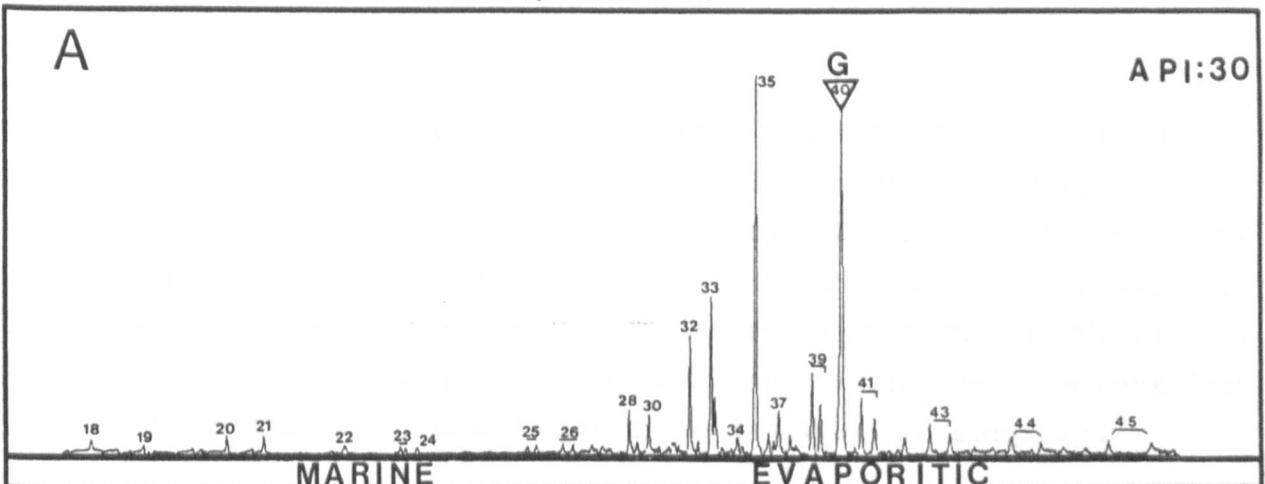
et al., 1985; Fu Jiamo et al., 1986), have, however, since reported it in samples from marine carbonate and hypersaline environments. The only known biologically-occurring compound with a gammacerane-type skeleton is tetrahymanol, a constituent of a non-marine protozoan (Hills et al., 1966; Whitehead, 1974), although any precursor/product relationship has not been verified from sediment data (Brassell and Eglinton, 1986). Recently, Moldowan et al. (1985) have stated that gammacerane cannot be used to distinguish between marine and non-marine samples, since it occurs in several different environments. Such evidence suggests the possibility of a bacterial origin for gammacerane, given its fairly widespread occurrence in time and space. In the light of this possibility, and bearing in mind the detection of this compound in several different depositional environments (e.g. lacustrine freshwater, lacustrine saline water, hypersaline and marine carbonate), it seems that the value of gammacerane as an environmental indicator lies in its abundance, rather than simply in its presence (see Chapters II and III). The high abundance (sometimes the major triterpane) in hypersaline organic-rich sediments and oils from the Brazilian marginal basins (e.g. Fig. 21) indicates that this it may be a good indicator of the salinity of a depositional environment, being a diagnostic biological marker for hypersaline episodes of sedimentation (Mello et al., 1984, 1988a, b); Moldowan et al., 1985; ten Haven et al., 1985; 1988; Fu Jiamo et al., 1986). Indeed, the more saline the environment, the higher appears to be the abundance of gammacerane (Mello et al., 1988a, b). Supporting such an assumption, extremely high concentrations of gammacerane, sometimes as the major peak in m/z 191 chromatograms, have been reported for sediments and petroleums from hypersaline environments; e.g. the Green River, USA, Amposta-Marino, Spain and Prinos, Greece (Moldowan et al., 1985), Messinian basin, northern Italy (ten Haven et al., 1985; Shengli oilfield and Jiangnan basin, China (Shi Ji-Yang et al., 1982; Fu Jiamo et al., 1986), Ceará basin, Brazil

Figure 21- Partial m/z 191 chromatograms for alkane fraction from sediment extracts and an oil from different depositional environments and vitrinite reflectance (Ro%) and API data; A: marine evaporitic (CES-41); B: lacustrine saline water (RD-1); C and D: marine evaporitic (CES-7 and CES-41; for peak assignments see appendix I).

M/Z 191

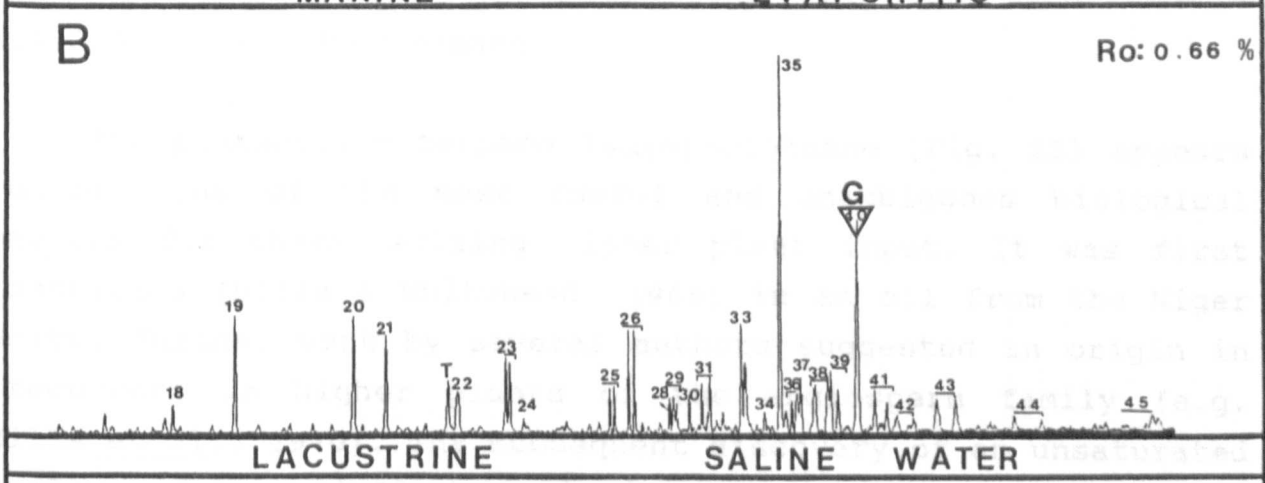
A

API:30



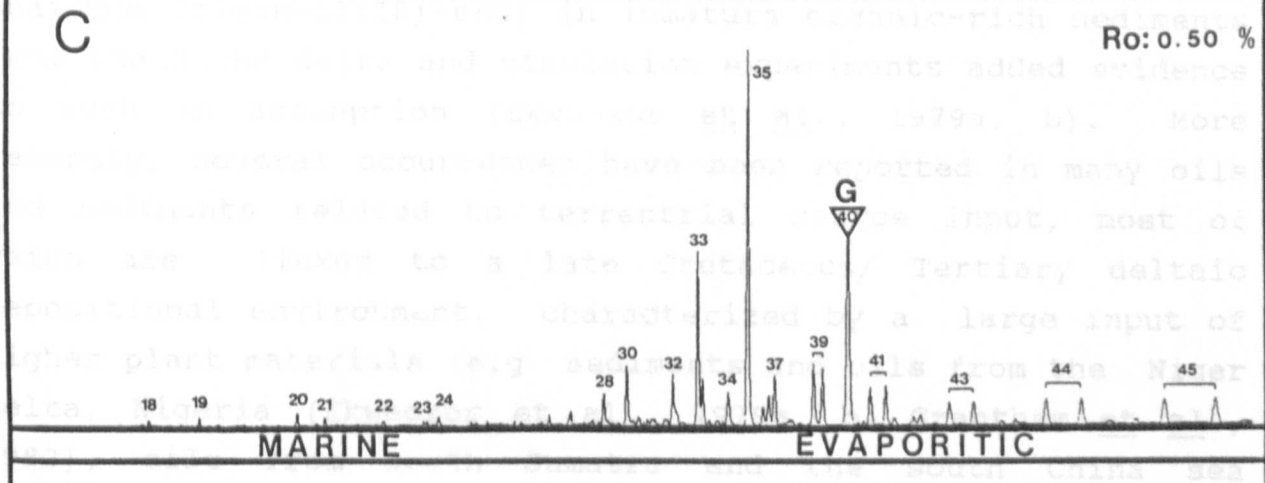
B

Ro: 0.66 %



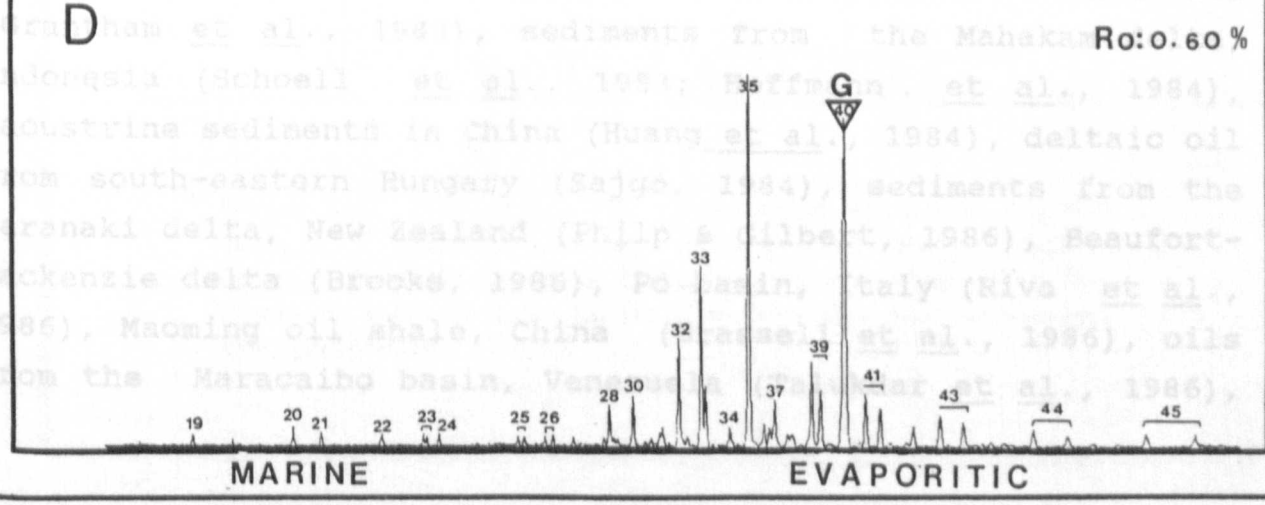
C

Ro: 0.50 %



D

Ro: 0.60 %

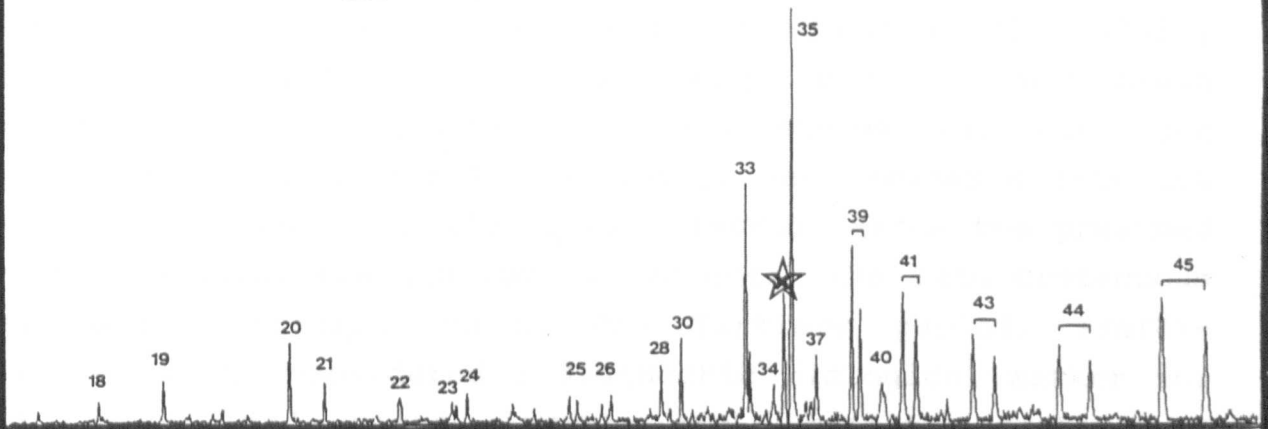


(Mello et al., 1984; Cerqueira et al., 1984; Espirito Santo, Sergipe-Alagoas, Potiguar and Ceará basins in the Brazilian continental margin (Mello et al., 1988a, b and Chapters II and III). Furthermore in the present study (Chapters II and III) much lower abundances were found (low or trace) in samples from open marine and marine deltaic environments, with medium abundances in samples from a lacustrine saline environment but greater than those in the lacustrine freshwater samples.

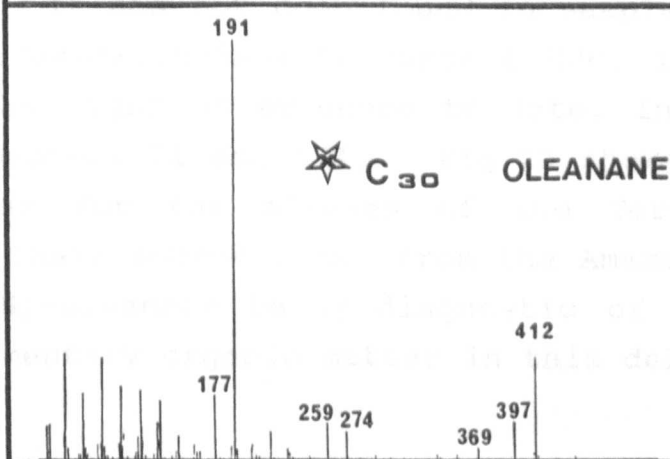
4.3.2.3.4 18 α (H)-Oleanane.

The pentacyclic terpane 18 α (H)-Oleanane (Fig. 22) appears to be one of the most useful and unambiguous biological markers for characterizing higher plant input. It was first identified (Hills & Whitehead, 1966) in an oil from the Niger delta. Further work by several authors suggested an origin in precursors in higher plants of the angiosperm family (e.g. Hills et al., 1970). The subsequent discovery of an unsaturated analogue (olean-13(18)-ene) in immature organic-rich sediments from the Niger delta and simulation experiments added evidence to such an assumption (Ekweozor et al., 1979a, b). More recently, several occurrences have been reported in many oils and sediments related to terrestrial source input, most of which are linked to a late Cretaceous/ Tertiary deltaic depositional environment, characterized by a large input of higher plant materials (e.g. sediments and oils from the Niger delta, Nigeria (Ekweozor et al., 1979a, b; Grantham et al., 1983), oils from south Sumatra and the south China sea (Grantham et al., 1983), sediments from the Mahakam delta, Indonesia (Schoell et al., 1983; Hoffmann et al., 1984), lacustrine sediments in China (Huang et al., 1984), deltaic oil from south-eastern Hungary (Sajgó, 1984), sediments from the Taranaki delta, New Zealand (Philp & Gilbert, 1986), Beaufort-Mackenzie delta (Brooks, 1986), Pó basin, Italy (Riva et al., 1986), Maoming oil shale, China (Brassell et al., 1986), oils from the Maracaibo basin, Venezuela (Talukdar et al., 1986),

M/Z 191

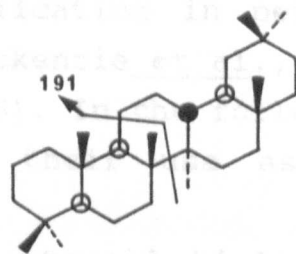


MASS FRAGMENTOGRAM



MASS SPECTRUM

18 α (H) OLEANANE



COMPOUND STRUCTURE

Figure 22- Partial m/z 191 chromatogram of alkane fraction from a typical sediment extract from marine deltaic environment with carbonate influence (APS-36) showing 18 (H)-oleanane with its spectrum and structure (for peak assignments see appendix I).

Coals of the Kutai basin, Indonesia (Thompson et al., 1985), sediments and oils from the the Congo delta, Angola basin (Connan et al., 1988), upper Cretaceous shales from the Niger delta, Nigeria (Ekweozor & Udo, 1988), and sediments from the Amazon delta, Brazil (Mello et al., 1988b). Since the presumed precursor angiosperms did not evolve until the late Cretaceous epoch and flourished during the Tertiary period, $18\alpha(H)$ -Oleanane can be considered a diagnostic biological marker for both source(land plant input) and age(late Cretaceous/Tertiary). Indeed, it has not been found in samples older than late Cretaceous (Maastrichtian; Ekweozor & Udo, 1988; Riva et al., 1988), in the light of evidence to date. In relation to the studies in Chapters II and III, Fig.23 shows the m/z 191 mass chromatograms for the alkanes of two Tertiary marine deltaic oils and their source rock from the Amazon delta, the presence of $18\alpha(H)$ -oleanane being diagnostic of higher plant input to the sedimentary organic matter in this deltaic system.

4.4 STEROIDS

Steroids are as widely used as terpenoids in biological marker studies. Recently, several reviews about their origins transformation and application in petroleum exploration have been published (e.g. Mackenzie et al., 1982a, b ; Philp, 1982; Seifert & Moldowan, 1986). In the following, only those aspects which are related to their use as source indicators are discussed.

A wide number of steroid biological markers have been reported to occur in sedimentary rocks and petroleums. Steroids are derived from sterols (e.g. Mackenzie et al., 1982a, b; de Leeuw & Bass, 1986). Generally, only the saturated components have been used in the assessment of source input and the depositional environment. The most significant are considered separately in the following sections.

M/Z 191

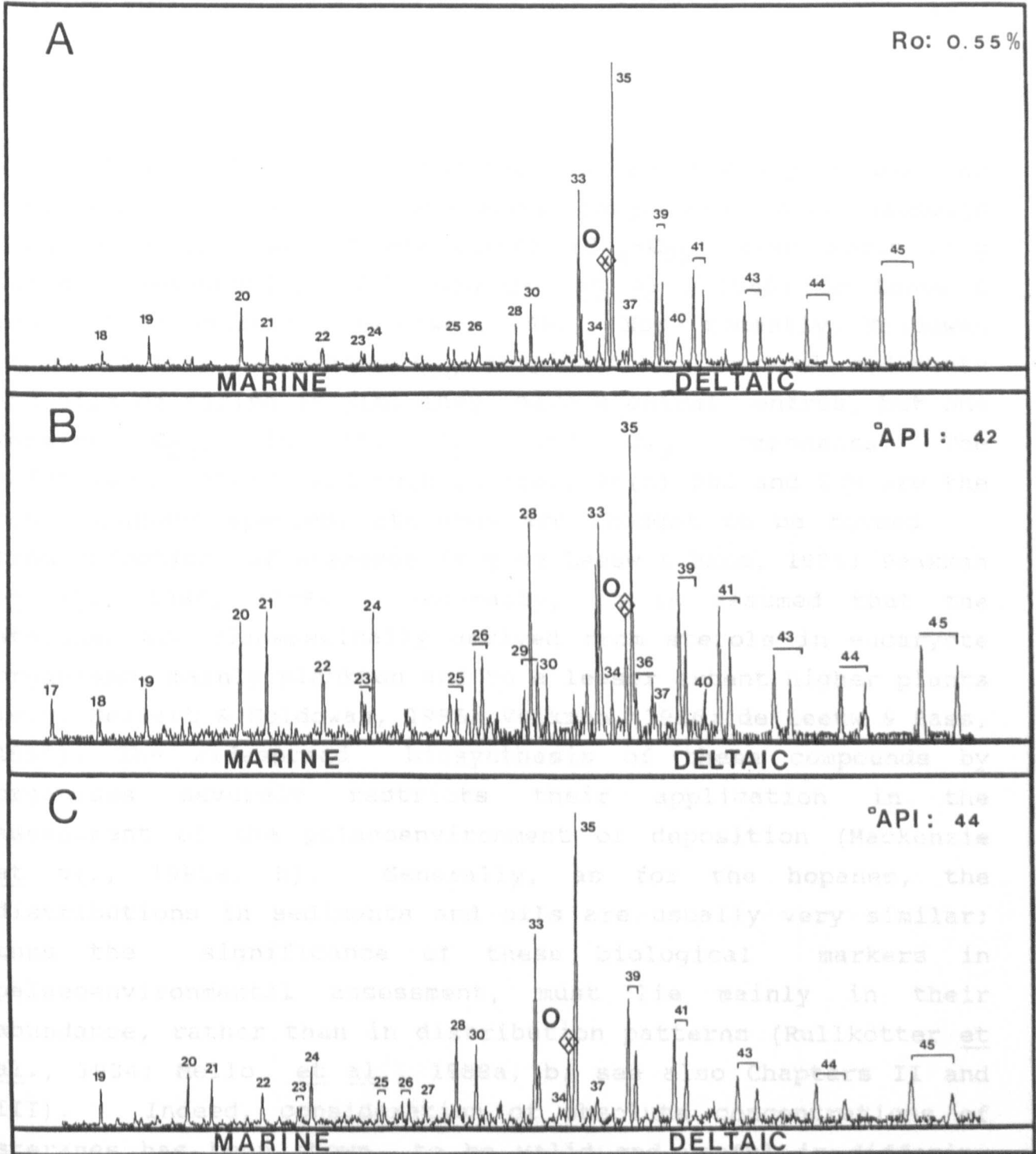


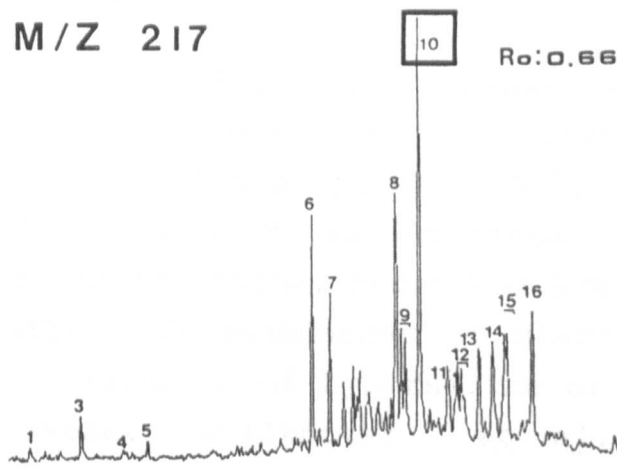
Figure 23- Partial m/z 191 chromatograms for alkane fraction of typical oil samples and a sediment extract from marine deltaic environment with carbonate influence, vitrinite reflectance (Ro%) and API data; A: (APS-36); B: (PAS-9); C: (PAS-11; for peak assignments see appendix I).

4.4.1 Steranes

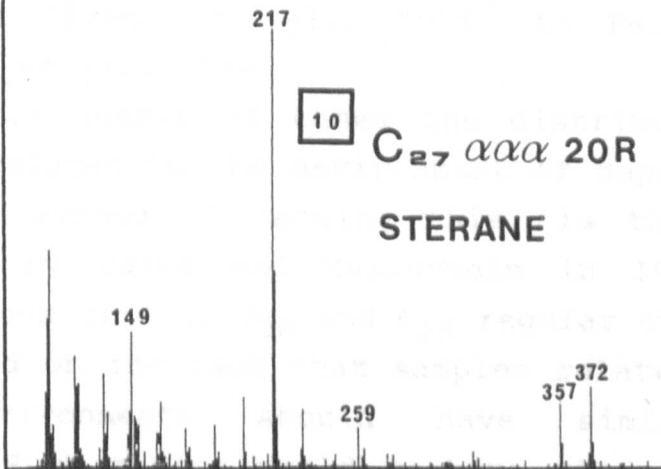
The most common steranes in sedimentary rocks and petroleum are C_{27} - C_{29} components (e.g. Fig. 24), although lower molecular weight components (C_{21} - C_{22}) also occur (e.g. Huang & Meinschein, 1978; Connan et al., 1980; de Leeuw & Bass, 1986; Seifert & Moldowan, 1986). More recently, Moldowan et al. (1985) recognized C_{30} components in several sediments and oils of marine origin. They have 8 chiral centres, but one more (at C_{24}) in the C_{28} and C_{29} components. The $5\alpha(H), 14\alpha(H), 17\alpha(H)$ and $5\alpha(H), 14\beta(H), 17\beta(H)$ 20S and 20R are the most abundant species. Steranes are thought to be formed from reduction of sterenes (e.g. de Leeuw & Bass, 1986; Peakman et al., 1986, 1988). Generally, it is assumed that the steranes are diagenetically derived from sterols in eucaryote organisms, mainly plankton and to a lesser extent higher plants (e.g. Seifert & Moldowan, 1986; Volkman, 1986; de Leeuw & Bass, 1986). The widespread biosynthesis of these compounds by organisms severely restricts their application in the assessment of the palaeoenvironment of deposition (Mackenzie et al., 1982a, b). Generally, as for the hopanes, the distributions in sediments and oils are usually very similar; thus the significance of these biological markers in palaeoenvironmental assessment, must lie mainly in their abundance, rather than in distribution patterns (Rullkötter et al., 1984; Mello et al., 1988a, b; see also Chapters II and III). Indeed, consideration of absolute concentrations of steranes has been shown to be valid and useful in differing environments of deposition. Mello et al. (1988a, b; Chapter II and III) in a study of a suite of 24 oils and 48 organic-rich rock samples from Brazilian basins, reported great differences in the sterane concentrations among samples from different depositional environments. Specifically, there was a paucity of steranes (low concentrations) in lacustrine freshwater and saline water environments in contrast to higher concentrations in marine related samples. Also, abnormally high

M/Z 217

Ro: 0.66

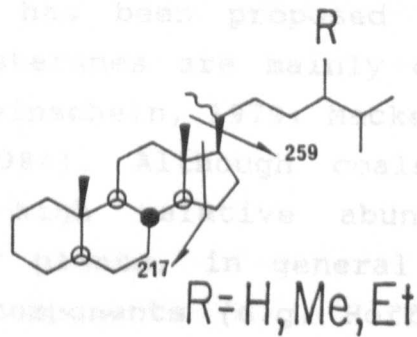


MASS FRAGMENTOGRAM



MASS SPECTRUM

ααα-STERANES



COMPOUND STRUCTURE

Figure 24- Partial m/z 217 chromatogram of alkane fraction from a typical sediment extract from lacustrine saline environment (RD-1) showing the sterane distribution pattern with the spectrum of the C₂₇ ααα 20R component and the 5α(H), 14α(H), 17α(H) regular steranes structure (for peak assignments see appendix I).

concentrations (sometimes higher than hopanes, were detected in the samples related to hypersaline environments. Lending support to these results, Moldowan et al. (1985) and McKirdy et al. (1986), reported a paucity of steranes in lacustrine freshwater oils from Brazil, China, Sudan and Australia. On the other hand, abnormally high abundances of steranes have been reported in oils and sediments of hypersaline origin (e.g. the Ghareb Formation, Israel, Rullkötter et al., 1984b; the Messinian basin, Italy, ten Haven et al., 1985; Jiangnan basin, China, Fu Jiamo et al., 1986; La Felicidad well, Guatemala, Connan et al., 1986).

In a limited number of cases the distribution pattern does seem to be related to the environment of deposition. The most widely used method of showing this, is the triangular diagram proposed by Huang and Meinschein in 1979, for the relative proportions of C₂₇, C₂₈ and C₂₉ regular steranes. This parameter is based on the fact that samples related to similar depositional environments should have similar sterane proportionality. Such ratios would perhaps also reflect the contributing organisms (plankton vs higher plants) as ecological indicators (Huang & Meinschein, 1979; Seifert & Moldowan, 1986). It has been proposed that the precursor sterols of the C₂₉ steranes are mainly derived from higher plants (e.g. Huang & Meinschein, 1979; Mackenzie et al., 1982; Hoffmann et al., 1984). Although coals and organic-rich sediments containing high relative abundances of components from higher plants, in general, appear to show a predominance of C₂₉ components (e.g. Hoffmann et al., 1984; Philp & Gilbert, 1986) the corollary is not true since C₂₉ steranes have been reported in samples from the Cambrian age, ie. before the onset of higher plants (Seifert, 1980; McKirdy et al., 1986). Furthermore, Volkman, (1986) demonstrated that C₂₉ sterols do occur in relatively high abundance in certain marine algae. Also, C₂₉ components have been found to predominate in the sterane distribution of several sediments and oils which are not related to a higher plant origin (Fowler

& Douglas, 1984; McKirdy et al., 1986; Farrimond, 1987; Mello et al., 1988a,b, and c; see also Chapters II and III). Hence, interpretation of a predominance of C₂₉ steranes as an indication of higher plant input, or as a characteristic of a non-marine environment must be made with caution. Also, many authors have reported that the triangular sterane diagram approach has proved to be too simplistic for general use, since the input sources of precursor sterols are not uniform (e.g. Seifert & Moldowan, 1986; Volkman, 1986; see also Chapter III). Fig. 25 illustrates the restriction in such an application, since no pattern differences are observed for a number of samples from seven different well established depositional environments from Brazilian marginal basins (Mello et al., 1988b).

Recently, Moldowan et al. (1985) studied a sample suite of nearly forty oils from marine and lacustrine sources, and suggested that the occurrence of C₃₀ regular steranes could be a definitive marker indicator of marine-derived organic matter. More recently, Summons et al. (1987) and Mello et al. (1988a, b; Chapter II and III) reported the absence of these compounds in a number of non-marine sediments and petroleums, in contrast with their presence in marine related ones. This is exemplified using selected Brazilian samples in Fig. 26, where linked scan GC-MS shows the absence of C₃₀ steranes in samples of non-marine origin (A to C), but its presence and increasing abundance towards the more established "normal" marine environments (D to F). The precise origin of such compounds is not established but it is thought that they arise from C₃₀ sterol constituents of marine algae (Djerassi, 1981).

The occurrence of low molecular weight steranes (C₂₁ and C₂₂; e.g. Fig. 27) in sediments and petroleums has been attributed to side chain cleavage, through diagenesis and/ or catagenesis of the high molecular steranes (e.g. Connan et al., 1980). Recent studies, however, suggest that they may arise from natural precursors, probably low molecular weight sterols (Restle, 1983; ten Haven et al., 1985; de Leeuw & Bass,

Figure 25- Carbon number (C_{27} , C_{28} , C_{29}) distributions of steranes for a number of sediment extracts from different depositional environment in the Brazilian continental margin.

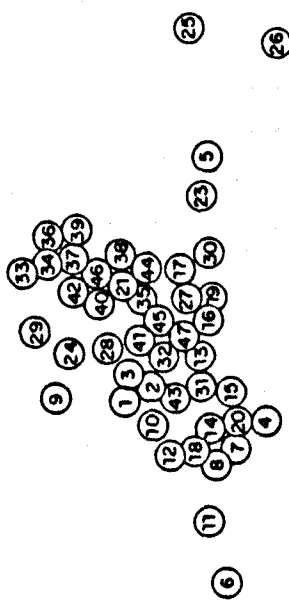
**ORGANIC RICH SEDIMENTS
BRAZILIAN MARGINAL BASINS**

- 1 TO 7 - LACUSTRINE FRESHWATER
- 8 TO 15 - LACUSTRINE SALINE WATER
- 16 TO 23 - MARINE EVAPORITIC
- 24 TO 33 - MARINE CARBONATE
- 34 TO 42 - OPEN MARINE HIGHLY ANOXIC
 - PREDOMINANCE OF CALCAREOUS
 - MUDSTONE LITHOLOGY
- 43 TO 46 - OPEN MARINE PREDOMINANCE
 - SILICICLASTIC LITHOLOGY
- 47 - MARINE DELTAIC

C28

5 α (H), 14 α (H), 17 α (H) 20 R CHOLESTANE

22



C27

C29

M/Z 414 - 217

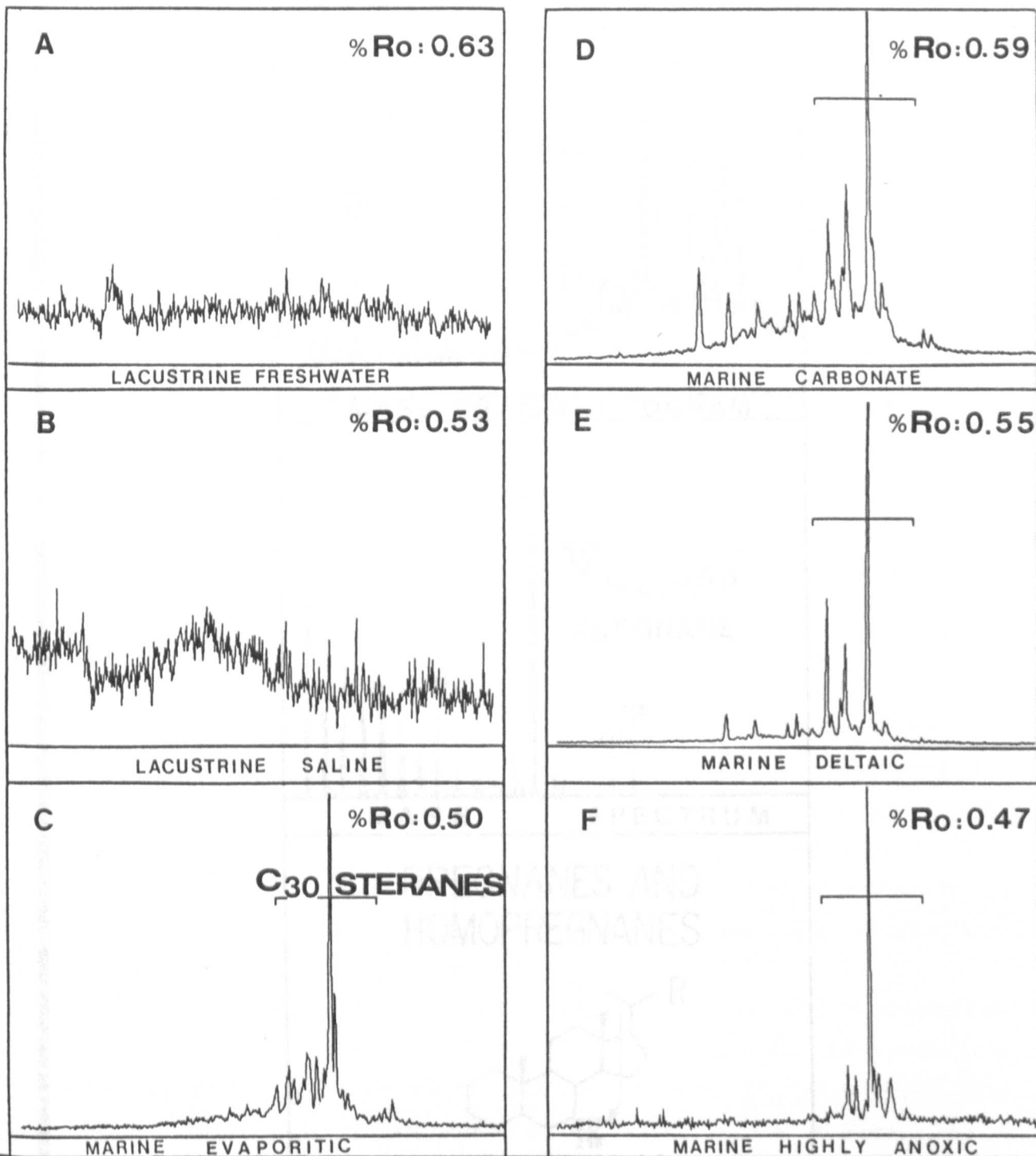


Figure 26- Mass chromatograms from metastable ion monitoring of transition m/z 414-217 (C₃₀ steranes), and vitrinite reflectance data from sediment extracts from different depositional environments from Brazilian marginal basins; A: lacustrine freshwater (CS-1); B: lacustrine saline water (RJS-51); C: marine evaporitic (CES-7); C: marine carbonate (CAU-3); D: marine deltaic with carbonate influence (APS-36); E: open marine highly anoxic environment with dominance of calcareous lithology (CES-50).

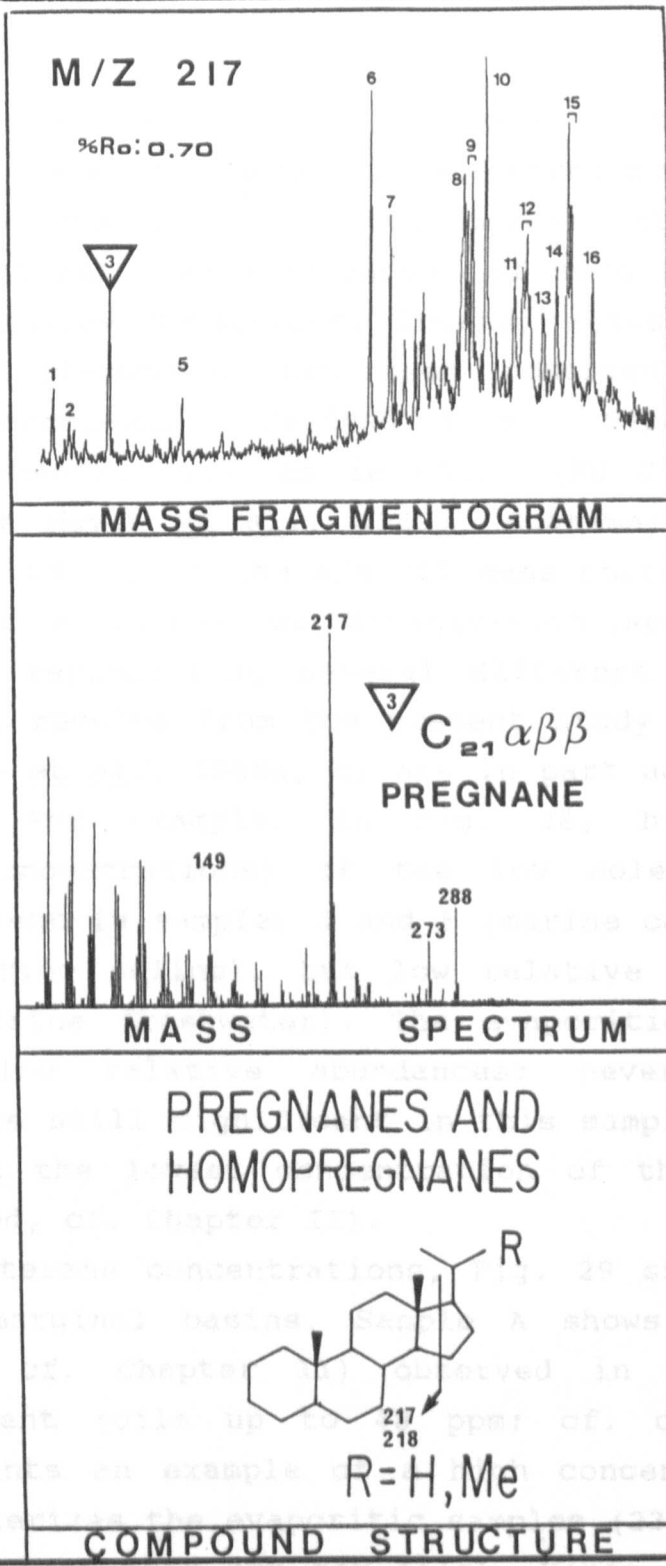


Figure 27- Partial m/z 217 chromatogram of alkane fraction from a typical oil sample derived from marine deltaic environment with carbonate influence (PAS-9) showing the low molecular weight sterane distribution pattern with the spectrum of the $C_{21} 5\alpha(H), 14\beta(H), 17\beta(H)$ component and the pregnanes and homopregnanes structure (for peak assignments see appendix I).

1986). Mackenzie et al. (1982a, b) suggested that immature marine sediments tend to show higher abundances of these compounds than non-marine ones. ten Haven et al. (1985) proposed that high relative abundances of such compounds are typical of hypersaline conditions. Indeed, although not well understood, this phenomenon has been observed in several sediments and petroleums derived from hypersaline and carbonate environments, such as in China (Fu Jiamo et al., 1986), Italy (ten Haven et al., 1985), Guatemala (Connan et al., 1986). Fig. 28 shows the m/z 217 mass chromatograms for the alkanes from a number of organic-rich sediments from Brazilian basins representing several different depositional environments. The results from the present study (Chapters II and III and Mello et al., 1988a, b) are in part agreement with these findings. For example, in Fig. 28, high relative abundances (and concentrations) of the low molecular weight steranes are present in samples D and F (marine carbonate) and B and C (lacustrine saline), but low relative abundance in sample A (lacustrine freshwater). The evaporitic sample (E) has, however, low relative abundances; nevertheless the concentrations are still significant in this sample (chosen as the example with the lowest concentration of the evaporitic sediments examined, cf. Chapter II).

In relation to sterane concentrations, Fig. 29 shows examples from Brazilian marginal basins. Sample A shows the maximum value (31 ppm; cf. Chapter II) observed in a lacustrine freshwater sediment (oils up to 48 ppm; cf. chapter III). Sample E represents an example of a high concentration that generally characterizes the evaporitic samples (230 to 1600 ppm for sediments; 537 to 2080 ppm for oils). Hence, hypersaline marine related samples tend to show the highest concentrations. The lacustrine saline water samples have low concentrations (sediments < 90 ppm (C in Fig. 29), although higher than the freshwater samples. In contrast, the other marine samples tend to show, except for the marine highly anoxic samples (see Chapters II and VII), medium to high concentrations (> 180 ppm;

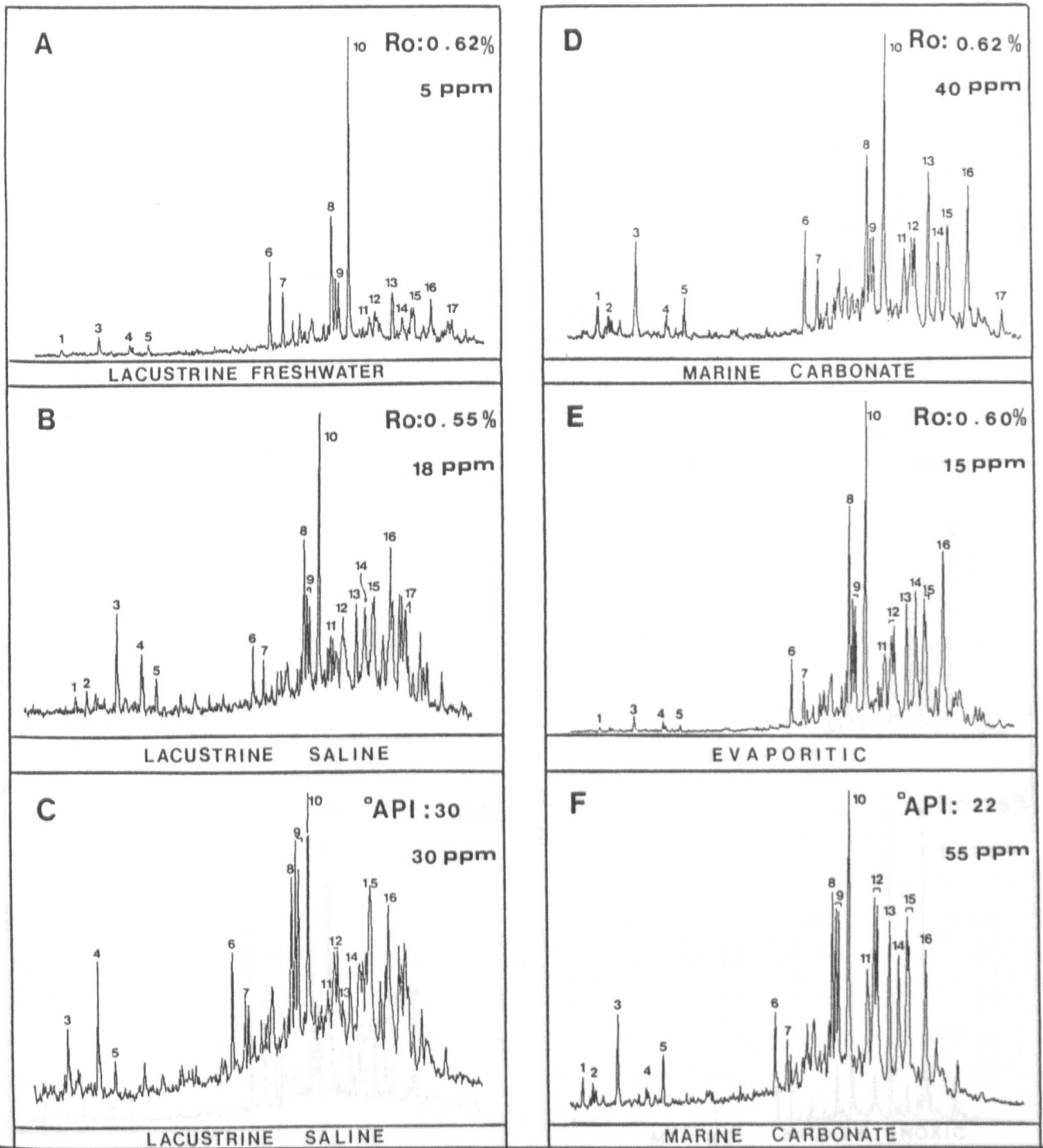


Figure 28- Partial m/z 217 chromatograms for alkane fraction from sediment extracts and oils from different depositional environments, $C_{21} + C_{22}$ low molecular weight steranes concentration (ppm) and vitrinite reflectance (Ro%) data; A: lacustrine freshwater (CS-1); B and C: lacustrine saline water (RJS-71 and RJS-49); D: marine carbonate (APS-31); E: marine evaporitic (CES-41); F: marine carbonate (APS-27; for peak assignments and concentration procedures see appendices I and II).

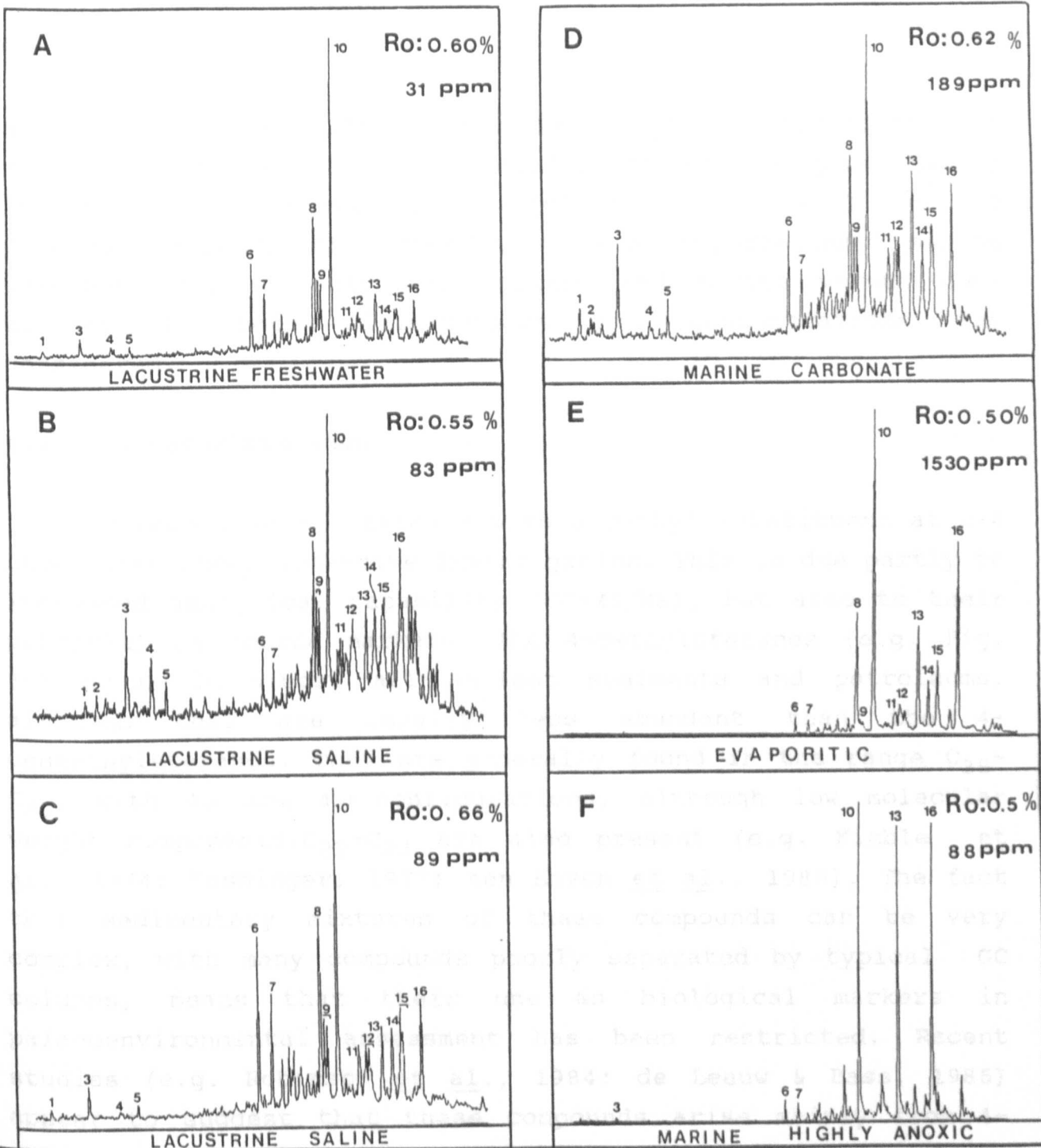


Figure 29- Partial m/z 217 chromatograms for alkane fraction from sediment extracts from different depositional environments, sterane concentrations (ppm) and vitrinite reflectance ($Ro\%$) data; A: lacustrine freshwater (CS-1); B and C: lacustrine saline water (RJS-71 and RD-1); D: marine carbonate (APS-31); E: marine evaporitic (CES-7); F: open marine highly anoxic environment with dominance of calcareous lithology (CES-19; for peak assignments and concentration procedures see appendices I and II).

see Chapters II and III and also Mello et al., 1988a, b). In summary, steranes can be considered useful as biological marker indicators of source input (plankton) as well as of palaeoenvironment of deposition (e.g. hypersaline, marine carbonate versus shaly environments and marine versus non-marine) if both distributions and concentrations are considered.

4.4.2 4-methylsteranes

In recent years steranes with a methyl substituent at C-4 have been under intensive investigation. This is due partly to increased analytical capability (GC-MS/MS), but also to their potential as source markers. The 4-methylsteranes (e.g. Fig. 30) occur in almost all ancient sediments and petroleums, although they are usually less abundant than the 4-desmethylsteranes. They are generally found in the range C₂₈-C₃₀, with 4 β and 4 α configurations, although low molecular weight components (C₂₂-C₂₃) are also present (e.g. Kimble et al., 1974; Ensminger, 1977; ten Haven et al., 1985). The fact that sedimentary mixtures of these compounds can be very complex, with many compounds poorly separated by typical GC columns, means that their use as biological markers in palaeoenvironmental assessment has been restricted. Recent studies (e.g. Robinson et al., 1984; de Leeuw & Bass, 1986) appear to suggest that these compounds arise mainly from 4-methylsterols produced by dinoflagellates. Since dinoflagellates are ubiquitous constituents of most aquatic environments (marine and lacustrine) the value of the 4-methylsteranes as biological markers would appear to lie only in their source specificity rather than as environmental markers (but see below). Brassell et al. (1986) and McKirdy et al. (1986) reported high relative abundances of 4-methylsteranes associated with lacustrine freshwater source rocks from China and Australia. Conversely, Mello et al., 1988a, b and Chapter II and III) reported the paucity of these

compounds in lacustrine freshwater and saline samples against high relative abundances in marine hypersaline and carbonate environments in oils and sediments from Brazilian basins. Clearly, measurements of 4-methylsterane concentrations (cf. steranes) are required to investigate their value as environmental indicators. On the other hand, recent advances in analytical conditions (use of GC-MS/MS) allowed some authors to suggest that the 4-methylsterane distribution patterns can be useful in distinguishing marine from non-marine environments (Summons et al., 1987; Goodwin et al., 1988). The idea is based on the distribution pattern of specific C₃₀ 4-methylsterane structural isomers. Specifically, lacustrine organic-rich sediments appear to possess only C₃₀ components with a 24-ethylcholestane structure, while both 24-ethylcholestane and 4 α ,23,24-trimethyl-5 α (H)-cholestane(dinosterane) structures are present in marine organic-rich sediments. Although both studies reported finding the 4 α ,23,24-trimethyl-5 α (H)-cholestane (dinosterane) type of structure only in marine oils and sediments more detailed studies of these compounds are needed in order to establish the usefulness of this parameter, i.e. by using a range of depositional environments, such as those represented by the oils and sediments from the Brazilian marginal basins. Fig. 30 exemplifies the approach which will need to be used, by way of MS-MS data from a lacustrine saline water sediment (RJS-71). As can be noted this sample does not contain the 4 α ,23,24-trimethyl-5 α (H)-cholestane (dinosterane) type of compound, although the compound type was found in samples from a marine depositional environment (see Chapter II). Recently, it has been proposed that abnormally high relative abundances of low molecular weight 4-methylsteranes (cf. peak 4 in Fig. 31) are typical of a hypersaline environment of deposition (ten Haven et al., 1985, 1988). The results in Chapters II and III and Mello et al., 1988a, b are partly in agreement with this idea since there is a tendency towards a high relative abundance in enhanced salinity environments (B and C in Fig. 28; but see C

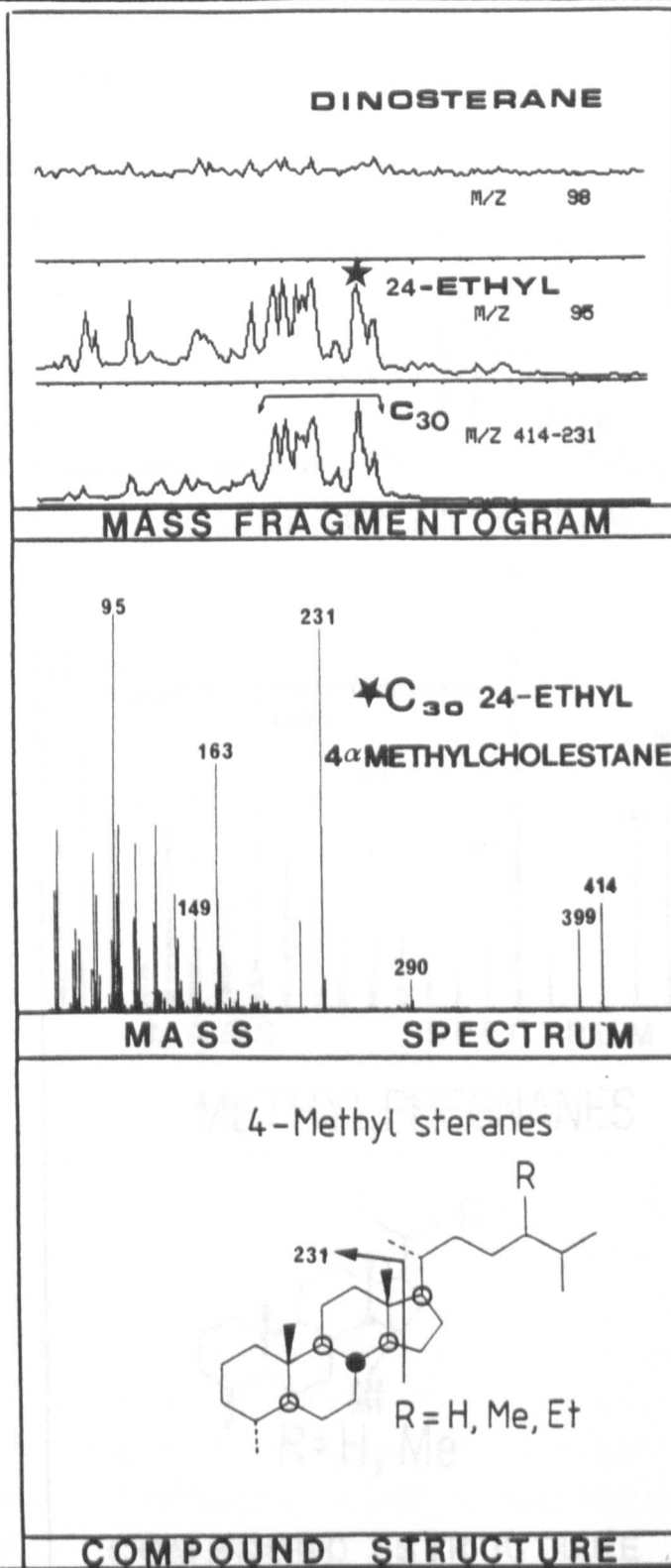
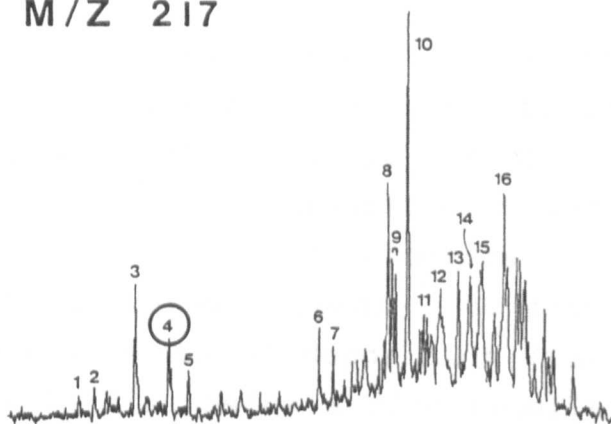
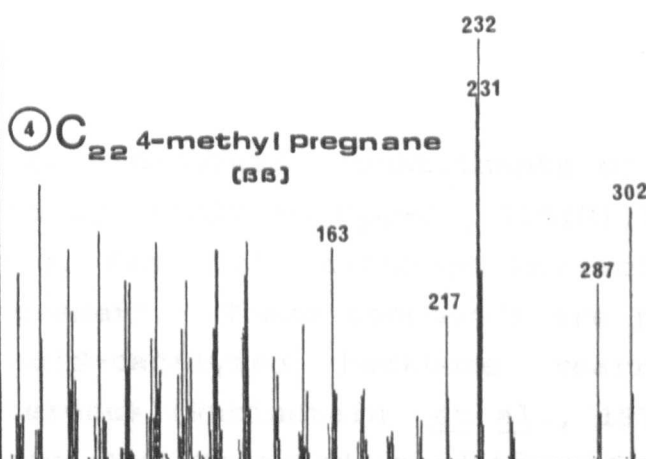


Figure 30- MS-MS mass chromatogram of transitions m/z 414-231, 414-95 and 414-98 of alkane fraction from a typical sediment extract from lacustrine saline water environment (RJS-71) showing the C_{30} 4-methyl steranes distribution pattern with the spectrum of the C_{30} 24-ethyl-4 methylcholestane component and the 4-methyl steranes structure.

M/Z 217



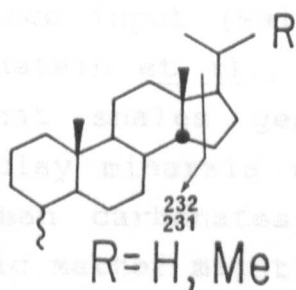
MASS FRAGMENTOGRAM



④ C₂₂ 4-methyl pregnane
(88)

MASS SPECTRUM

METHYLPREGNANES



COMPOUND STRUCTURE

Figure 31- Partial m/z 217 chromatogram of alkane fraction from a typical sediment extract from lacustrine saline water environment (RJS-71) showing the low molecular weight 4-methyl steranes distribution pattern with the spectrum of the C₂₂ 5 α (H),14 β (H),17 β (H) 4-methyl homopregnane component and the methylpregnanes structure (for peak assignments see appendix I).

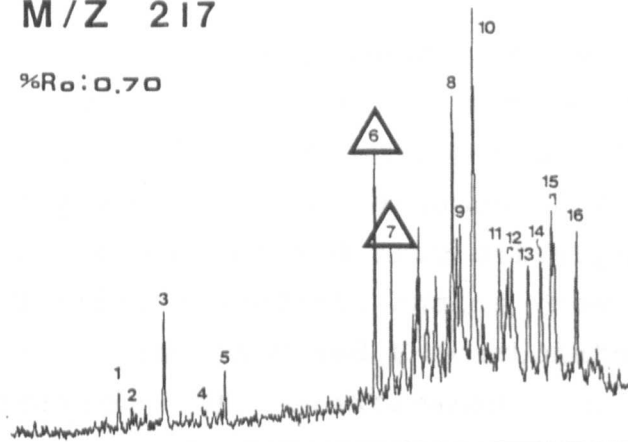
in Fig. 29). The evaporitic samples, on the other hand, have low relative abundances (Chapters II and III and Figs. 28 and 29) although the concentrations would appear to be high. Again further studies, using an appropriate standard to measure concentrations using m/z 231 chromatograms are required. In summary, 4-methyl steranes appear to show promise in differentiating environments of deposition (marine versus non-marine) as well as in diagnosing a dinoflagellate input to the sedimentary record, but more studies are required.

4.4.3 Diasteranes

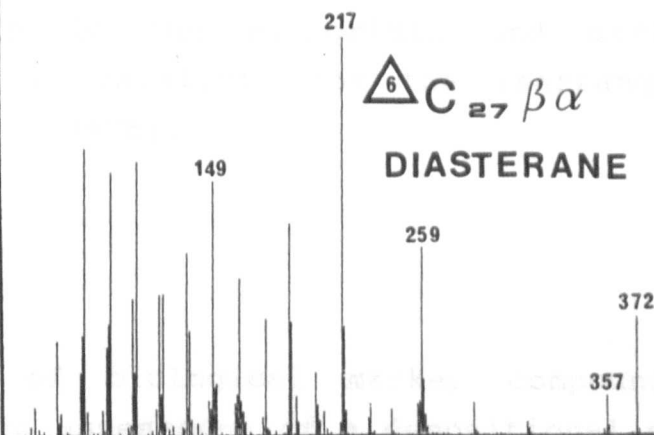
Diasteranes are widespread constituents of sediments and petroleums. They occur mainly as C₂₇-C₂₉ 13 β (H),17 α (H) 20S and 20R components (e.g. Fig. 32), although low molecular weight species are also present. These compounds are presumed to be formed by an acid-catalyzed backbone rearrangement and reduction of diasterenes (Rubinstein et al., 1975; Peakman et al., 1988). Since the reported condition for diasteranes formation is acid catalysis, the source significance of these compounds should lie more in the characteristics of the inorganic matrix of the host sediments than in those of the contributing organic source input (Seifert & Moldowan, 1986). Many authors (e.g. Rubinstein et al., 1975; Sieskind et al., 1979) have reported that shales generally have a higher availability of acidic clay minerals to catalyse the sterene rearrangement process than carbonates. Hence, carbonate and hypersaline-source organic matter might be expected to contain lower amounts of diasteranes than those derived from shale rich depositional environments (e.g. lacustrine, open marine and marine deltaic). Indeed, several examples of sediments and oils containing low amounts of diasteranes have been observed in samples from both hypersaline and carbonate environments (McKirby et al., 1983; ten Haven et al., 1985; Connan et al., 1986; Fu Jiamo et al., 1986; Mello et al., 1988a, b). Therefore, diasteranes can be applied as a biological marker

M/Z 217

%R₀: 0.70

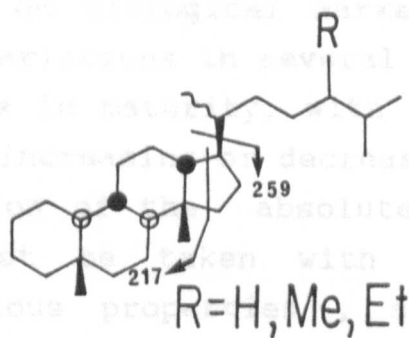


MASS FRAGMENTOGRAM



MASS SPECTRUM

DIASTERANES



COMPOUND STRUCTURE

Figure 32- Partial m/z 217 chromatogram of alkane fraction from a typical sediment extract from open marine environment with dominance of siliciclastic lithology (ESS-46) showing the diasteranes distribution pattern with the spectrum of the C₂₇ 13β(H), 17α(H) 20 S and/or R components and the diasteranes structure (for peak assignments see appendix I).

indicator of depositional environments where only low clay minerals are available such as, marine carbonate and hypersaline environments. As an example, Fig. 33 shows the m/z 217 mass fragmentograms of the alkanes from organic-rich sediments and an oil sample derived from different depositional environments from Brazilian marginal basins (see Chapter II and III). It is clear that samples D and E (carbonate related) have the lowest proportion of diasteranes in the sterane distributions when compared with samples A, B, C, and F) (more shaly). Such a feature probably arises from the virtual absence of clay minerals in the evaporitic and marine carbonate samples, to act as catalysts for the rearrangement process (Rubinstein et al., 1975).

4.5 CONCLUSIONS

The application of biological marker compounds as source markers and in the assessment of a depositional environment is useful but should be made with caution. It is important to stress the need to understand and disentangle the effects of source and maturity on biological marker properties. It is well recognised that variations in several molecular parameters occur with an increase in maturity, with the relative amounts of specific compounds increasing or decreasing (see Chapter V). Therefore, consideration of the absolute concentration of a biological marker must be taken with care. Nevertheless, consideration of various properties, such as distribution pattern, presence or absence of specific marker compounds and absolute concentrations can provide criteria for the assessment of source input and the depositional environment. In the author opinion the main contribution, however, of the use of biological markers in source input/ palaeoenvironmental assessment is in ascertaining the type of depositional environment of the source rocks and the organisms which contributed to them, using only the biological marker analysis

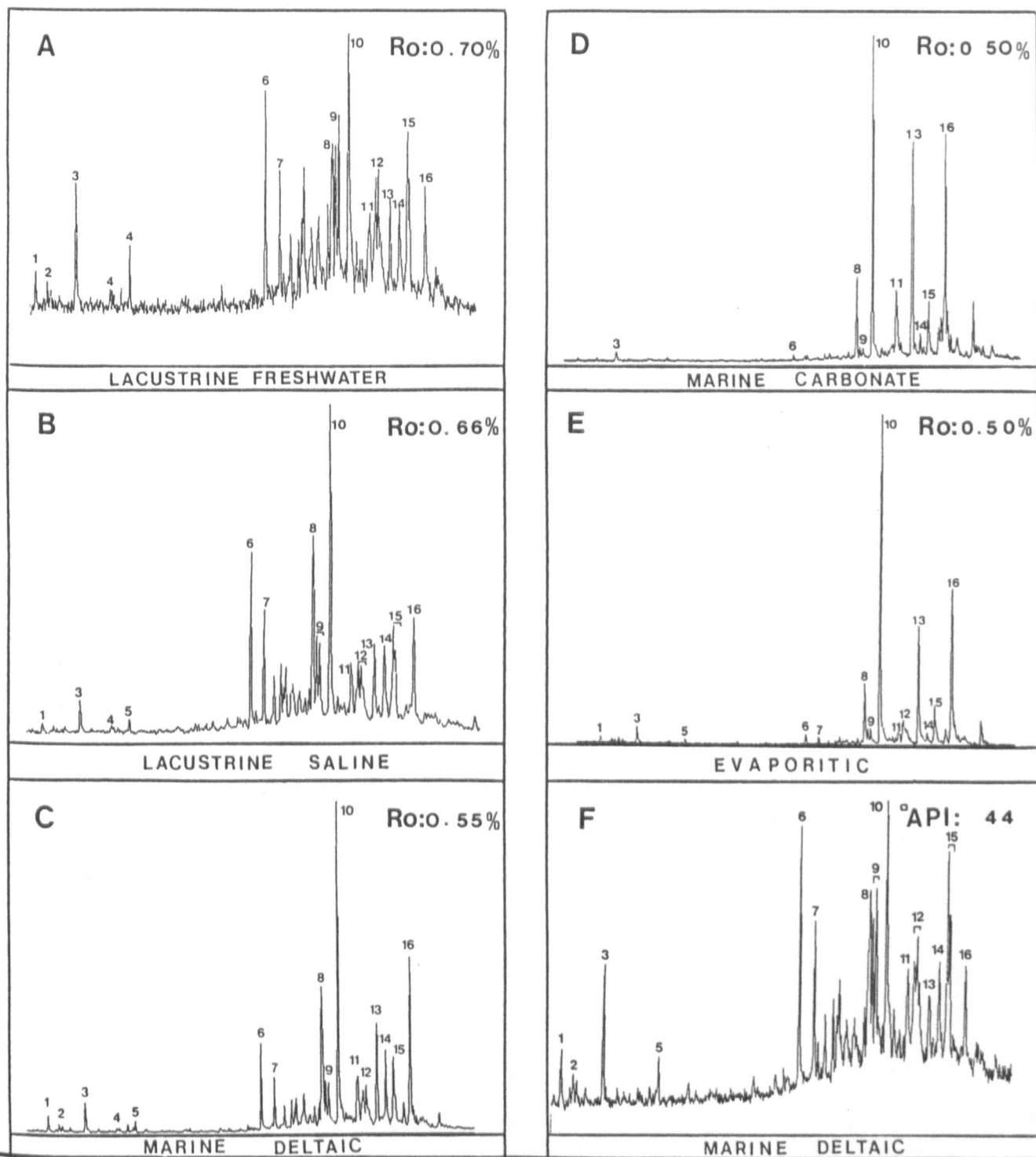
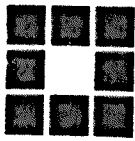


Figure 33- Partial m/z 217 chromatograms for alkane fraction from sediment extracts and an oil from different depositional environments and vitrinite reflectance ($Ro\%$) data; A: lacustrine freshwater (RNS-53); B: lacustrine saline water (RD-1); C: marine deltaic with carbonate influence (APS-36); D: marine carbonate (CES-56); E: marine evaporitic (CES-7); F: marine deltaic with carbonate influence (PAS-11; for peak assignments see appendix I).

of the oil. Indeed, there is no other chemical or geological method suitable for such a task.



CHAPTER V

CHAPTER V

MATURITY ASSESSMENT OF SEDIMENTARY ROCKS - A CASE
STUDY OF BIOLOGICAL MARKER DISTRIBUTIONS AND CONCENTRATIONS.

This chapter reviews and extends the application of bulk and biological marker properties to the assessment of the thermal maturity of a given sedimentary sequence. It aims to address some key questions relating to the understanding of the effects of maturity on the composition and absolute concentration of biological markers from organic-rich sediments.

5.1 INTRODUCTION.

In the past fifteen years, organic geochemistry has played an increasing role in petroleum exploration. Among the recent advances in petroleum geochemistry, several have had a major impact on exploration. One of the most applied has been the assessment of the extent of thermal maturation of organic matter in sedimentary basins.

Thermally induced reactions cause many systematic changes in the physical and chemical properties of sedimentary organic matter. These changes can be used as indicators of sediment maturity and, hence can be important parameters in assessing burial and time-temperature histories. Physical (mainly optical), chemical and predictive methods (mathematical models) have been developed to attempt the assessment of maturity levels as well as palaeotemperatures of organic-rich sequences in sedimentary basins. Maturation indicators based on physical properties generally give qualitative to semiquantitative information. Those based on chemical and predictive analyses tend to be quantitative (Staplin, 1982).

In the last decade the assessment of the thermal history of organic-rich sediments based on physical and chemical changes has been the subject of a large number of studies (e.g. Dow, 1977; Espitalié et al., 1977, 1980; Seifert & Moldowan, 1978; Hunt, 1979; Mackenzie et al., 1980; Mackenzie et al., 1981; Mackenzie & Maxwell, 1981; Van Grass et al., 1982; Mackenzie, 1982, 1984; Radke & Welte, 1983; Radke et al., 1982, 1984; Tissot, 1984; Tissot & Welte, 1984; Rullkötter et al., 1984, 1985; Cassani & Eglinton, 1986; ten Haven et al., 1986; Teichmüller, 1986; Abbott & Maxwell, 1988; Curiale, 1988; Cassani et al., 1988; Larcher et al., 1988). The application of optical methods is a result of the recognition of "rank" in coals (Staplin, 1982). Later on, both physical and chemical methods were developed, with the emphasis on Rock-Eval pyrolysis and changes in the composition and abundance of hydrocarbons. In the early eighties, the application of

biological marker ratios to the assessment of the thermal maturity of petroleum source rocks, added a significant dimension to the basin analysis studies.

5.2 OVERVIEW OF GEOCHEMICAL PARAMETERS USED IN MATURATION STUDIES.

Of the bulk and molecular parameters for the assessment of thermal maturation in sediments, only those related to the ones utilized in the present study are reviewed in the following sections. The following are the most commonly used physical, chemical, bulk and molecular parameters for the assessment of thermal maturation of sedimentary organic matter:

5.2.1 Physical methods.

Among the physical methods, vitrinite reflectance and spore coloration index are the most widely used.

5.2.1.1 Vitrinite reflectance.

Vitrinite is a humic organic constituent of most sedimentary kerogens, and is itself a source of gas (Tissot & Welte, 1984). It is formed during diagenesis by the humification of lignin and cellulose in plant cells. With burial and associated temperature rise, the aromatic lamellae become more ordered, resulting in a systematic increase in reflectivity (Dow, 1977). The reflectivity (R_o) is measured by a sophisticated microscope system, using a sample immersed in oil and incident light, giving the reflectance index ($R_o \%$) which can be used as a direct maturity indicator. The increase in reflectivity depends on the maximum palaeotemperature reached and also on the length of heating time (Dow, 1977).

Although many views have been expressed about the boundaries of the oil window in terms of vitrinite reflectance levels (Dow, 1977; Alpern, 1980; Tissot & Welte, 1984) the consensus of

opinion is that there are no precise reflectance levels defining the oil window. Indeed, the onset of oil generation may vary according to the kerogen type as well as the mineral matrix (Fig. 1; Espitalié et al., 1980; Tissot, 1984; Teichmüller, 1986). In general, it is widely accepted that the onset of generation occurs around 0.6 % Ro, and the "end of oil generation" around 1.3-1.4 % Ro (Rogers, 1980). Condensates occur mostly between 1.0-2.1 % Ro and the dry gas "death line" between 2.5-3.5 % Ro (Fig. 1; Dow, 1977; Teichmüller, 1986). Although widely applied, this method presents several limitations, the most important being the following:

- i) Scarcity or absence of syngenetic vitrinite in type I and sometimes type II kerogen (Alpern, 1980);
- ii) Definitive identification of primary vitrinite particles in kerogen concentrates is sometimes difficult;
- iii) Sediments of pre-Devonian age do not contain vitrinite, since the higher plants had not yet evolved; and
- iv) when vitrinites are impregnated with bituminous substances reflectance values are lowered (Teichmüller, 1986).

Despite these limitations, when it is measured carefully, it can be a consistent and reliable indicator of maturity (e.g. Teichmüller, 1986).

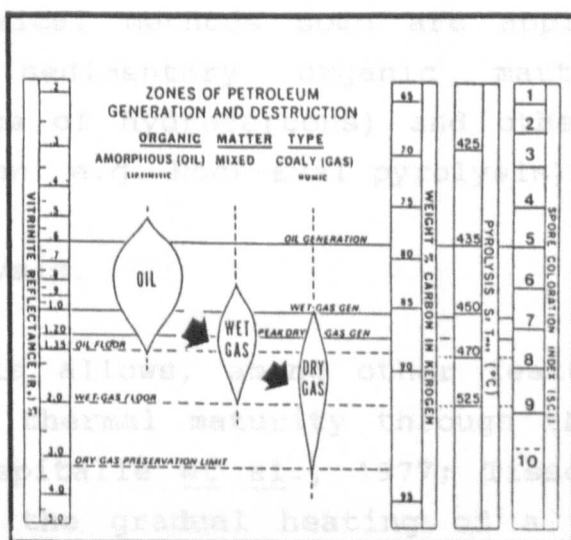


Figure 1- Generalised correlation of vitrinite reflectance, T-max and spore coloration index with the zones of petroleum generation and destruction. Taken from Dow & O'connor (1982).

5.2.1.2 Spore Coloration Index (SCI or TAI).

The basis of this property is that certain organic components of kerogen such as pollens, spores and cuticles change colour from yellow to brown to black in response to an increase in temperature (e.g. Correia, 1969; Staplin, 1982). The colour is compared with a standard index and the results according to many authors (e.g. Tissot & Welte, 1984; Staplin, 1982) may be interpreted as follows:

- 1.0 to 5.0 - immature
- 5.0 to 8.0 - oil window
- 8.0 to 10 - overmature.

However, as for vitrinite reflectance, no generally accepted opinion exists on these boundaries, but most workers accept SCI values around 5.0 as the level that defines the onset of oil generation (Fig. 1; Tissot & Welte, 1984).

5.2.2 Chemical methods.

Among the chemical methods some are applicable to solvent extracts of sedimentary organic matter (e.g. composition and abundance of hydrocarbons) and others to the insoluble portion (kerogen; e.g. Rock-Eval pyrolysis).

5.2.2.1 Rock-Eval Pyrolysis.

Rock-Eval pyrolysis allows, among other features, a rapid assessment of the thermal maturity through the thermal breakdown of kerogen (Espitalié *et al.*, 1977; Tissot, 1984). This technique involves the gradual heating of a pulverized sample and/or isolated kerogen up to 550 °C. Two parameters are provided: T-max and a modified Van Krevelen type diagram (Tissot & Welte, 1984; Tissot, 1984). T-max is the temperature corresponding to the maximum yield of pyrolysis products (Fig.

2). Although the boundaries can vary with organic matter and changes in the mineral matrix, the results may be interpreted as follows:

up to 435 °C - immature
 435 to 470 °C - oil window
 higher than 470 °C - overmature

The decrease in hydrogen and oxygen during thermal evolution of the kerogen can be used as a qualitative estimate of the maturity level of sedimentary organic matter. The modified Van Krevelen type diagram is derived from the traditional one by replacing H/C and O/C ratios by the hydrogen index (S2/TOC) and the oxygen index (S3/TOC; Fig. 2).

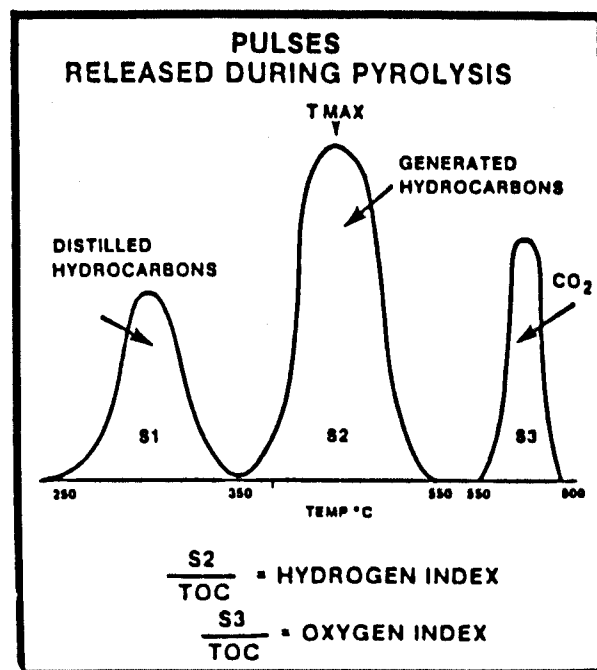
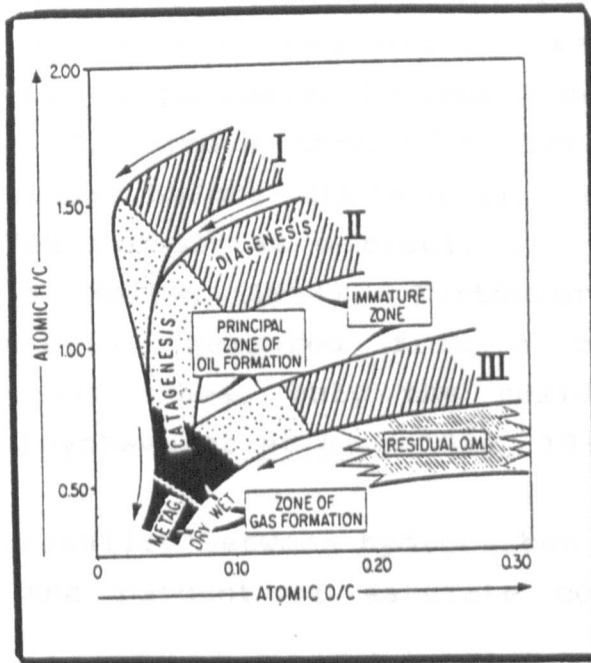


Figure 2-Pulses of products released during pyrolysis Rock-Eval, showing the evolved hydrocarbons and CO₂ as a function of temperature. T-max, represents the temperature of maximum generation of hydrocarbons from thermal cracking of the kerogen. Taken from Espitalié et al., (1977).

Increasing maturity tends to result in kerogens plotting progressively closer to the origin of the diagram (Fig. 3). Both parameters (T-max and Van Krevelen's diagram) have proved, when carefully used, to be reliable methods for characterising the evolutionary stages of organic matter as a function of increase maturation (see below).



PRINCIPAL PRODUCTS OF KEROGEN EVOLUTION




 $\text{CO}_2, \text{H}_2\text{O}, \text{BIOGENIC CH}_4$
 OIL
 GAS

Figure 3- Kerogen evolution scheme, based on van Krevelen's diagram, showing the main stages of hydrocarbon formation and destruction. Taken from Tissot & Welte (1984).

5.2.2.2 Composition and abundance of hydrocarbons.

In recent years a number of parameters have been used which involve the analysis of the organic-extractable fraction of the organic matter (bitumen). Major problems are the possibility of contamination by migrated hydrocarbons (Leythaeuser et al., 1984) and dependence upon the nature of the organic matter (Hunt, 1979; Tissot & Welte, 1984). Among the most widely parameters used are:

5.2.2.3 Amount of extractable hydrocarbons and bitumen.

The amount of total extract (ppm) can be used to evaluate thermal maturity. The variation in this parameter is a function of the increase of thermal stress on the kerogen resulting in a gradual increase in hydrocarbon production. Generally, inside the same sedimentary facies, sediments yielding less extractable material are less mature. Care must be taken, however, since such a parameter is source dependent and is only valid in the oil window threshold. The amount of bitumen reaches a maximum before decreasing, as the kerogen is progressively "exhausted" as a result of its breakdown (Hunt, 1979; Tissot & Welte, 1984). Furthermore, the amount of extractible material measured from a mature source rock represents in most cases, only the residual material after expulsion (cf. Leythaeuser et al., 1984, 1988).

5.2.2.4 Proportionality between hydrocarbon and non-hydrocarbon fractions and the percent of saturate compounds related to aromatics.

With increasing temperature, the gradual breakdown of the kerogen results in gross compositional changes in the solvent extract. The higher the thermal maturity, the higher the proportion of hydrocarbons (saturates plus aromatics) to heavy non-hydrocarbons (i.e. NSOs plus asphaltenes), and the proportion of saturates to aromatic compounds. Such trends are thought to be due to chemical rearrangements and expulsions from the kerogen structure as it attempts to compensate for the instability caused by increasing thermal stress and overburden during late diagenesis and catagenesis (Milner, 1982; Tissot & Welte, 1984). As mentioned above, care must be taken in its application, due to source dependence, expulsion effects, and the fact that most of the labile hydrocarbons are eliminated before the end of the oil window (catagenetic stage; Hunt, 1979; Tissot & Welte, 1984; Leythaeuser et al., 1984, 1988).

5.2.2.5 Carbon preference index (CPI) and the odd/even carbon preference (OEP).

Both coefficients are based on the ratio of n-alkanes having odd numbers of carbons to those having even numbers. The carbon preference index (CPI) was originally proposed by Bray & Evans (1961). It has been observed that immature sediments often contain a large proportion of odd numbered n-alkanes to even, resulting in CPI values greater than unity. With a progressive increase in maturity and thermal breakdown of the kerogen, n-alkanes are generated with no carbon number preference, causing by dilution the progressive decrease in the odd-numbered molecules. It is commonly accepted that hydrocarbons will show CPIs and OEPs near unity by the time the peak of oil generation is reached (Tissot & Welte, 1984). Although both parameters have been widely applied, there are limitations to their use, one of the most important being their dependence upon source input (e.g. mature samples from carbonate and/or evaporitic environments often show an even predominance, with CPI and OEP values less than unity (Tissot & Welte, 1984; Fu Jiamo et al., 1986; Mello et al., 1988a, b).

5.3 MOLECULAR MARKER INDICATORS.

Recently, several parameters based on biological marker compounds, have been proposed as indicators of thermal maturity. Together with the fact that these compounds are ubiquitous in organic-rich sediments, there is also apparent alteration towards thermal equilibrium, as the individual molecules adapt to increases in thermal stress. These changes appear to be relatively consistent with increasing extent of thermal maturity and hence have allowed the evaluation of burial and time-temperature histories of sedimentary basins. Biological marker studies are now important parts of hydrocarbon exploration programmes (Hunt, 1979; Tissot & Welte,

1984; Mackenzie, 1984).

The assessment of the thermal evolution of organic-rich sediments using molecular parameters has recently been reviewed (Tissot & Welte, 1984; Mackenzie, 1984; Abbott et al., 1985; Cassani & Eglinton, 1986; ten Haven et al., 1986; Cassani et al., 1988; Larcher et al., 1988; Rullkötter & Marzi, 1988). Although several limitations to their use have been pointed out by some of these authors, it has been accepted that, when used carefully, the application of molecular parameters is reliable and compares favourably with other physical and chemical techniques. This is particularly true just before and within the oil window (late diagenetic and early catagenetic stages; Mackenzie, 1984; Tissot & Welte, 1984). The chemical reactions most commonly used in the assessment of the extent of thermal maturity in organic-rich sequences are:

5.3.1 Extent of isomerism at C-20 in $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ steranes.

With increasing thermal maturity, the abundance of the biologically-inherited configuration (20R) gradually decreases relative to the geological isomer (20S). The maximum value is reached when $20S/(20S + 20R)$ is around 50-55% (Mackenzie et al., 1982; Tissot & Welte, 1984; Mackenzie, 1984; Cassani & Eglinton, 1986). The change, measured using C_{29} components due to coelution problems, is complete before the peak of oil generation has been reached (Fig. 4).

Generally, oil generation is associated with a value of ca. 40% (Mackenzie, 1982, 1984). Care must be taken in the use of this parameter, since some mature samples derived from hypersaline environments tend to show high amounts of 20R steranes relative to the 20S isomers (Rullkötter et al., 1984; ten Haven et al., 1986; Mello et al., 1988b).

5.3.2 Extent of isomerism at C-14 and C-17 in $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$ steranes.

With increasing maturation, there is an increase in 5 α (H), 14 β (H), 17 β (H) steranes (ca.1:1 mixture of 20S + 20R) relative to 5 α (H), 14 α (H), 17 α (H) steranes(20R + 20S). The parameter $\beta\beta / \beta\beta + \alpha\alpha$ for 20R + 20S isomers, is again measured from the C₂₉ components, due to the partial absence of co-elution problems.

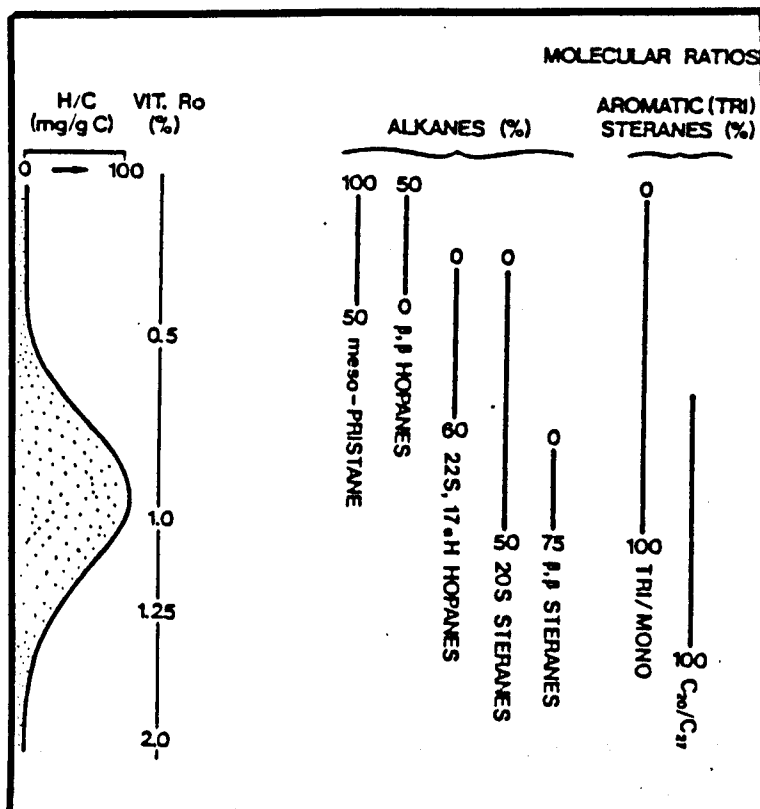


Figure 4- Generalized ranges of molecular ratio measurements of maturation against the hydrocarbon generation curve and vitrinite reflectance data. Taken from Tissot & Welte (1984).

The reaction reaches the reported maximum value of around 65 to 75% just before peak oil generation (Fig. 4; Mackenzie & Maxwell, 1981; Van Grass *et al.*, 1984; Tissot & Welte, 1984), although there is some doubt about this value(see below). Recently, some authors have pointed out that these $\beta\beta$ components, instead of being solely isomerization products of less stable steranes (Mackenzie, 1984), could also be products of a concentration effect as less stable steranes are degraded

(Peakman et al., 1986) having arisen initially from specific precursor steroids present in the original depositional environment (Rullkötter et al., 1984; Peakman et al., 1986). Variation in the input of such precursors could explain the observations of high amounts of $\alpha\beta\beta$ steranes species in some immature hypersaline environments (ten Haven et al., 1986). Another limitation to this parameter, is the coelution problem of the more unstable 20R 5 β (H), 14 α (H), 17 α (H) sterane with the 5 α (H), 14 β (H), 17 β (H) steranes that sometimes precludes measurement of a precise ratio (Mackenzie, 1984) in immature samples.

From the above, it is apparent that caution must be taken when using this parameter as a maturity index.

5.3.3 Extent of isomerism at C-17 and C-21 in the hopanes (C₂₉, C₃₀-C₃₅).

Several authors (e.g. Ensminger et al., 1977; Van Dorsselaer et al., 1977; Seifert & Moldowan, 1980) have suggested that increasing maturation would involve the conversion of $\beta\beta$ species (predominantly biosynthesised) to more stable configurations (e.g. $\alpha\beta$; cf. steranes above). This parameter is best calculated by measuring C₃₀ $\alpha\beta$ /C₃₀ $\alpha\beta$ + C₃₀ $\beta\beta$ hopanes. Although such a parameter has little value in exploration (a value of 100% is reached before the onset of oil generation; Fig. 4), the presence of 17 β (H), 21 β (H) hopanes is an indicator of the immature character of the sedimentary section analysed. More recently, laboratory simulation showed that the increase of 17 α (H), 21 β (H) hopanes in more mature sediments may be due to the selective removal of the thermodynamically less stable 17 β (H), 21 β (H) hopanes, rather than to their isomerization (Larcher et al., 1988). Another parameter that involves isomerism at these positions is concerned with the change in the ratio of 17 β (H), 21 α (H) hopanes to the more stable 17 α (H), 21 β (H) configuration (Mackenzie et al., 1980; Seifert & Moldowan, 1980). This

parameter is calculated by measuring $C_{30} \alpha\beta / C_{30} \alpha\beta + C_{30} \beta\alpha$ hopanes. Based on previous work (Seifert & Moldowan, 1980), this ratio can show changes even inside the peak of oil generation.

5.3.4 Isomerism at C-22 in the $17\alpha(H)$, $21\beta(H)$ C_{31} to C_{35} hopanes.

With the increase of maturity the preference for the biological configuration (22R) is lost and the more thermally stable isomer (22S) tends to increase. The maximum value is reached before peak oil generation, when $22S / (22S + 22R)$ is around 55-60% (Fig. 4; Ensminger et al., 1977; Seifert & Moldowan, 1980; Mackenzie et al., 1980). Recently, Seifert & Moldowan (1986) suggested that when 22S/22R ratios are less than 1.0, oil generation is unlikely; values in the 1.0-1.2 range mean that the onset of oil generation has taken place and higher than 1.3 mean that the peak of oil generation has been reached or even surpassed. Again recent studies have suggested that caution must be exercised when using this parameter as a maturity indicator, since source input could play an important role (e.g. hypersaline sediments can show a series of hopanoids fully isomeric at C-22 derived from precursors at an early stage of diagenesis; ten Haven et al. , 1986).

5.3.5 Ratio of C_{27} $18\alpha(H)$ -trisnorneohopane (Ts) to C_{27} $17\alpha(H)$ -trisorhopane (Tm).

This parameter is based on the fact that the trisnorneohopane (Ts) is more resistant to thermal stress than the trisorhopane (Tm; Seifert & Moldowan, 1978). The boundary of the immature to mature stage is subject to discussion, since the nature of the mineral matrix and also source input may play a role which is superimposed on maturity effects (Seifert & Moldowan, 1986), so caution must be taken when using this parameter as a maturity indicator (Moldowan et al., 1985;

Seifert & Moldowan, 1986; Mello et al., 1988a and b). Generally, Ts/Tm ratios greater than 1.0 are reported to mean that the sample may have just entered the oil window.

5.3.6 Ratio of C₂₃ to C₂₁tricyclic terpanes.

The use of tricyclic terpanes in assessing maturity has not been established, although it appears that these compounds are more resistant to thermal degradation than the $\alpha\beta$ hopanes (Seifert & Moldowan, 1986). Earlier applications of tricyclic terpanes (C₂₃/C₂₁ ratio proposed by Ekweozor & Strausz, 1983), were based on the idea of a preferential generation of the C₂₁ component from functionalized precursors in the polar fractions and kerogen during catagenesis relative to the C₂₃ component (Cassani, 1985). Recently, such a parameter was used in a large set of Venezuelan source rocks by Cassani (1985) and Cassani et al., (1988).

5.3.7 Extent of aromatization of C-ring monoaromatic steroid hydrocarbons.

This proposed reaction is the only aromatization-type transformation that has been used as a maturation parameter (Mackenzie et al., 1981). The parameter is based on the idea of conversion of C-ring monoaromatic steroidal hydrocarbons to triaromatic steroids, and has been calculated by measuring C₂₈-tri/C₂₈-tri + C₂₉-monoaromatic. Although coelution problems occur (the C₂₉ 5 β (H) 20R monoaromatic coelutes with the C₂₈ 5 α (H) 20R monoaromatic; Mackenzie, 1984), the presumed maximum value has been reported as reaching around 100% with increasing maturity during late diagenesis at around the peak of oil generation. Generally, the onset of oil generation is reported to occur when the parameter equals 40-60% (Fig. 4; Mackenzie et al., 1982; Tissot & Welte, 1984; Mackenzie, 1984; Cassani & Eglinton, 1986). This parameter appears to be a more sensitive to temperature than the isomerism parameters and

hence is valuable in the assessment of the thermal history of sedimentary basins (Mackenzie et al., 1982).

Recently, however, Riolo & Albrecht (1985) and Moldowan & Fago (1986) have shown that the C₂₉ 5β(H) 20R monoaromatic peak in the m/z 253 mass chromatogram used in this parameter can in certain circumstances be a composite of a non-rearranged with a novel rearranged series having angular methyl group at C-5 instead of C-10. This finding suggests that care needs to be exercised in the application of the parameter to maturity assessment (Riolo & Albrecht, 1985; Moldowan & Fago, 1986; Abbott & Maxwell, 1988).

5.3.8 Ratio of low to high molecular weight triaromatic steroidal hydrocarbons.

Side-chain scission in the triaromatic steroids was used by Mackenzie (1980) and Mackenzie et al., (1981) as a maturity indicator in a study of Toarcian shales from the Paris basin and NW Germany. The parameter was based on the idea of carbon-carbon bond cracking in the side chain with increasing thermal stress resulting in an increase in the relative amount of C₂₀ relative to C₂₇ triaromatic steroids. The maximum value is reached with increased maturity over the range of late diagenesis to the peak of oil generation (reported to be around 100%; Fig. 4; Mackenzie et al., 1982). Mackenzie, (1984) in a review, changed the ratio to C₂₀/C₂₀ + C₂₈, due to coelution problem with the C₂₇ component. Recently, some authors have pointed out that the C₂₀ and C₂₁ components, instead of being cracking products of triaromatics (Mackenzie, 1984), could merely be products of a concentration effect as the less stable components (C₂₆-C₂₈) are progressively thermally degraded (Riolo et al., 1986).

Given the limitations related to the application of the two aromatic parameters described above (e.g. occasional complexity of the monoaromatic distribution (i.e. rearranged vs non-rearranged, and subsequent coelution problems), it is

clear that further studies need to be undertaken before such parameters can be considered truly reliable indicators of maturity changes in sedimentary organic matter.

5.4 PREDICTIVE METHODS.

The predictive methods were initially developed to be applied in areas where samples were few or unavailable. In the early seventies a semi-empirical model to assess the thermal maturity of organic matter in sedimentary rocks was proposed by Lopatin (Lopatin, 1971). Waples (1980) as an extension of Lopatin's work, introduced a time-temperature index of maturity (TTI). This index, based on the residence time of the sedimentary organic matter, in a given temperature range, is able to define the thresholds of the various maturation stages (Waples, 1980). During the past decade, changes in computing facilities have made possible the development of sophisticated quantitative mathematical models which take into account a broad variety of effects from hydrocarbon reaction kinetics to sub-surface fluid flow modelling which can facilitate prospect evaluation (Yükler et al., 1978; Welte et al., 1981; Welte & Yükler, 1982; Yükler, 1988). Basic data input used in this approach generally includes knowledge of the regional geology (structural, palaeontological and sedimentological data), hydrocarbon reaction kinetics, hydrodynamics and geothermics. Well established geochemical maturity parameters (e.g. vitrinite reflectance, Rock-Eval pyrolysis, and biological marker ratios) play a very important role since they are used to constrain the results of such models. This new approach is gaining in importance, since it can offer a quantitative way of treating the complex interrelation of geochemical and geological processes involved in petroleum generation.

5.5 THIS STUDY.

From the above review it is becoming increasingly clear that many of the parameters first proposed as being solely maturity dependent are also source dependent. Hence, changes in source input are one of the major limitations in the assessment of maturity using geochemical properties (e.g. Tissot & Welte, 1984; Rullkötter *et al.*, 1984; ten Haven *et al.*, 1986). Hence a re-investigation of these parameters is needed, a key requirement being uniform sedimentary sequences spanning the oil window. Ideally, the sediments in each sequence should also be derived from the same or similar depositional environment and have been deposited over a short period of geological time. These conditions would provide a rare opportunity to study such effects, since it should be possible to recognise differences in source rock composition due to thermal influences, independent of lithological changes, variations of organic facies and heat flow.

In this work a set of carefully selected cuttings and core samples from a single wildcat well in the Sergipe-Alagoas basin in the Brazilian continental margin (Fig. 5, 6) has been studied in detail. The aims were to determine the extent of thermal maturity and its effect on the bulk and molecular parameters of a uniform sedimentary sequence as a function of temperature and geological time.

Specifically, eight organic-rich samples, spanning depths from 945m to 3693m (A to H; Fig. 7), were selected for microscopic analysis of kerogen, and elemental, bulk, GC, GC-MS and linked scan GC-MS analysis of aliphatic and aromatic fractions. Furthermore, a specific GC-MS study, with the addition of the deuteriated sterane standard (cf. Chapter II), was carried out in order to assess the continuous sequence of appearance, transformation and disappearance of aliphatic biological markers (for sample preparation and methods, see Chapter VIII). Sample C (1557m) was also chosen as the

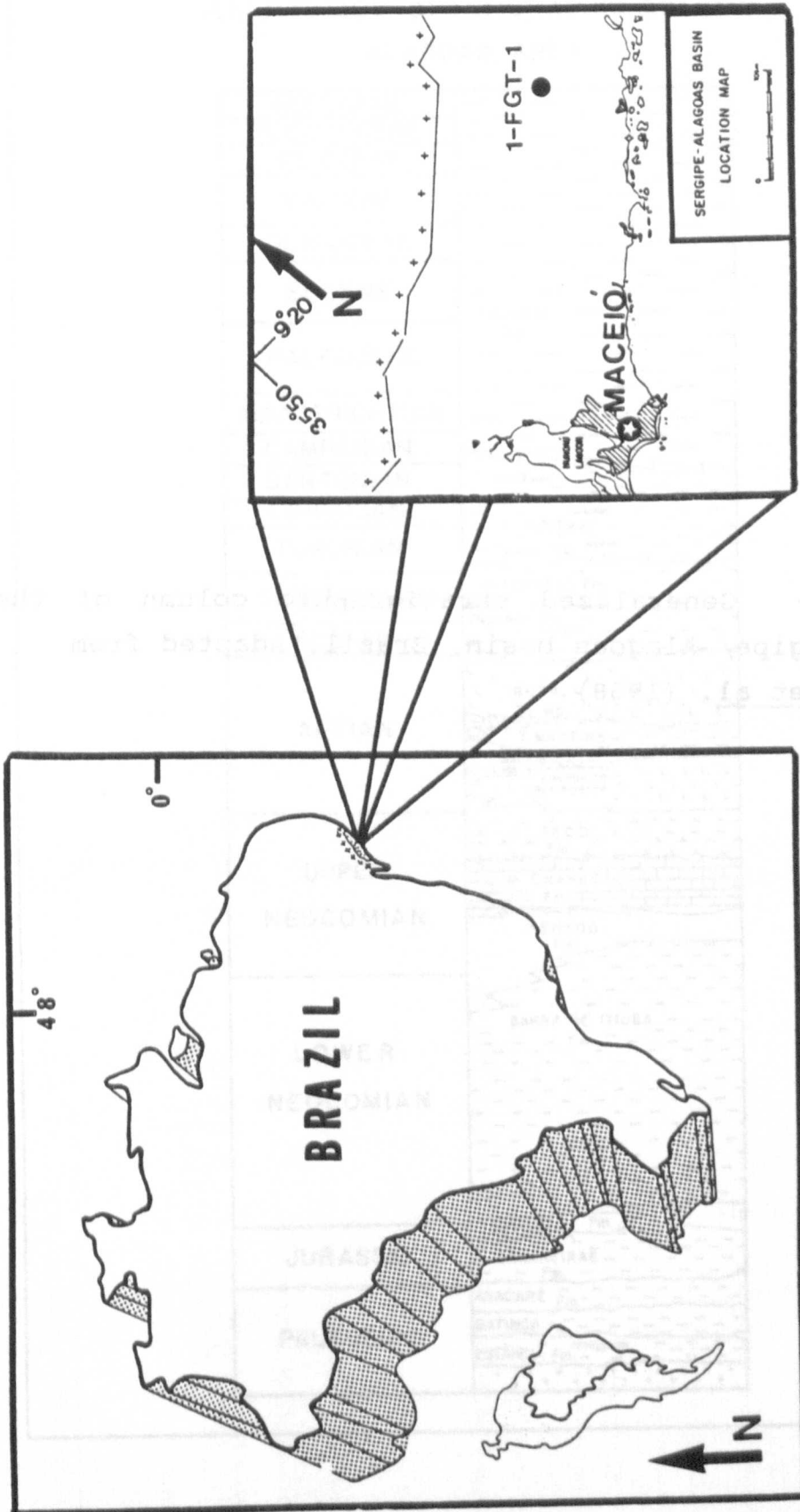


Figure 5- Location map of well 1-FGT-1-AL in the Alagoas area of Sergipe/ Alagoas basin, onshore Brazil.

Figure 6- Generalized stratigraphic column of the Alagoas area, Sergipe/ Alagoas basin, Brazil. Adapted from Schaller et al. (1968).

**GENERALIZED STRATIGRAPHIC COLUMN
ALAGOAS AREA**

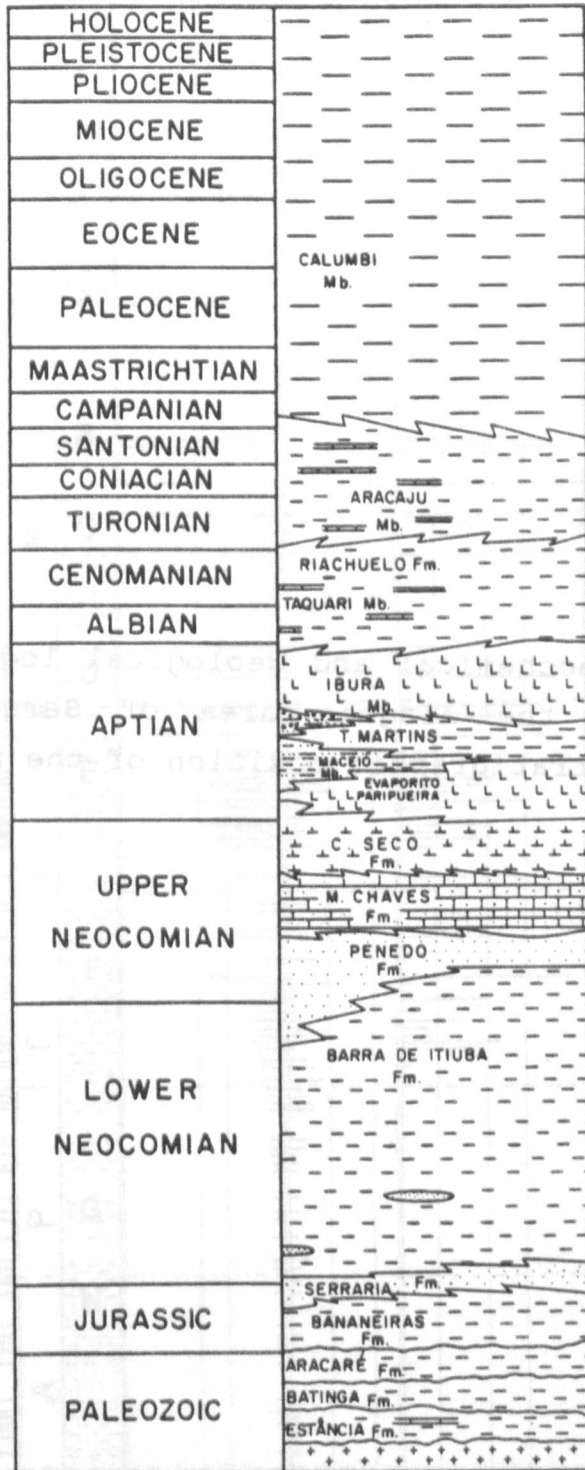
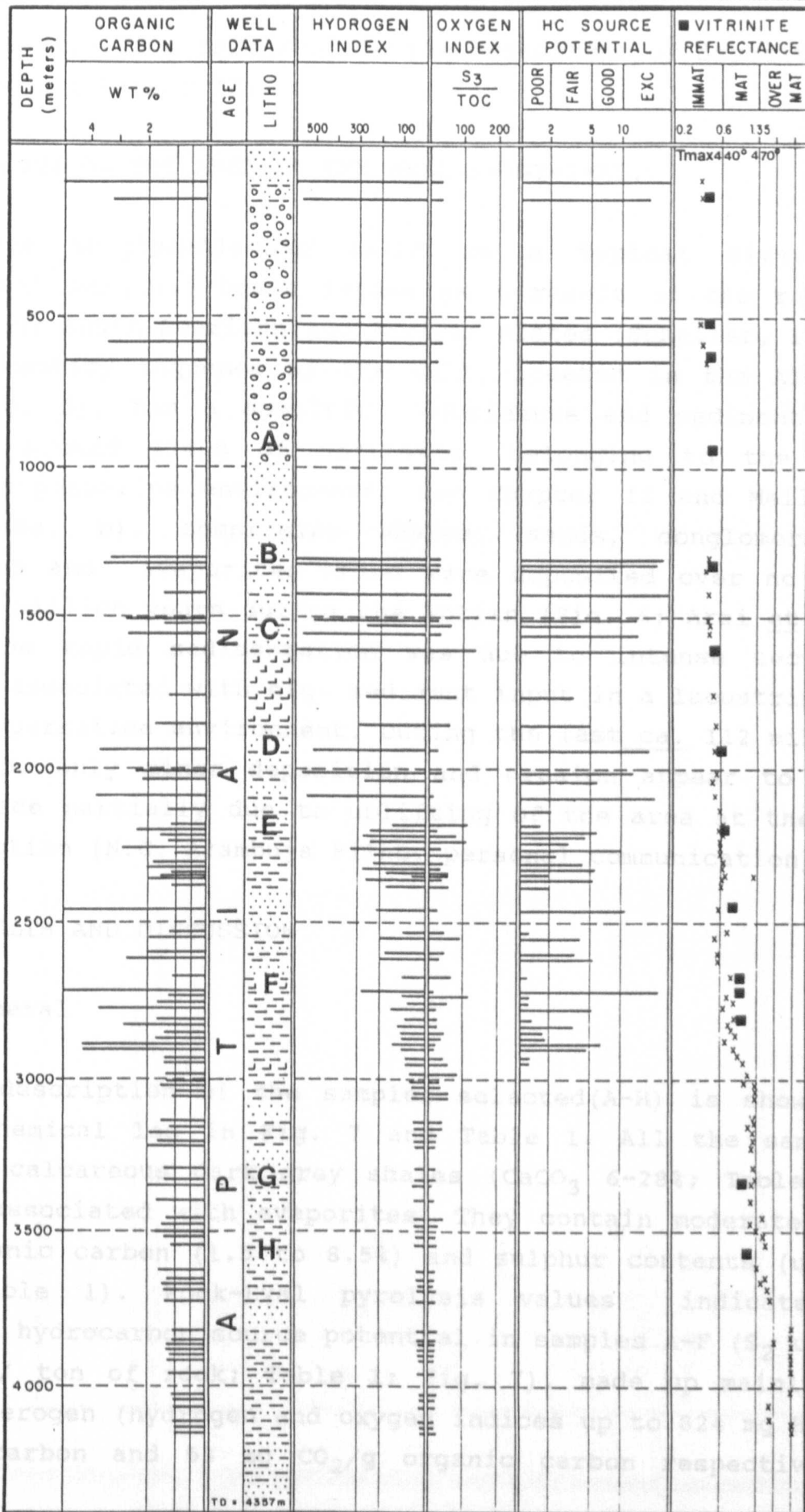


Figure 7- Geochemical and geological log of well 1-FGT-1-AL, localized in the Alagoas area of Sergipe/ Alagoas basin, showing the stratigraphic position of the samples A to H.



TD = 4357 m

representative from this well in the assessment of depositional environment (Chapter II).

5.6 GEOLOGY OF THE AREA OF THE WELL 1-FGT-1-AL.

The Sergipe-Alagoas basin is a typical divergent, continental marginal basin formed as a result of the rupture between the South American and African plates (Schaller, 1979). The sedimentary sequence of the well, located in the Alagoas area (Fig. 5), has a specific subsidence and sedimentation history. Around 4340m of sediments, belonging to the same facies (hypersaline environment; see Chapter II and Mello *et al.*, 1988a, b), comprising shales, sands, conglomerates, carbonates and evaporites which were deposited over no more than six million years during the Aptian (Fig. 6; Arai *et al.*, 1987). The rapid sedimentation was due to intense tectonic activity associated with high sediment input in a lacustrine to marine hypersaline environment. During the last ca. 112 million years b.p. only minor deposition and erosion appear to have taken place partially due to uplifting of the area at the end of the Aptian (N.C. Azambuja Filho, personal communication).

5.7 RESULTS AND DISCUSSION

5.7.1 General

A description of the samples selected (A-H) is shown in the geochemical log in Fig. 7 and Table 1. All the samples comprise calcareous dark grey shales (CaCO_3 6-28%; Table 1), usually associated with evaporites. They contain moderate to high organic carbon (1.5 to 8.5%) and sulphur contents (up to 0.7%; Table 1). Rock-Eval pyrolysis values indicate an excellent hydrocarbon source potential in samples A-F (S_2 up to 24 Kg Hc/ ton of rock; Table 1; Fig. 7), made up mainly of type-II kerogen (hydrogen and oxygen indices up to 824 mg Hc/ g organic carbon and 53 mg CO_2 /g organic carbon respectively;

TABLE 1 - Elemental, Pyrolysis Rock-Eval, Optical and Bulk Geochemical Data for a Series of Organic-Rich Samples(A to H), from Well I-FGT-1-AL.

I-FGT-1-AL	A	B	C	D	E	F	G	H
DEPTH (m)	945	1311	1557	1938	2259	2724	3402	3693
% CaCO ₃	28	26	26	24	14	7.5	6.0	6.0
% SULPHUR	0.25	0.3	0.5	0.55	0.7	0.45	0.2	0.2
% T.O.C	2.1	3.3	2.7	3.7	3.0	8.5	1.7	1.5
S ₂ (kgHc/ton rock)	18	24	15	19	10	24	0.7	0.4
HYDROGEN INDEX	824	747	543	500	334	280	43	27
T-MAX	433	428	430	434	439	440	465	489
VITRINITE RO%	0.46	0.5	0.56	0.6	0.66	0.77	0.83	0.94
EXTRACT (ppm)	395	1400	2524	2555	3755	5098	162	94
% SATURATES	26	28	32	35	51	54	40	30
% AROMATICS	13	20	16	16	13	17	4	6
% NSO	61	52	52	49	36	29	56	64
ODD/EVEN	<1	<1	<1	≤1	-1	-1	-1	-
PR/PH	0.4	0.93	0.9	0.9	0.8	0.9	1.1	-

Table 1; Figs. 7 and 8). The results of the elemental, bulk and biological marker investigation show a typical distribution (Tables 1, 4; e.g. Fig. 9) that characterize sediments deposited in an evaporitic environment (see Chapter II). The most significant are; moderate to high sulphur content, generally low pristane/ phytane ratios, heavy $\delta^{13}\text{C}$ values, and high abundance of long chain isoprenoids such as C_{25} regular and C_{30} (squalane), high concentrations of β -carotane, gammacerane, hopanes and steranes, except in the deepest samples. The fact that all the samples are derived from a similar depositional environment provides the opportunity to study the changes in the source rock composition due to thermal influences, virtually independent of lithological differences and variations of organic facies.

5.7.2. Microscopic, bulk and chemical parameters.

Figs. 7, 8, 10 and 11 and Tables 1 and 2 show a good correlation between the microscopic, bulk and chemical maturation parameters. This is clearly suggested by a uniform increase in the maturity indicators with depth (e.g. T-max and vitrinite reflectance in Figs. 7, 10 and 11; Dow, 1977; Milner, 1982; Tissot & Welte, 1984). Vitrinite reflectance data (%Ro) rise with depth, ranging from 0.46% (immature) at sample A (945m) to 0.60% (around onset of oil generation) at sample D (1938m) reaching 0.94% (base of the oil window) at sample H (3693m; Table 2; Figs. 7 and 10). Fig. 11 shows Ro (%) and T-max values plotted against depth for different samples in the same well. As can be observed, there is a good correlation between the Ro(%) and T-max values. Also, the same is observed between the spore colour index (SCI) and the Rock-Eval T-max data, which show values ranging from 3.0 and 433 °C (sample A, 945m) to 7.5 and 465 °C (sample H, 3693m) respectively; Table 2). Figs. 7, 8 and 10 and Tables 1, 2 show also uniform decrease in hydrogen index (HI) and hydrocarbon source potential (S_2) with the increase of maturity.

Table 2 - Bulk and Microscopic Maturation and Kerogen Type Data of Rock Samples from the Well 1-FGT-1-AL, Sergipe/Alagoas Basin, Brazil.

Samples	Age	Depth (m)	T-max (°C)	Vitrinite Reflectance (%Ro)	Spore Colour Index	Extracted Organic Matter (EOM, ppm)	Hydrocarbon/ Non-HC (%)	Saturates/ Aromatics (%)	CPI	$\delta^{13}C$ (‰ PDB)	Type of Organic Matter		
											Amorph. (%)	Herbac. (%)	Wood/Coaly (%)
A	Aptian	945	433	0.46	3.0	395	39	66	1.2	-27.6	50	10	40
B	Aptian	1311	428	0.50	4.5	1400	48	58	1.5	-24.1	50	5	45
C	Aptian	1557	430	0.56	4.5	2524	48	66	1.0	-24.2	60	5	35
D	Aptian	1938	434	0.60	5.0	2555	51	68	1.0	-23.6	40	15	45
E	Aptian	2259	439	0.66	5.0	3755	64	79	1.1	-23.6	80	5	15
F	Aptian	2724	440	0.77	6.0	5098	71	76	1.08	-22.5	90	5	5
G	Aptian	3402	465	0.83	6.5	162	44	90	1.03	-23.3	5	60	35
H	Aptian	3693	489	0.94	7.5	94	36	83	1.0	-	5	50	45

This decrease becomes especially noticeable during the last stages of the oil window (samples G and H; 3402 and 3693 m respectively) when the high maturity level tends to result in S_2 and HI values becoming close to zero (residual carbon). Fig. 8 and 10 show the variation in hydrogen and oxygen indices with depth and vitrinite reflectance. It is clear that the increasing maturity (indicated by both burial depth and $\%Ro$) tends to result in kerogen characteristics plotting progressively closer to the origin of the diagrams, indicating the gradual disappearance of aliphatic hydrocarbon chains, with consequently no more hydrocarbon generation (base of the oil window (Tissot & Welte, 1984)).

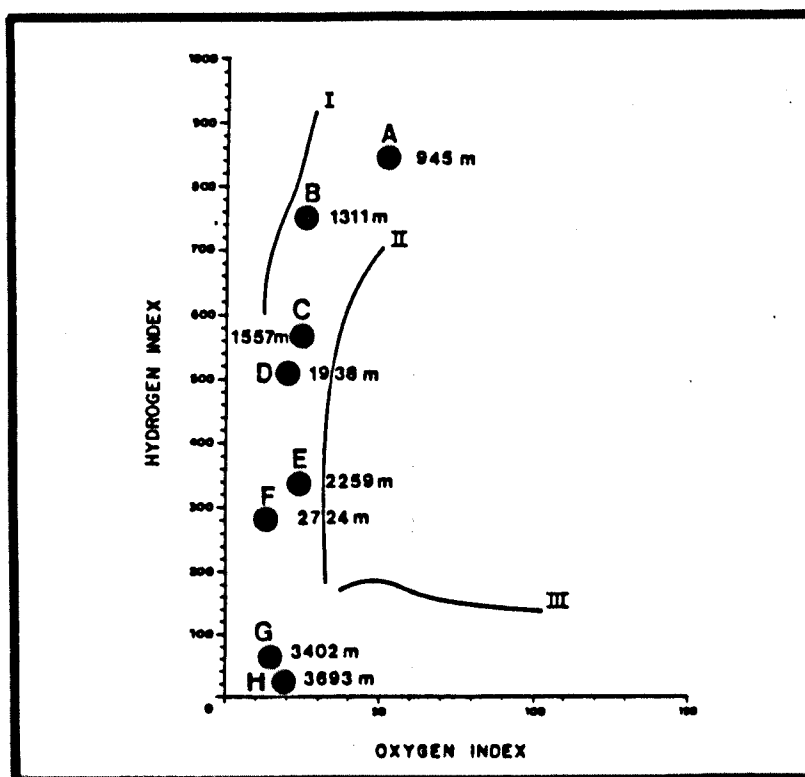
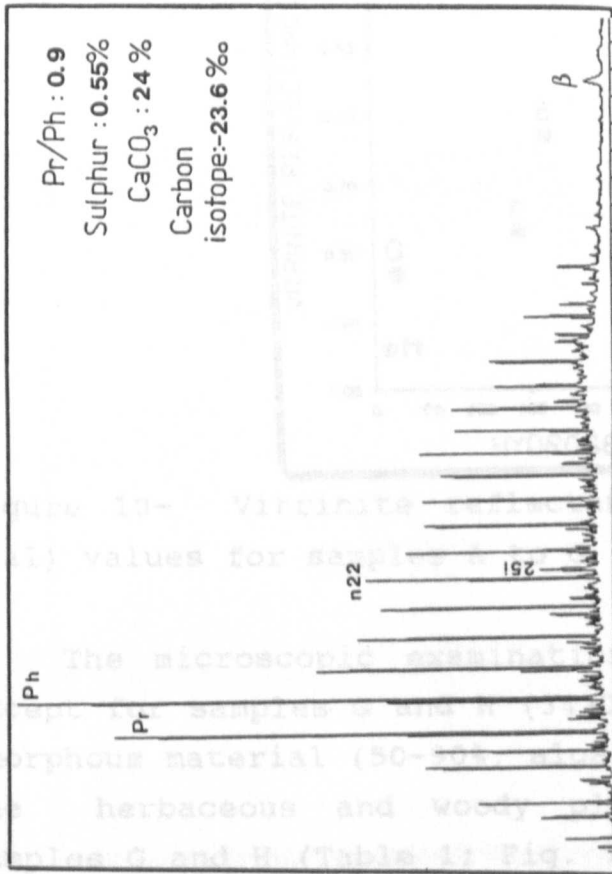
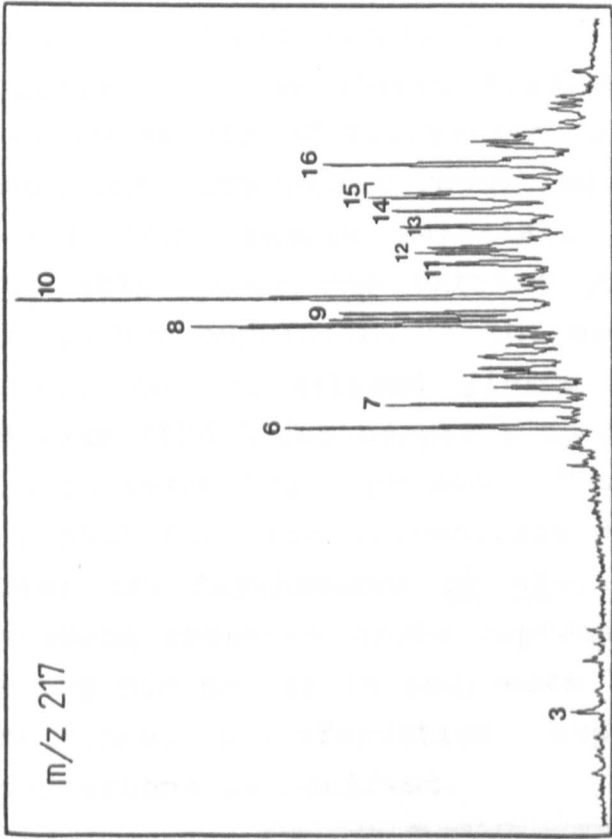


Figure 8- Hydrogen index (S_2/TOC) vs oxygen index (S_3/TOC), presented on van Krevelen type diagram, of samples A to H from well 1-FGT-1-AL.

Such phenomena are also associated with changes in the amount of extract obtained. From sample A to F, the amount of "EOM" ranges from 395 to 5098 ppm, maximising at sample F (2724m), the hydrocarbon/ non-hydrocarbon ratio varies from 39



Pr/Ph : 0.9
 Sulphur : 0.55%
 CaCO₃ : 24 %
 Carbon
 isotope:-23.6 ‰

Figure 13- Viridite fluorescence vs hydrogen index (Evl) values for samples from well 1-FGT-1-AL. The microscopic examination of the kerogen type, shows that samples G and H (50-100 m and 1963 m) a predominance of amorphous material (50-100 m and bacterially derived) over the herbaceous and woody material (1963 m). Samples G and H (Table 1; Fig. 13), show a drastic decrease in

to 71% and the amount of saturates reaches up to 54% (Tables 1 and 2). Samples deeper than 2724m (G and H), also exhibit a decrease in these values (Tables 1, 2), suggesting that, at advanced levels of maturation, breaking of carbon-carbon bonds occurs more frequently resulting in the conversion/ destruction of the more labile material. However, this explanation is simplistic since the extract yields are also the result of hydrocarbon expulsion. If the extract yields are normalised to T.O.C., the normalised yields for samples E and F show a decrease (125.2 for sample E to 39.9 mg/g T.O.C. for sample F). This suggests that the peak of oil generation is nearer sample E (2259m) than the unnormalised data would suggest (5098 ppm at 2724m; cf. Leythaeuser *et al.*, 1984, 1988). Summarizing, the phenomena observed above represent the cycle of evolution of the organic matter in sediments, where a continuous sequence of appearance, transformation, expulsion and disappearance of hydrocarbons is manifest.

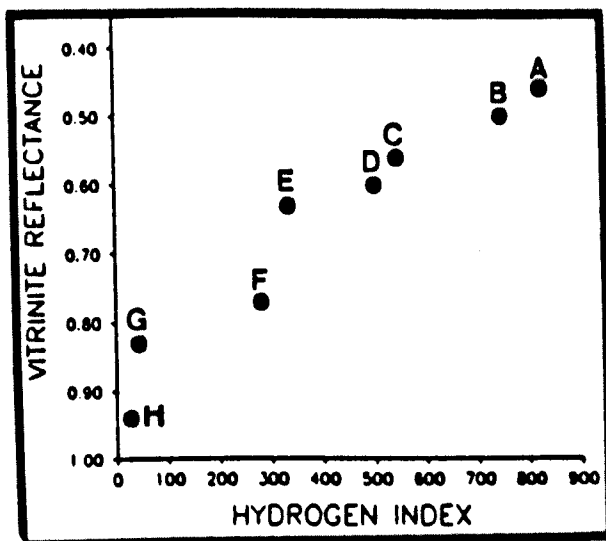
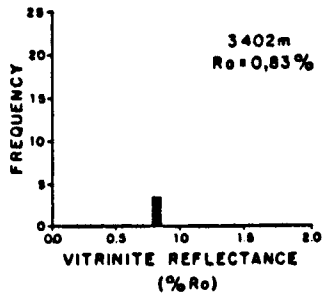
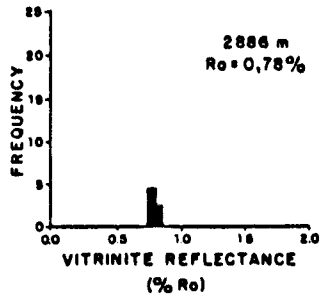
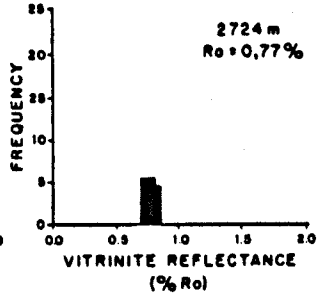
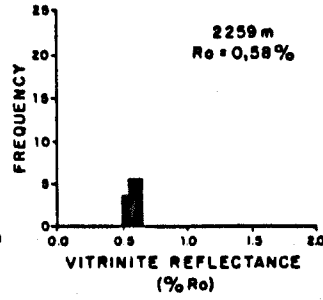
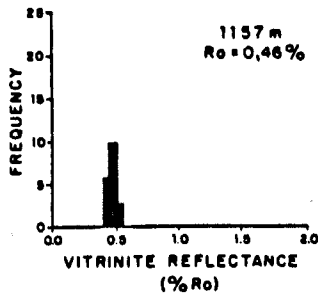
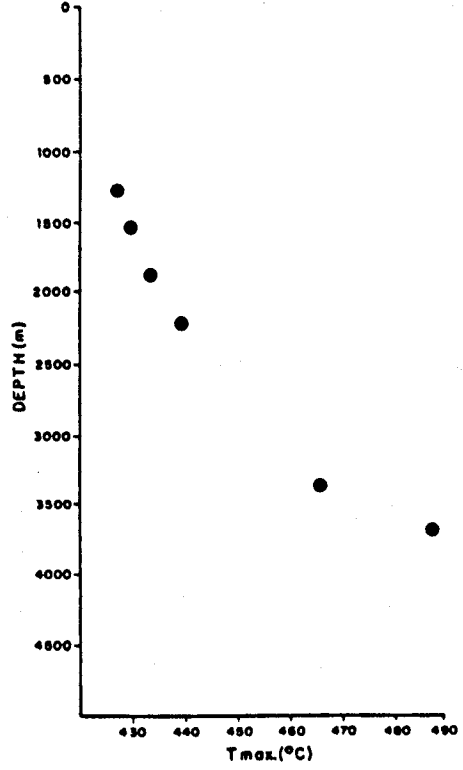
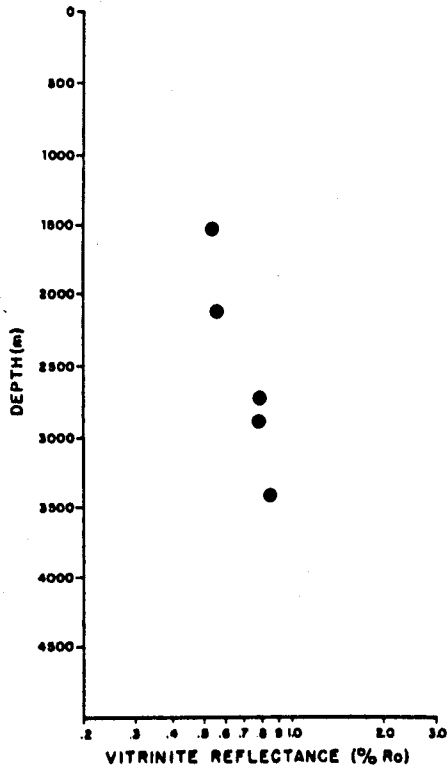


Figure 10- Vitrinite reflectance vs hydrogen index (Rock-Eval) values for samples A to G from well 1-FGT-1-AL.

The microscopic examination of the kerogen type, shows, except for samples G and H (3420 and 3963 m) a predominance of amorphous material (50-90%, algal and bacterially derived) over the herbaceous and woody plus coaly material (Table 2). Samples G and H (Table 1; Fig. 7), show a drastic decrease in

Figure 11- Vitrinite reflectance and T-max (Rock-Eval) values plotted against depth for other samples than A to G from well 1-FGT-1-AL.

WELL: 1-FGT-1-AL



the proportion of amorphous organic matter relative to the other samples (from 90% in sample F (2724m) to 5% in sample G and H; Table 2). This reduction can be explained by the fact that at the maturity levels of these samples (R_o equals 0.83 and 0.94% respectively), the more labile kerogen (algal and bacterial, hydrogen rich) has been preferentially converted to hydrocarbons relative to the more resistant herbaceous and woody plus coaly material (Tissot & Welte, 1984). It is interesting to note that similar behaviour of $\delta^{13}C$ values (whole extract) with depth are also observed. Initially, as expected, with increasing maturity (continuous breakdown of the kerogen tends to cause an isotope fractionation, with preferential breaking of $^{12}C-^{12}C$ bonds over $^{13}C-^{12}C$ bonds; Galimov, 1973; Tissot & Welte, 1984), resulting in a rise in $\delta^{13}C$ values (-27.6 at 945m to -22.5% at 2724m; Table 2). The slight change in this trend, with sample G (3402 m), showing a lighter $\delta^{13}C$ value (-23.3%; Table 2), is perhaps significant. This behaviour has been observed previously at an advanced level of maturation (base of the oil window), since the proportion of $^{13}C-^{12}C$ bonds being broken will increase as a reflection of the relative increase of NSO compounds plus asphaltenes (Table 1; Galimov, 1973; Silverman, 1967; Tissot & Welte, 1984). Summarizing the microscopic and bulk chemical data, it is clear that there is a good correlation between the different maturity indicators and their variation with depth and maturity (Tables 1, 2). As a whole it seems that samples A to C can be considered immature (no significant oil generation), sample D has barely entered the oil generation stage, whereas for the samples E to F the peak of oil generation has been reached, and in the samples G and H, it has been surpassed (base of the oil window, beginning of the "death line of oil". The zonation of the main stages of the thermal evolution of sedimentary organic matter in this well, once again, shows the importance of a combination, in a multiparameter approach, of physical and chemical methods in the assessment of thermal maturity.

5.7.3 Biological markers

This section, considered the main scope of this study, has as its primary objective the checking, under "ideal" conditions (relatively independent of lithological changes and variations in organic facies), of some of the most widely accepted biological marker parameters ratios used in the assessment of the thermal maturity of sedimentary organic matter. Extending such a study, it aims also to monitor the ratios against the absolute concentrations of biological marker compounds, these concentration being considered important in oil-oil correlation and maturity assessment (Rullkötter et al, 1984) and in the assessment of the palaeoenvironment of deposition (Chapter II; Mello et al., 1988a, b).

Overall, the molecular data obtained are in general agreement with the maturity order suggested by the optical, bulk and chemical data collated in Tables 2 and 3. In order to gain a better understanding of the relationship, each of the individual molecular parameters is discussed separately in the following sections:

5.7.3.1 Hydrocarbon composition and n-alkane distribution.

The basic concept of the changes in the hydrocarbon composition and n-alkane distribution with increasing maturity is clearly observed in Fig. 12. Originally, in the immature stage (samples A-C), there is a high abundance of cycloalkanes and long chain isoprenoids relative to n-alkanes, linked with CPI values higher than or equal to 1.0 (Table 2; Fig. 12). With increasing maturity, n-alkanes are generated, causing the dilution and subsequent destruction of the cycloalkanes and long chain isoprenoids (samples D-F; Fig. 12). Following on from this stage, the CPI values are around unity (Table 2). At the later stages of the oil generation process (sample G; Fig. 12), the increased cracking of C-C bonds, produces an increase in the relative proportion of light hydrocarbons (low molecular

Table 3 - Vitrinite Reflectance of Kerogen and GC-MS Maturity Parameters of the Alkane and Aromatic Fractions of Rock Samples from the Well 1-FGT-1-AL Sergipe/Alagoas Basin, Brazil.

Samples	Depth (m)	Vitrinite Reflectance (%Ro)	Ts/ ¹ Ts+Tm (%)	22S/ ² 22S+22R (%)	C ₃₀ αβ/ ³ C ₃₀ αβ+C ₃₀ βα	C ₂₃ /C ₂₇ Tri-cyclic terpanes ⁴	20S/ ⁵ 20S+20R (%)	αBB/ ⁶ αBB+ααα (%)	Tri/ ⁷ Tri+Mono (%)	C ₂₀ Tri/ ⁸ C ₂₀ +C ₂₀ Tri (%)
A	945	0.46	36	30	21	1.2	11	<26	44	0
B	1311	0.50	39	43	23	0.9	23	<26	66	2
C	1557	0.56	49	54	16	1.4	30	<28	74	6
D	1938	0.60	56	60	15	2.0	44	45	86	33
E	2259	0.66	65	62	16	1.2	40	50	-	81
F	2724	0.77	64	58	24	1.1	46	55	-	-
G	3402	0.83	65	63	32	2.5	44	53	-	-
H	3693	0.94	Tr	Tr	Tr	Tr	Tr	Tr	-	-

¹ C₂₇ 18α(H) Trisnorhopane (Ts) / C₂₇ 17α(H) Trisnorhopane (Tm) ⁵ C₂₀ 5α(H), 14α(H), 21α(H) 20S + 20R Ethylcholestone*

² C₃₁ 17α(H), 21β(H) Homohopanes

³ C₃₀ 17α(H), 21β(H) / C₃₀ 17β(H), 21α(H) Hopanes

⁴ C₂₃/C₂₇ Tricyclic terpanes

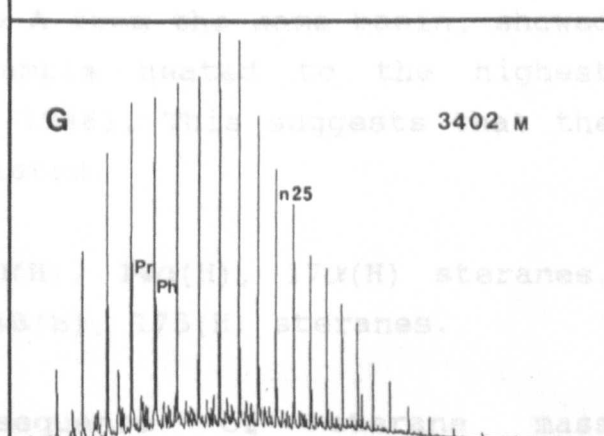
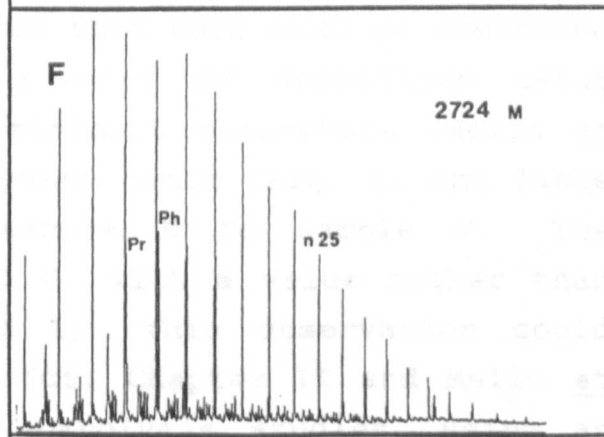
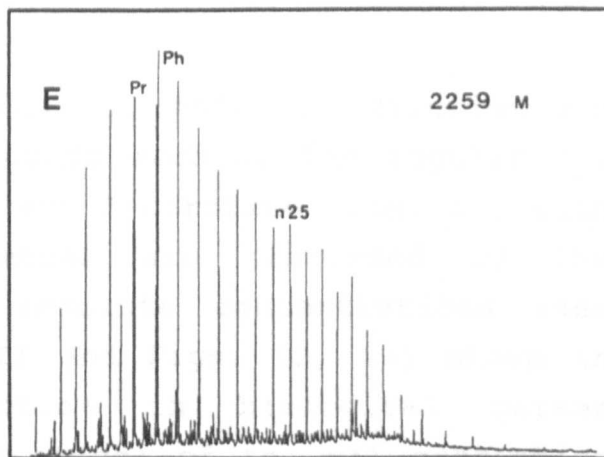
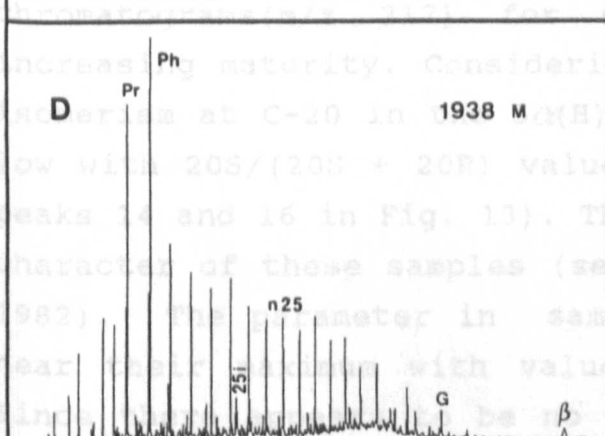
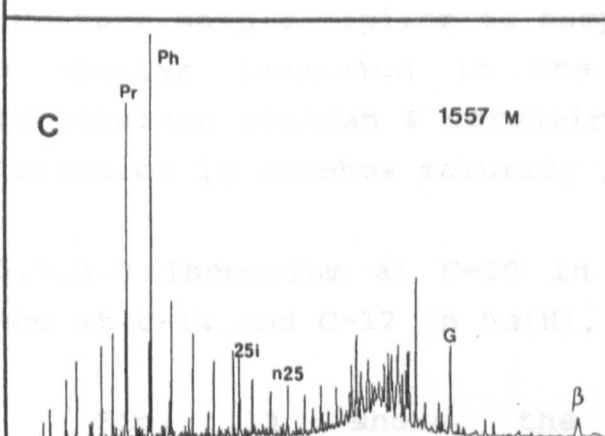
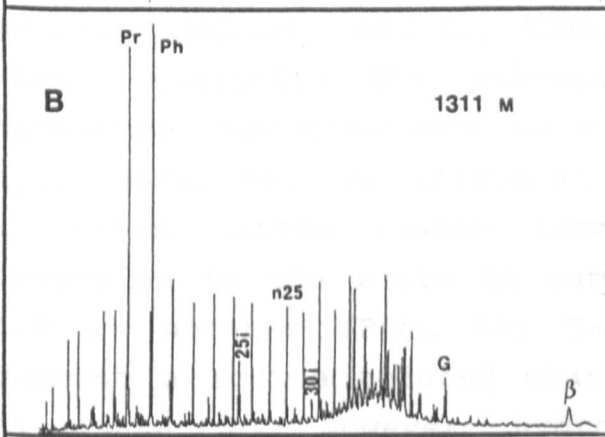
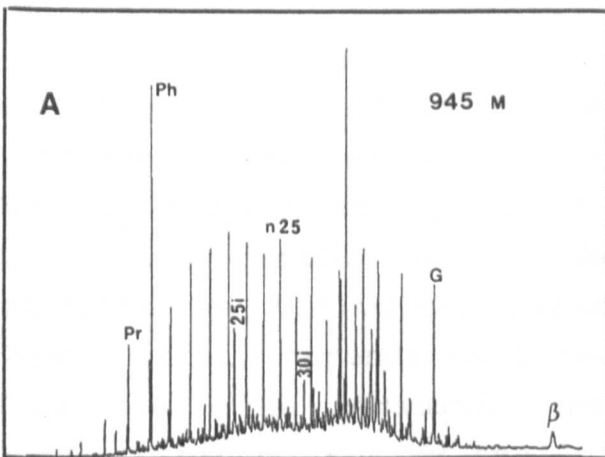
⁶ C₂₀ 5α(H), 14β(H), 21β(H) 20S + 20R / Total C₂₀ Ethylcholestone*

⁷ C₂₀ 20R Triaromatic/C₂₀ 20R Triaromatic+C₂₀ 5α(H) 20R Monoaromatic*

⁸ C₂₀ Triaromatic/C₂₀ Triaromatic + C₂₀ 20R Triaromatic

* See Experimental for measurement procedures

Figure 12- Gas chromatograms of total alkanes of extract of samples A to H, from well 1-FGT-1-AL.



COMPOUND ASSIGNMENT.

- Pr- 2,6,10,14-tetramethylpentadecane (pristane).
- Ph- 2,6,10,14-tetramethylhexadecane (phytane).
- 25i- C₂₅ 2,6,10,14,18-pentamethyleicosane (regular)
- 30i- C₃₀ regular isoprenoid (Squalane) et al.
- n25- C₂₅ n-alkane.
- G- Gammacerane.
- beta- beta-Carotane.

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weight species). It is interesting to note the dilution and subsequent disappearance of compounds such as the regular C_{25} and C_{30} isoprenoids, gammacerane and β -carotane (Fig. 12) with increasing depth. Such decreases are confirmed by the quantitative biological marker absolute concentrations (see Experimental, appendices I and II and Figs. 12, 13) shown in Table 4. The dramatic reduction in biological marker concentrations during the later stages of the oil generation process (samples G and H), indicates that care must be exercised when assessing the palaeoenvironment of deposition using biomarker concentrations as discriminant parameters (Mello *et al.*, 1988a, b). The pristane/ phytane ratio (Fig. 12 and Table 1) shows little change from sample B to sample F. The inversion in the ratio in sample G, with a value higher than 1.0 is notable (Fig. 12; Table 1). This observation could suggest a source related change (cf. Chapter II and Mello *et al.*, 1988a, b); however, hydrous pyrolysis studies, using an immature sample similar to sample A from the same basin, showed a similar inversion in the sample heated to the highest temperature (Soldan & Cerqueira, 1986). This suggests that the inversion is somehow maturity related.

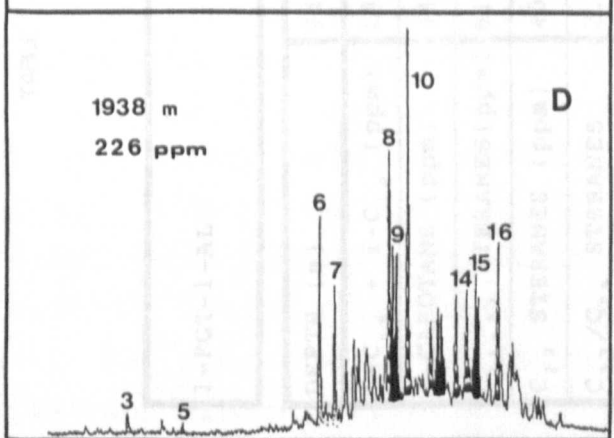
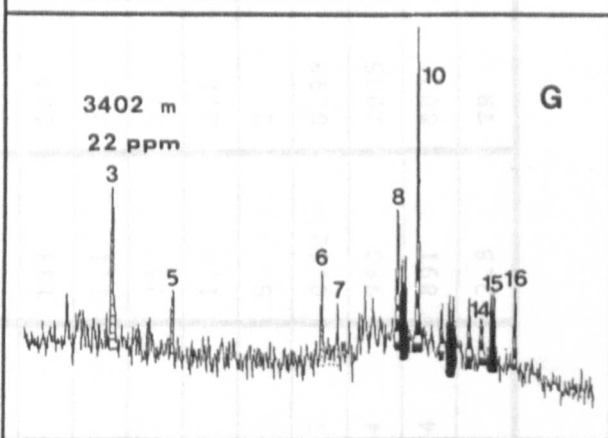
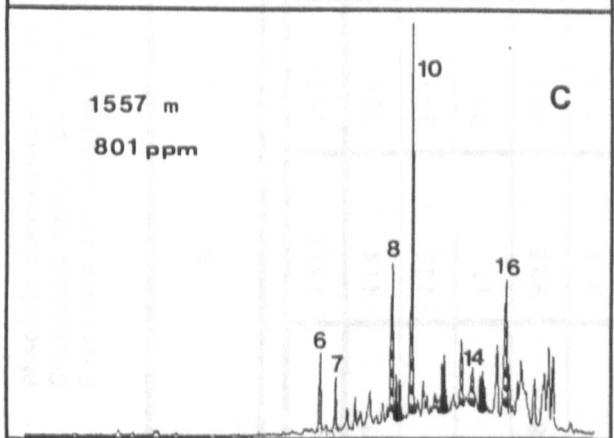
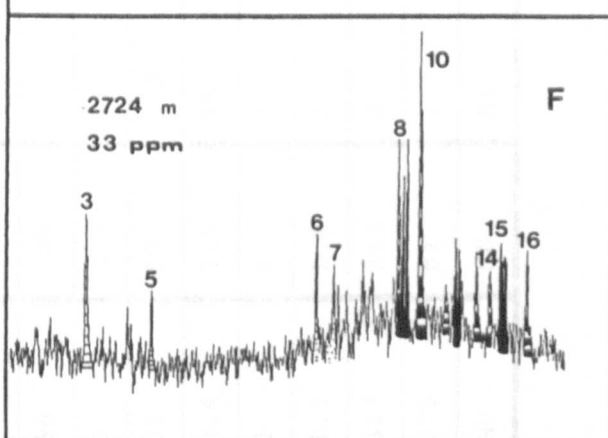
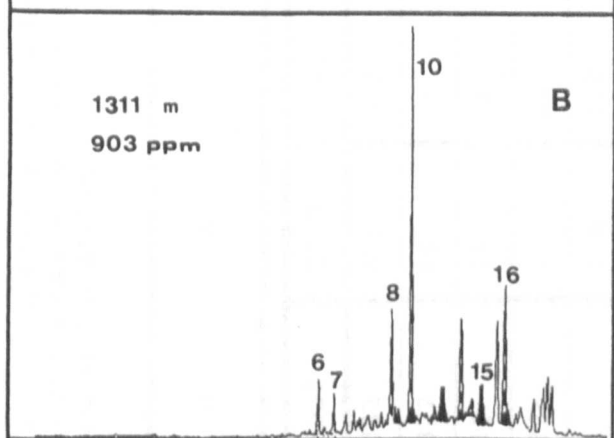
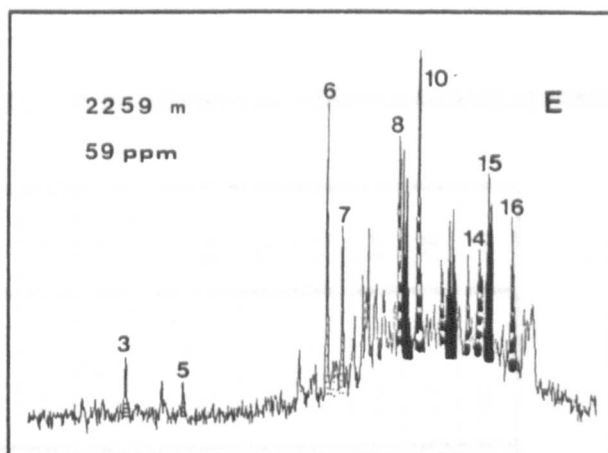
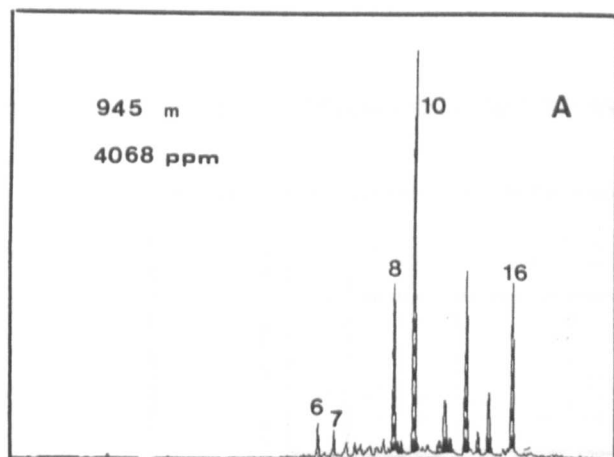
5.7.3.2 Isomerism at C-20 in $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ steranes, and at C-14 and C-17 in $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$ steranes.

Fig. 13 shows the sequence of sterane mass chromatograms (m/z 217) for samples A-G as a function of increasing maturity. Considering samples A to C, the extent of isomerism at C-20 in the $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ C_{29} steranes is low with $20S/(20S + 20R)$ values ranging from 11-30% (Table 3; peaks 14 and 16 in Fig. 13). These results confirm the immature character of these samples (see above; e.g. (Mackenzie *et al.*, 1982). The parameter in samples D to G appears to be at or near their maximum with values around 44 to 46% (Table 3). Since there appears to be no coelution problem connected with this ratio in these samples (the ratios were checked using

Figure 13- Partial m/z 217 chromatograms and C₂₇ ααα (S + R) steranes concentrations (ppm of extract) for samples A to G from well 1-FGT-1-AL (for biological marker quantitation see appendix II).

m/z 217

m/z 217



COMPOUND ASSIGNMENT.

- 3- 5 α (H),14 β (H),17 β (H) + 5 α (H),14 α (H),17 α (H) pregnane (C₂₁)
- 5- 5 α (H),14 β (H),17 β (H) + 5 α (H),14 α (H),17 α (H) homopregnane (C₂₂)
- 6- 13 β (H),17 α (H)-dicholestone, 20S diasterane.
- 7- 13 β (H),17 α (H)-dicholestone, 20R diasterane.
- 8- 5 α (H),14 α (H),17 α (H) + 5 β (H),14 α (H),17 α (H), 20S cholestanes.
- 9- 5 α (H),14 β (H),17 β (H), 20R + 20S cholestanes
- 10- 5 α (H),14 α (H),17 α (H), 20R cholestane.
- 14- 5 α (H),14 α (H),17 α (H), 20S 24-ethylcholestone.
- 15- 5 α (H),14 β (H),17 β (H), 20R + 20S + (5 β (H),14 α (H),17 α (H), 20R . 24-ethylcholestanes.
- 16- 5 α (H),14 α (H),17 α (H), 20R 24-ethylcholestone.

- 5 α (H), 14 α (H), 17 α (H) Steranes
- 5 α (H), 14 β (H), 17 β (H) Steranes

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TABLE 4 - Absolute Concentrations (ppm of extract) and Compound Ratios from Biological Marker GC-MS Analysis of the Alkanes and Porphyrins Fractions for Samples A to H, from Well 1-FGT-1-AL.

1-FGT-1-AL	A	B	C	D	E	F	G	H
DEPTH (m)	945	1311	1557	1938	2259	2724	3402	3693
i-C ₂₅ + i-C ₃₀ (ppm)	1417	414	796	382	491	352	103	TR
β-CAROTANE (ppm)	348	235	343	322	84	42	TR	TR
C ₂₁₊₂₂ STERANES (ppm)	61	11	22	12	26	26	20	TR
C ₂₇ STERANES (ppm)	4068	903	801	226	59	33	22	TR
C ₂₇ /C ₂₉ STERANES	2.1	2.3	2.0	1.7	1.5	3.0	2.0	TR
DIASTERANE INDEX	9	16	21	46	67	29	42	TR
4-Me STERANE INDEX	7	163	223	66	108	TR	TR	TR
HOPANE/STERANES	0.6	1.1	2.7	5.3	3.3	1.1	1.7	TR
TRICYCLIC INDEX	20	36	27	38	89	452	278	TR
C ₃₄ /C ₃₅ HOPANES	1.0	1.4	2.2	2.4	2.5	TR	TR	TR
BISNORHOPANE INDEX	58	5	2	3	4	14	23	TR
TS/TH	0.57	0.62	0.98	1.2	1.9	1.7	1.9	TR
C ₃₀ αβ HOPANE (ppm)	1184	960	1005	323	213	43	60	TR
GAMMACERANE (ppm)	1474	891	803	270	61	10	29	TR
Ni/V=O PORPHYRINS	3.2	2.8	TR	ND	ND	ND	ND	ND

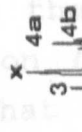
linked scan GC-MS), it appears that the end point of the reaction corresponds to slightly smaller values than the ones proposed by Mackenzie et al. (1982), which were around 50-55% (Fig. 4). A similar situation occurs with the extent of isomerism at C-14 and C-17 in the $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$ C_{29} steranes (peak 15 in Fig. 13; Table 3). The values are low in the shallow samples (quoted as a maximum since no allowance was made for the co-eluting $\beta\alpha\alpha$ 20R isomer in these immature samples) and increase with depth to a maximum value around sample F (around 55%; Table 3). In this case there are significant differences from the maximum value proposed in earlier studies (around 65-75%; Mackenzie et al., 1984). The differences are difficult to explain but presumably arise at least in part from the inherent inaccuracy in the measurement and from the lower resolution in earlier studies (Mackenzie et al. (1984) appreciated the difficulties by quoting a range of maximum values and mentioning coelution problems). With the column (DB 1701) and conditions used herein, there is some contribution from the $\beta\alpha\alpha$ isomer to the $\alpha\beta\beta$ components in immature samples (cf. peak 15 in Fig. 13). However, with increasing maturity such a contribution tends to be minimised. In Fig. 13 significant amounts of the $\beta\alpha\alpha$ species are present only in samples A, B and C (peak 15; Fig. 13). The increase in $\alpha\beta\beta$ components with maturity is confirmed by the low molecular weight C_{22} 4-methyl steranes where the maximum values occur around the same point (Fig. 14).

Recently, some authors have pointed out that these $\alpha\beta\beta$ components could be derived from specific steroid precursors present in the original depositional environment (Rullkötter et al., 1984) arising specifically from Δ^7 sterols (ten Haven et al., 1986; Peakman et al., 1986, 1988). Hence, rather than being isomerization products of steranes (Mackenzie & Maxwell, 1981; Mackenzie et al., 1982) they could merely or also be products of a concentration effect as less stable steranes are preferentially degraded (Peakman et al., 1986, 1988). The results of this work, based on a quantitative

Figure 14- Partial m/z 231 (4-methyl homopregnanes)
chromatograms for samples B to E from well 1-FGT-1-AL.

1938 m

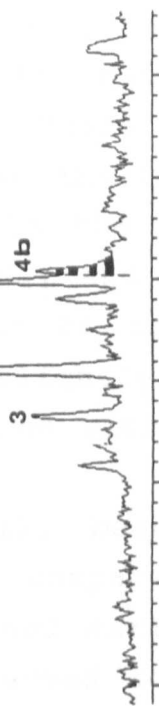
D



R: 60 %

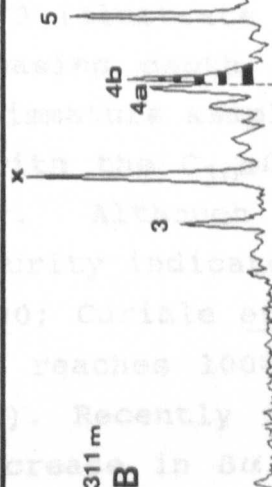
1938 m

D



1311 m

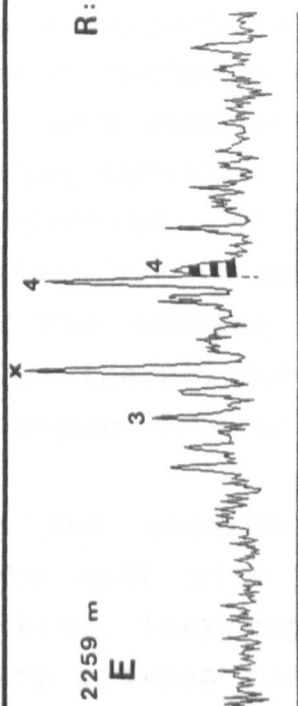
B



R: 45 %

2259 m

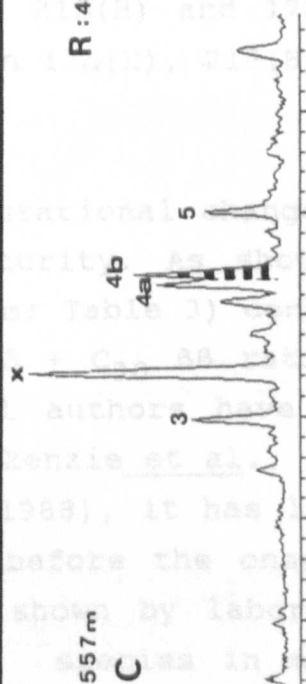
E



R: 82 %

1557 m

C



R: 48 %

3- 5 α (H),14 β (H),17 β (H) + 5 α (H),14 α (H),17 α (H)-pregnane (C₂₂)

4- 4 α -methyl-5 α (H),14 β (H),17 α (H)-homopregnane (C₂₂)

4a- 4 α -methyl-5 α (H),14 β (H),17 β (H)-homopregnane (C₂₂)

4b- 4 α -methyl-5 α (H),14 α (H),17 α (H)-homopregnane (C₂₂)

5- 5 α (H),14 β (H),17 β (H) + 5 α (H),14 α (H),17 α (H)-homopregnane (C₂₂)

R: 4a/(4a + 4b)

M/Z 231

M/Z 231

biological marker approach, showing ($C_{27} \alpha \alpha \alpha$ S + R concentrations dropping from 4068 ppm at 945m to 22 ppm at 3402m; Table 4), give some support to this idea. Whatever the origin and the evolutionary pathways of these compounds, it is clear that there is a good correlation between the sterane ratios above and increasing maturity (Tables 2, 3). The slight variation in the concentration of the low molecular weight steranes (C_{21} and C_{22} steranes) in most of the samples (ranging from 11 to 26 ppm in the samples B-G; Table 4), suggests perhaps a slightly higher thermal stability of such compounds, in comparison with the higher molecular weight steranes (Table 4).

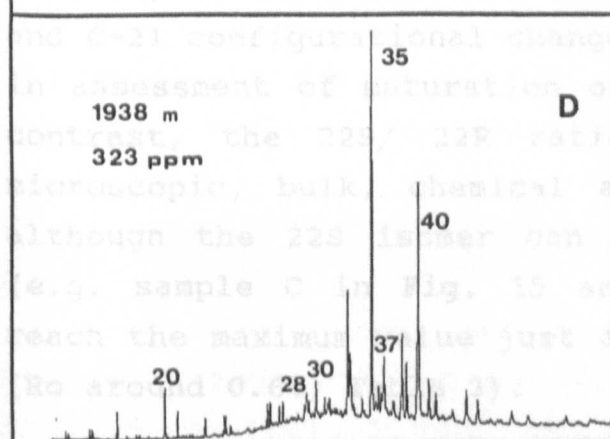
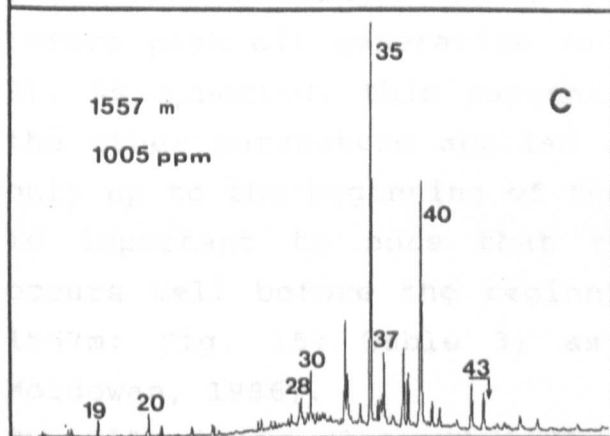
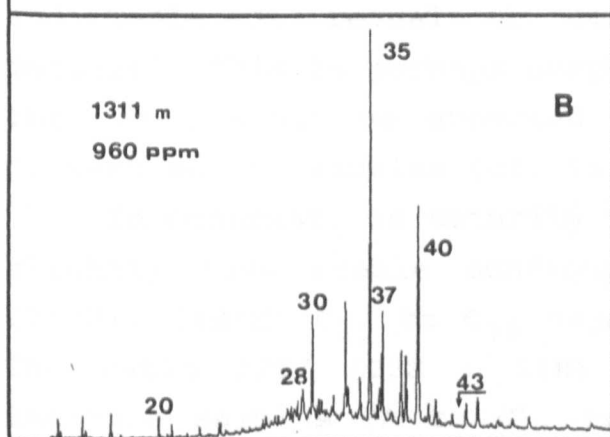
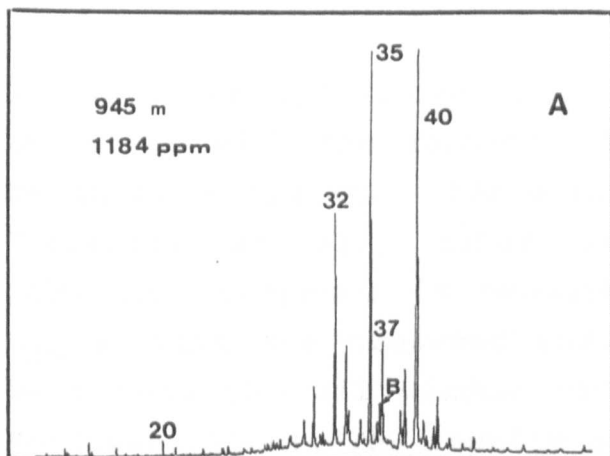
Overall, based on the results above, the two sterane parameters compare quite well with the generalized maturity data proposed earlier. Also, they appear to reach the highest values observed somewhere between the onset of oil generation (R_o around 0.6%) and the oil peak generation (R_o around 0.8%; Table 3).

5.7.3.3 Isomerism at C-17, C-21 in $17\beta(H)$, $21\beta(H)$ and $17\beta(H)$, $21\alpha(H)$ hopanes (C_{29} , C_{30} - C_{35}) and at C-22 in $17\alpha(H)$, $21\beta(H)$ C_{31} to C_{35} hopanes.

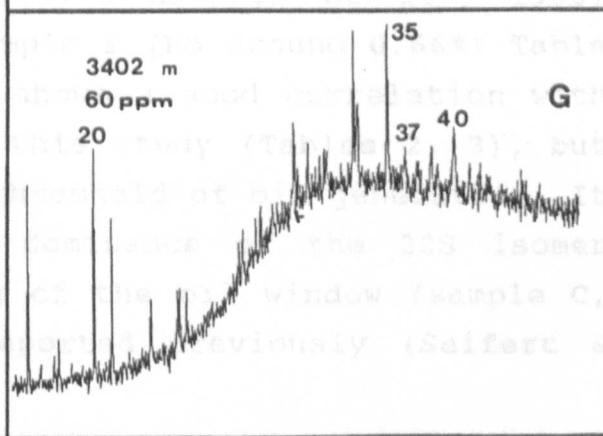
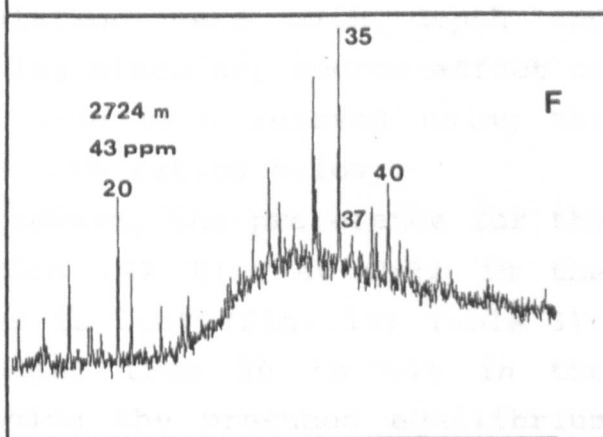
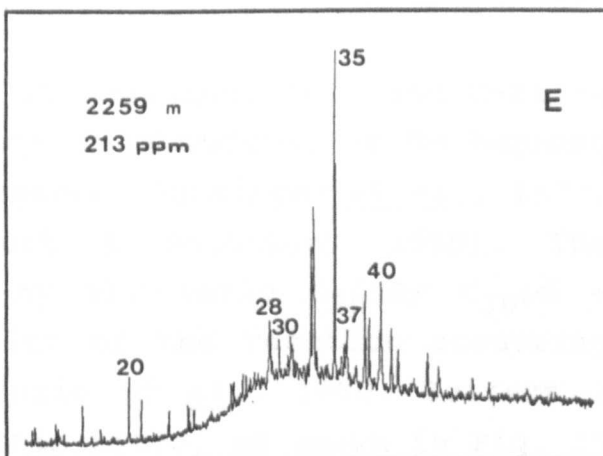
Fig. 15 and Table 3 illustrate configurational changes in the hopanes with increasing depth and maturity. As shown in Fig. 15, only the most immature sample (945m; Table 3) contains a $\beta\beta$ hopane (peak B) with the $C_{30}\alpha\beta / C_{30}\alpha\beta + C_{30}\beta\beta$ ratio in samples B-F being 100%. Although several authors have used this parameter as a maturity indicator (Mackenzie et al., 1980; Seifert & Moldowan, 1980; Curiale et al., 1988), it has little value, since the ratio reaches 100% well before the onset of oil generation (Fig. 4). Recently it was shown by laboratory simulation that the increase in $\beta\alpha$ and $\alpha\beta$ species in mature samples may be due to selective removal of the less thermally stable $17\beta(H)$, $21\beta(H)$ hopanes, rather than to their isomerization (Larcher et al., 1988). Another parameter that

Figure 15- Partial m/z 191 chromatograms and C₃₀ αβ hopane concentrations (ppm of extract) for samples A to G from well 1-FGT-1-AL (for biological marker quantitation see appendix II).

m/z 191



m/z 191



COMPOUND ASSIGNMENT.

- 19- C₂₁ tricyclic terpene
- 20- C₂₂ tricyclic terpene
- 28- 18 α (H)-22,29,30-trisnorhopane (Ts).
- 30- 17 α (H)-22,29,30-trisnorhopane (Tn).
- 32- 17 α (H),18 α (H),21 β (H)-28,30-bisnorhopane.
- 35- C₃₀ 17 α (H),21 β (H)-hopane.
- 37- C₃₀ 17 β (H),21 α (H)-hopane.
- 40- Gammacerane.
- 43- 17 α (H),21 β (H)-trishomohopanes (22S + 22R).

RETENTION TIME →

involves configurational changes at positions C-17 and C-21 is concerned with the apparent change in abundance of $\beta\alpha$ hopanes relative to the more stable $\alpha\beta$ hopanes (Ensminger et al., 1977; Mackenzie et al., 1980; Seifert & Moldowan, 1980). The parameter proposed is measured by the ratio $C_{30}\alpha\beta / C_{30}\alpha\beta + C_{30}\beta\alpha$, with the presumed end point of the reaction occurring well into the oil window (Mackenzie et al., 1980; Seifert & Moldowan, 1980). The results of this ratio, as shown in Fig. 15 and Table 3, reveal no correlation here with depth and maturity. This is perhaps surprising since any source effect on the ratio might be expected to have been removed using the present set of samples (cf. $T_s/T_s + T_m$ ratios below).

In contrast, as maturity increases, the preference for the slightly less stable configuration (22 R) at C-22 in the $17\alpha(H)$, $21\beta(H)$ C_{31} to C_{35} hopanes is lost (Fig. 15; Table 3). The ratio $22S / (22S + 22R)$ ranges from 30 to 54% in the immature samples (A to C), reaching the presumed equilibrium (ca. 60%; Ensminger et al., 1977; Mackenzie et al., 1980) before peak oil generation in sample E (R_o around 0.66%; Table 3). As expected, this parameter shows a good correlation with the other parameters applied in this study (Tables 2, 3), but only up to the beginning of the threshold of oil generation. It is important to note that the dominance of the 22S isomer occurs well before the beginning of the oil window (sample C, 1557m; Fig. 15; Table 3) as reported previously (Seifert & Moldowan, 1986).

Overall, it is clear that the hopane parameters based on C-17 and C-21 configurational changes are of relatively little value in assessment of maturation of sedimentary organic matter. In contrast, the $22S / 22R$ ratio compares favourably with the microscopic, bulk, chemical and sterane maturity parameters, although the 22S isomer can be dominant in immature samples (e.g. sample C in Fig. 15 and Table 3). It also appears to reach the maximum value just after the onset of oil generation (R_o around 0.6%; Table 3).

5.7.3.4 Ratio of C₂₇ 18 α (H)-trisnorneohopane (Ts) to C₂₇ 17 α (H)-trisnorhopane (Tm).

This parameter, first proposed by Seifert & Moldowan. (1978), is based on the idea that Ts is more resistant to thermal stress than Tm. Recently it has been shown that it is strongly dependent on both source input and mineral matrix (e.g. Seifert & Moldowan, 1986; Mello *et al.*, 1988a, b). The coelution problems with tricyclic or tetracyclic terpanes (Seifert & Moldowan, 1986) were avoided using a DB 1701 column and, in any case, the samples were also analysed by linked scan GC-MS, monitoring the m/z 370 ion; Norsk Hydro, Norway). The results in Fig. 15 and Table 3 suggest that, in samples with a specific palaeoenvironment of deposition (evaporitic), this parameter can, however, still be used as a maturity indicator. As expected, the boundary of the immature to mature stage based on this ratio (Ts/ Ts + Tm ratio higher than 50%) occurs somewhere around the sample with Ro= 0.6% (1938m; Table 3; e.g. Seifert & Moldowan, 1987). The deep samples (2259 and 2724m; Fig. 15), show a ratio rising to 65% (Table 3). Since these are the deepest samples before the disappearance of these compounds, it is reasonable to suggest that ratios around 65% reflect the "end point" of the parameter. This value is in agreement with several other results from oils and mature source rocks from some types of depositional environments in the Brazilian marginal basins (unpublished data). However, it is important to bear in mind that mineral matrix and/ or source input may play an important role in the Ts/Ts + Tm parameter (see Chapters II and III), and care is needed when interpreting such data.

5.7.3.5 Ratio of C₂₃/ C₂₁tricyclic terpanes.

Although the use of tricyclic terpanes ratios in assessing maturity has not been established, it appears from Fig. 15 and Table 4, that these compounds are more resistant to

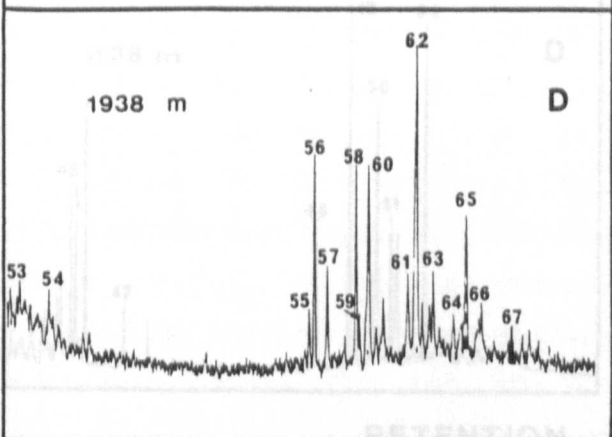
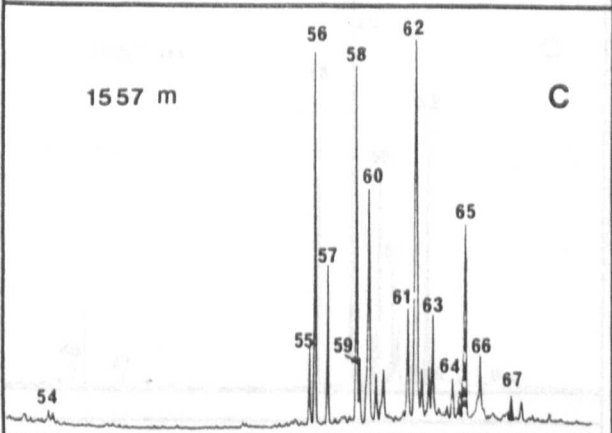
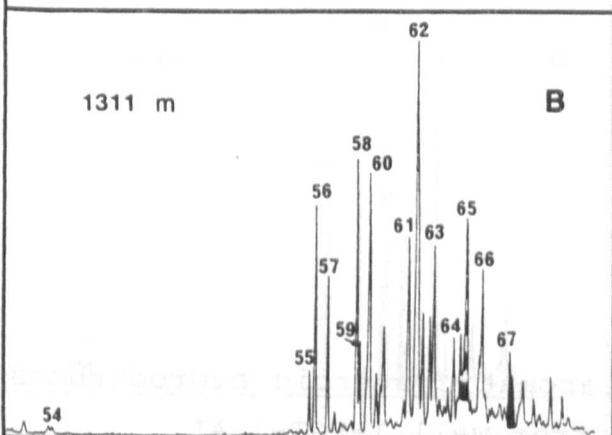
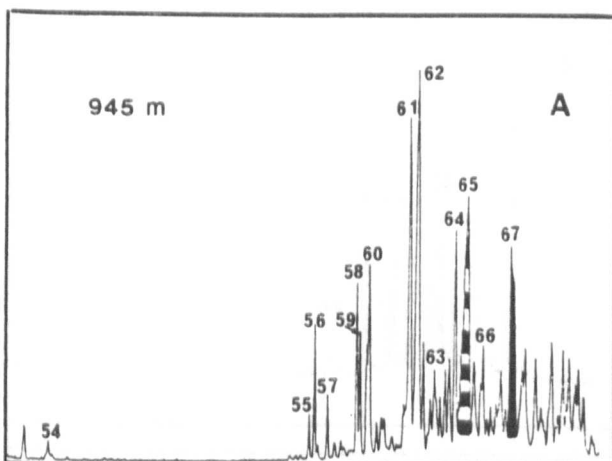
thermal degradation than the $\alpha\beta$ hopanes (tricyclic index rising from 20 in sample A(945m) to 452 in sample G (2724m; Table 4; cf. Seifert & Moldowan, 1986). The tricyclic terpane ratio C_{23}/C_{21} proposed by Ekweozor and Strausz (1983), and later by Cassani et al. (1988), showed, however, no correlation whatsoever with increasing maturity and depth as shown in Table 3 and Fig. 15.

5.7.3.6 Aromatization of C-ring monoaromatic steroid hydrocarbons.

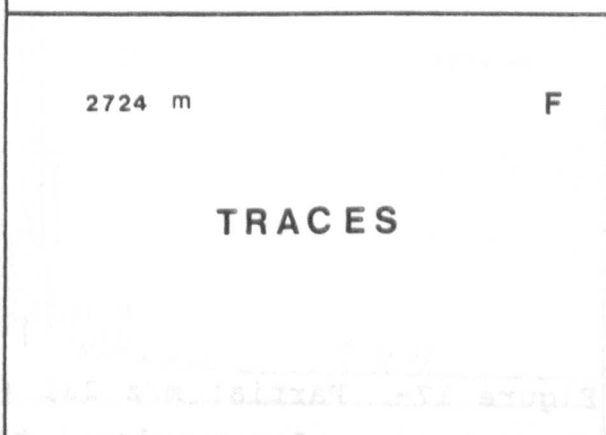
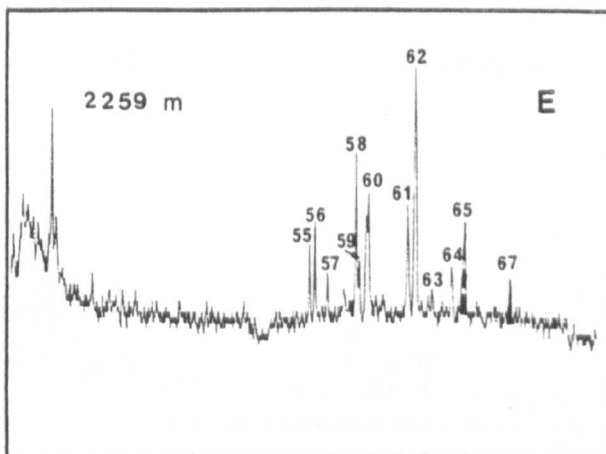
Fig 16 shows mass chromatograms of the monoaromatic steroid hydrocarbons (m/z 253). Recent studies (Riolo & Albrecht, 1985; Riolo et al., 1986; Moldowan & Fago, 1986) have shown that these distributions are more complex in some sample types (including hypersaline samples represented by the sample set herein) than previously supposed (e.g. Mackenzie et al., 1984). From these studies the peak assignments in Fig. 16 have been made by comparing relative retention times and elution orders (cf. Riolo et al., 1986). As a result of the complexities in the distributions which occur in some samples, Moldowan & Fago (1986) have pointed out that caution should be exercised in applying aromatisation ratios in a quantitative sense for assessment of thermal history of sedimentary basins (cf. Mackenzie & McKenzie, 1983) since different monoaromatic isomers may react at different rates. Furthermore, there can be coelution problems when measuring precise aromatisation ratios using the peaks in m/z 253 chromatograms as proposed by Mackenzie et al. (1982). The ratio uses peak 52 in Fig. 17 (triaromatics) and peaks 65 and 67 in Fig. 16 (monoaromatics). Originally, the derived ratio was given as C_{28} -20R tri/ C_{28} -20R tri + C_{29} 5 α (H) 20R + C_{29} 5 β (H) 20R-monoaromatic; a correction had to be made to allow for the contribution of the C_{28} 5 α (H) 20R component to peak 65 (Mackenzie et al., 1982). However, it is now known that peak 65 can contain in addition a C_{29} rearranged component in some types of samples (Riolo et al.,

Figure 16- Partial m/z 253 (monoaromatic steroid hydrocarbons) chromatograms for samples A to G from well 1-FGT-1-AL .

M / Z 253



M / Z 253



COMPOUND ASSIGNMENT.

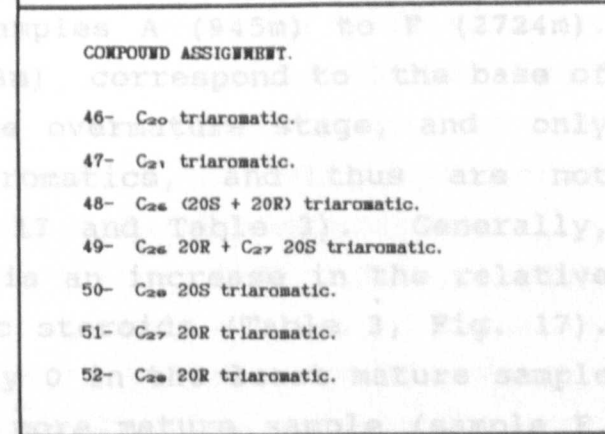
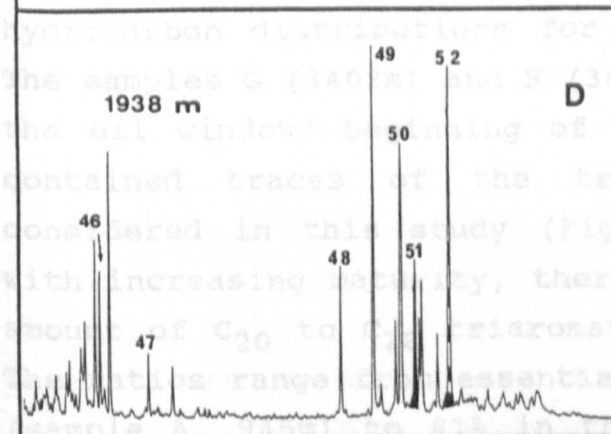
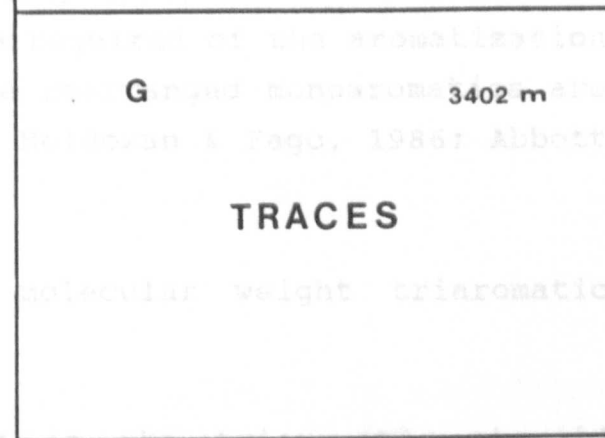
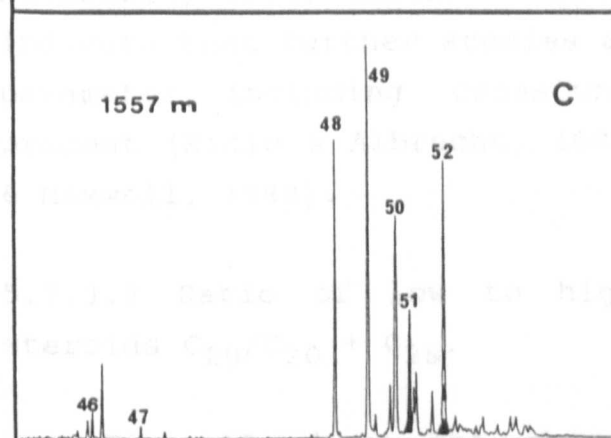
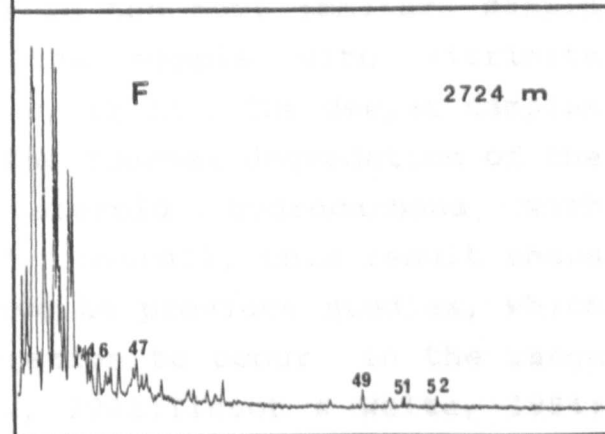
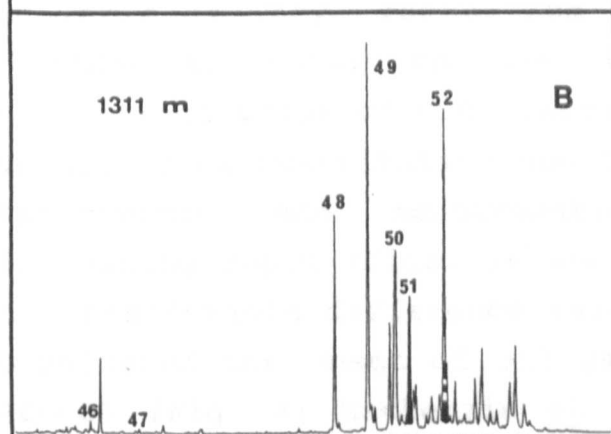
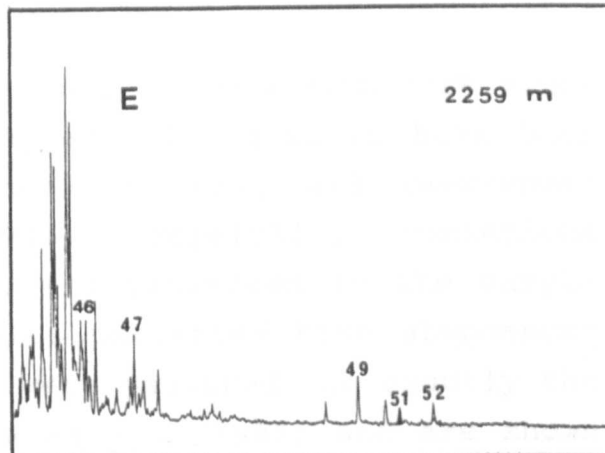
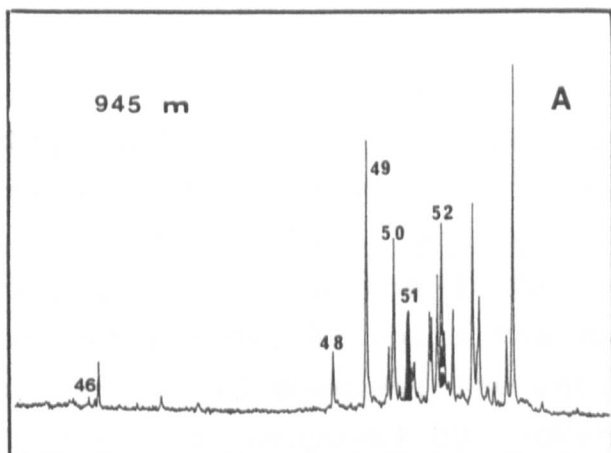
- 53- C₂₁ 5β(H) monocaromatic.
- 54- C₂₂ 5β(H) monocaromatic.
- 55- C₂₇ 5β(H), 20S monocaromatic.
- 56- C₂₇ 10β(H), 20S monocaromatic.
- 57- C₂₇ 10α(H), 20S monocaromatic.
- 58- C₂₇ 5β(H), 20R + C₂₇ 10β(H), 20S monocaromatic.
- 59- C₂₇ 5α(H), 20S monocaromatic.
- 60- C₂₈ 5β(H), 20S + C₂₇ 10α(H), 20R
+ C₂₈ 10β(H), 20S monocaromatic.
- 61- C₂₇ 5α(H), 20R + C₂₈ 5α(H), 20S monocaromatic.
- 62- C₂₈ 5β(H), 20R + C₂₈ 10β(H), 20R
+ C₂₉ 5β(H), 20S + C₂₉ 10β(H), 20S monocaromatic.
- 63- C₂₈ 10α(H), 20S monocaromatic.
- 64- C₂₈ 5α(H), 20S monocaromatic.
- 65- C₂₈ 5α(H), 20R + C₂₉ 5β(H), 20R
+ C₂₉ 10β(H), 20R monocaromatic.
- 66- C₂₉ 10β(H), 20R monocaromatic.
- 67- C₂₉ 5α(H), 20R monocaromatic.

RETENTION TIME →

Figure 17- Partial m/z 231 (triaromatic steroid hydrocarbons) chromatograms for samples A to G from well 1-FGT-1-AL .

M / Z 231

M / Z 231



RETENTION

TIME



1986). Hence, aromatization ratios must be used with care since there will be a source effect (hypersaline samples have been reported as having high abundances of ring A/B rearranged components; Riolo et al., 1986). Hopefully, variations resulting from source differences are minimised in the sample set used here. Although the samples presented high abundances of rearranged species, the ratios were measured in exactly the same way as proposed by Mackenzie et al. (1982) and are shown in Table 3. They range from 44% in the most immature sample (sample A, 945m) to 86% in the sample with vitrinite reflectance value of 0.6% (sample D, 1938m). The deeper samples do not allow quantitation due to the thermal degradation of the triaromatic and monoaromatic steroid hydrocarbons with increasing depth (Figs. 16 and 17). Overall, this result shows a considerable difference relative to previous studies, which considered the onset of oil generation to occur in the range 40-60% (Fig. 4; Mackenzie et al., 1982; Tissot & Welte, 1984; Mackenzie, 1984; Cassani & Eglinton, 1986). These differences indicate that further studies are required of the aromatization parameter, including cases where rearranged monoaromatics are present (Riolo & Albrecht, 1985; Moldowan & Fago, 1986; Abbott & Maxwell, 1988).

5.7.3.8 Ratio of low to high molecular weight triaromatic steroids $C_{20}/C_{20} + C_{28}$.

Fig. 17 shows the changes in the triaromatic steroid hydrocarbon distributions for samples A (945m) to F (2724m). The samples G (3402m) and H (3693m) correspond to the base of the oil window/ beginning of the overmature stage, and only contained traces of the triaromatics, and thus are not considered in this study (Fig. 17 and Table 3). Generally, with increasing maturity, there is an increase in the relative amount of C_{20} to C_{28} triaromatic steroids (Table 3, Fig. 17). The ratios range from essentially 0 in the least mature sample (sample A, 945m) to 81% in the more mature sample (sample E,

2259m; Table 3). Sample F (2724m) contains very low concentration of triaromatic steroids, and a ratio calculation was impossible (Fig. 17). It is noteworthy that although the previously-proposed maximum value (100%) has not been reached, the triaromatic species has been essentially degraded (samples G and H; Table 3; Fig. 17). In accordance with previous studies, the maximum value is normally obtained before the overmature stage has been reached (Fig. 4; Mackenzie *et al.*, 1982; Tissot & Welte, 1984). Recently, it has been pointed out that the C₂₀ components, instead of being cracking products of the higher molecular weight triaromatic steroid compounds (Mackenzie, 1984), could merely be products of a concentration effect (J.R. Maxwell and T.M. Peakman, personal communication).

Overall, the limitations related to the two aromatics parameters described above (e.g. sometimes complex monoaromatic distribution, dependence on source input and coelution problems), clearly indicate that caution must be exercised in the use of these parameters as maturity indices. Nevertheless, studies on samples from similar sedimentary facies, as discussed above, can provide results that compare favourably with other well established maturity parameters).

5.8 PREDICTIVE METHODS.

A computer model was applied to well 1-FGT-1-AL to illustrate that a predictive approach to the assessment of the maturity and hydrocarbon potential of a source rock, as a function of depth and geological time, can be useful (Norsk Hydro geochemistry section, Norway). The quantitation of the geological evolution of the basin and the hydrocarbon generation have been modelled using the deterministic model (Welte *et al.*, 1981; Welte & Yökler, 1982; Yökler, 1988). The input data for the model were; general geology of the area, present day thicknesses, lithology, average total porosity, geothermal gradient, palaeontological data, palaeobathymetry,

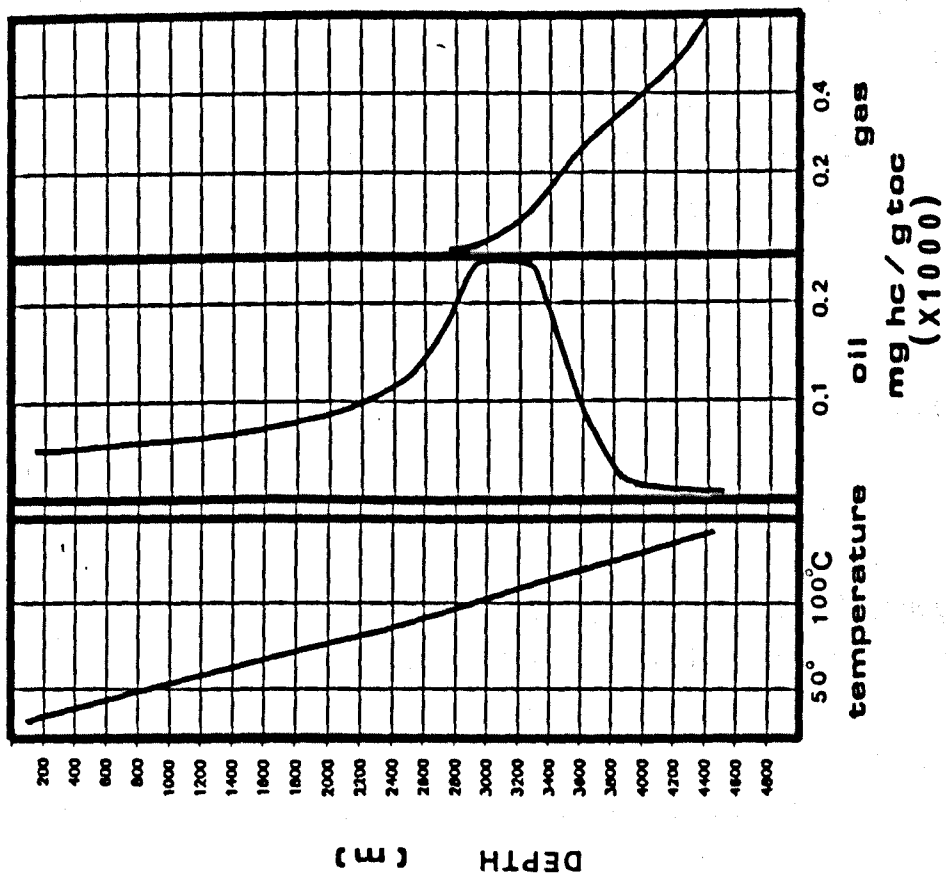
and heat flow. As a result, subsidence, compaction, pressure, temperature maturation and hydrocarbon generation as a function of space and time were calculated. These results were optimised by minimizing the errors between computed and measured porosities, pressures, temperatures and vitrinite reflectances. The bulk, Rock-Eval and biological marker data were used for checking the results from the model. Fig. 18 shows the computed evolution of the hydrocarbon generation curves (oil and gas) and the temperature profile with depth at the present time. The results suggest that the onset of oil generation occurs at around 2200 to 2400m, with the peak of oil generation ranging from 2900 to 3300m. Around 3600m, the peak of oil generation has been surpassed and the zone of destruction of the long aliphatic chain starts (base of the oil window). Microscopic, bulk, chemical and molecular parameters compare favourably with the maturation boundaries as defined by the predictive model (onset of the oil window between 1938 to 2259m (samples D and E), peak oil generation around sample F (2700-3000m), and the floor of the oil window/ top of the overmature zone between samples G and H (3400-3693m; see Tables 1-4)). Although there are small differences between the two approaches, it is clear that the predictive model can play a role in areas where samples are few or unavailable, since it offers a quantitative treatment of the complex interrelation of geochemical and geological processes as a function of temperature, time and pressure scales (Yükler et al., 1978; Welte et al., 1981; Welte & Yükler, 1980).

5.9) CONCLUSIONS

This work shows the value of a multiparameter approach (optical, bulk, chemical, biological marker, and predictive), and quantitative GC-MS in the assessment of the maturation effects in sedimentary organic matter. It is clear from the above discussion that the assessment of the extent of thermal maturity in sedimentary rocks has many problems. It is also

Figure 18- Computed diagram, modelled using a deterministic Yüklér model, showing the evolution of the oil and gas generation curves (mg Hc/g TOC) against depth(m) and temperature(C), for well 1-FGT-1-A1.

1-FGT-1 TIME: PRESENT



clear, that no single parameter is sufficient to assess maturity level with certainty. According to Mackenzie (1980), the ideal maturity parameter must be applicable to any sedimentary sequence, be irreversible, independent of the environment of deposition and not affected by catalytic reactions induced by lithological changes. For all the parameters in the present study, none of them satisfy all of these criteria. Nevertheless, consideration of the various parameters as a whole, together with the measurement of absolute concentrations of individual biological markers can assist in producing a result that may contribute to the precise assessment of the thermal evolution of organic-rich sediments. Figs. 19 and 20 show a comparison of most of the maturity parameters applied in this study and their evolutionary pathways with increasing maturity. As can be observed, there is a good correlation between the oil generation curve (ppm of extractable organic matter; Fig 19), decrease in hydrogen index and C_{30} $\alpha\beta$ hopane and C_{27} $\alpha\alpha\alpha$ (S + R) steranes absolute concentrations, with different maturity indicators, such as the vitrinite reflectance, T-max data and molecular parameters (Figs. 19, 20; Tables 2 and 3). The integration of all these data appears to define, with reasonable precision, the major boundaries of the evolution of the organic matter with increasing temperature. It is noteworthy that, since the differences in source input were hopefully minimized, the amount of hydrocarbons generated together with all the changes observed in the other maturity parameters can only be the result of thermal effects. Overall, the results (Fig. 19, 20; Tables 1-4) suggest that oil generation has not been significant at depths shallower than sample D (1938m), with samples A to C being immature. It is interesting to note that during this zone (945 to 1938m), the first drastic reduction in the hydrogen index (Fig. 19) and most of the biological marker compounds (e.g. C_{30} $\alpha\beta$ hopane in Fig. 19; C_{27} $\alpha\alpha\alpha$ S + R steranes in Fig. 20 and Table 4) occurs. Somewhere between samples D and E (1938-2259m), the beginning of

Figure 19- Composite diagram showing the relationship between physicochemical (pyrolysis Rock-Eval, extractible organic matter and absolute concentration of C₃₀ α/β hopane) and vitrinite reflectance data for samples A to H from well 1-FGT-1-A1.

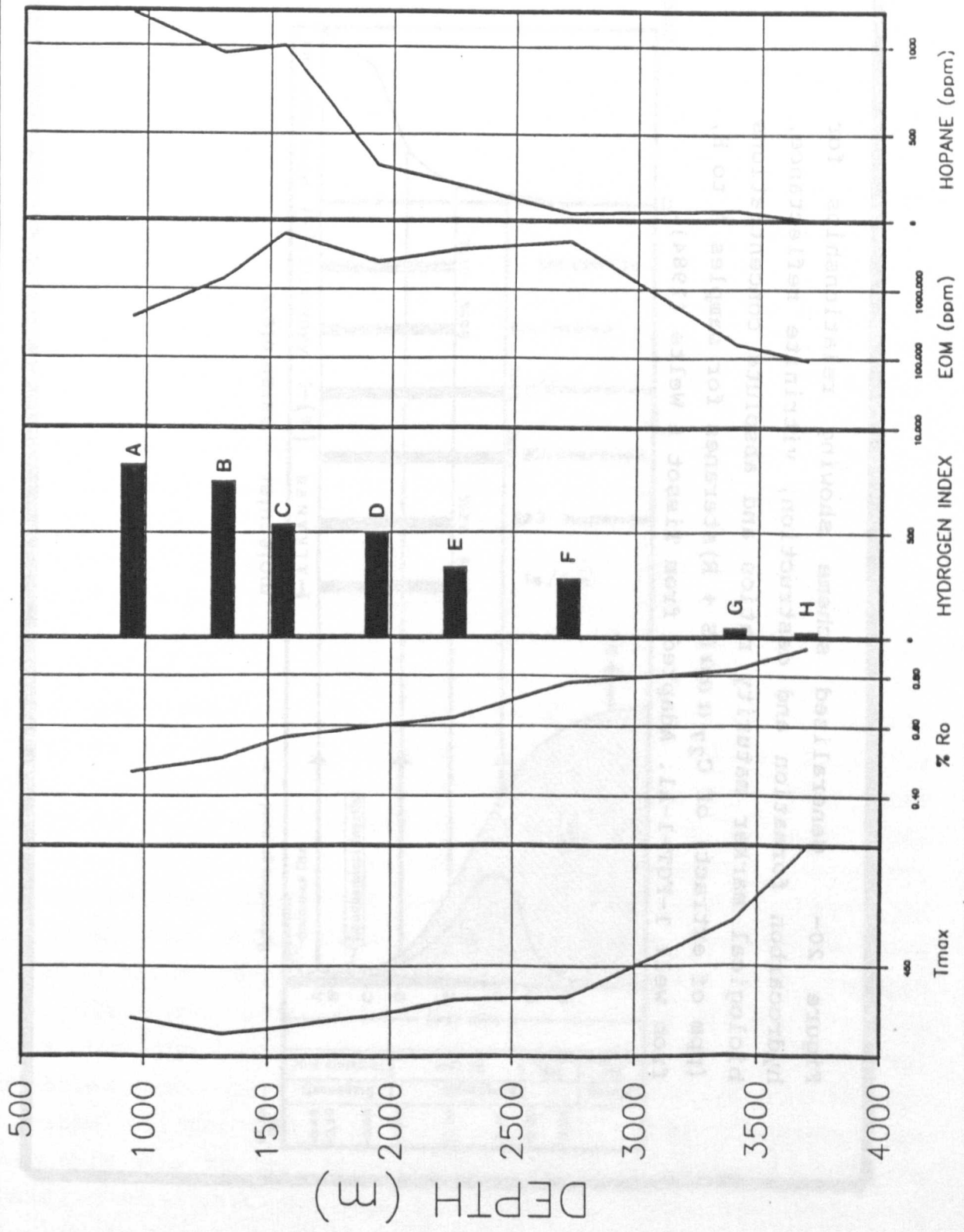
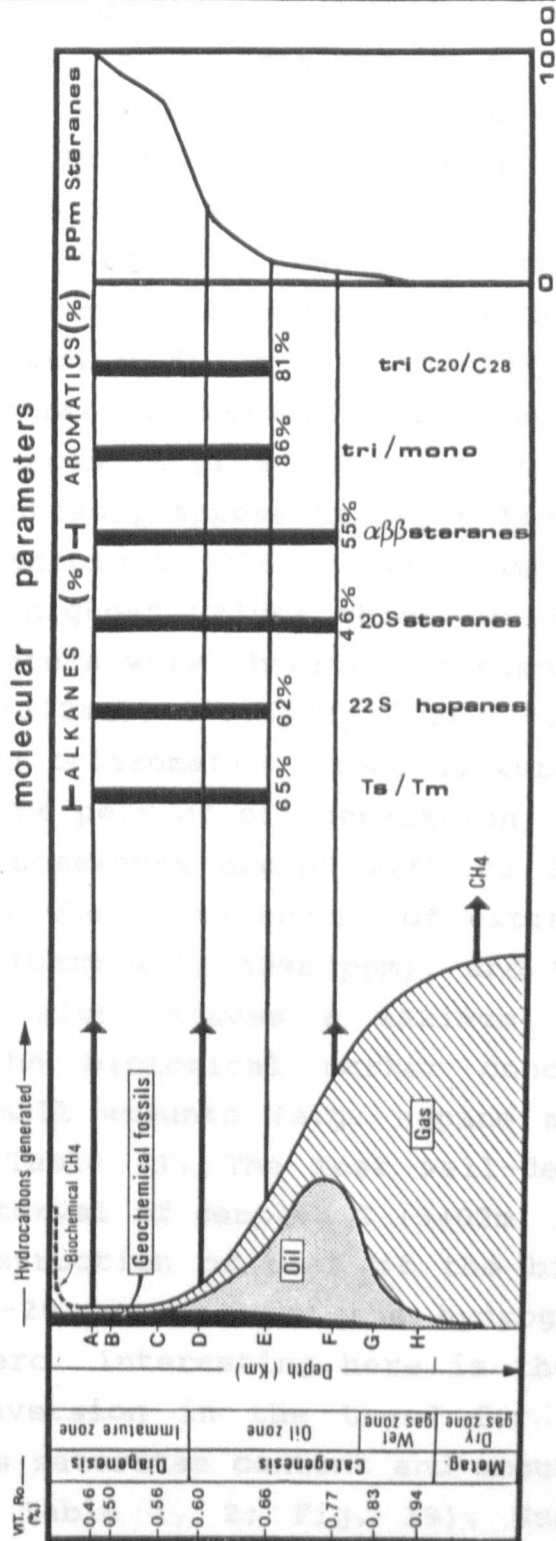


Figure 20- Generalized scheme showing relationships for hydrocarbon formation and destruction, vitrinite reflectance, biological marker maturity ratios and absolute concentrations (ppm of extract) of C₂₇ $\alpha\alpha\alpha$ (S + R)steranes for samples A to H, from well 1-FGT-1-A1. Adapted from Tissot & Welte (1984).



already formed hydrocarbons, as well as from the remaining hydrogen-depleted kerogen, and expulsion effects. At this

significant oil generation starts (Fig. 19, 20; Tables 2, 3). At this stage, with vitrinite reflectance values between 0.60 and 0.66%, a second significant reduction of the hydrogen index and biological marker concentrations (e.g. hopane, steranes; Figs. 19, 20; Table 4) occurs. These results lend support to the findings of Rullkötter et al. (1984) that the absolute concentrations of biological markers in sediment extracts decrease considerably between the onset and the peak of oil generation. It is also, interesting to note that some of the molecular ratios, such as $Ts/Ts + Tm$ and $22S/22S + 22R$ hopanes have reached their maximum values in this zone (Fig.20; Table 3), despite differences in presumed reaction type. The 20S and $\alpha\beta\beta$ steranes in contrast, appear to reach their highest values somewhere between sample E (2259m) and sample F (2724m; Fig. 20; Table 3). The highest values which could be measured for the aromatic parameters were observed in sample E (2259m; Fig. 20). In samples F (2724m), G (3402m), and H (3693m) only traces of monoaromatic and triaromatic compounds were detected (Figs. 16, 17; Table 3). The peak of oil generation, based on the data available, occurs somewhere around 2259 to 2724m (samples E, F). In this zone, where the amount of extract yield reaches the maximum value (sample F, 5098 ppm), and the extract yield normalised to TOC also reaches a maximum (sample E, 125.2 mg/g), most of the biological marker concentrations are reduced to very small amounts (e.g. hopane and sterane data, Figs. 19, 20 and Table 4). The most well-defined boundary, however, is the interval of samples G (3402m) and H (3693m). In this zone, the destruction of most of the biological markers (Table 4; Figs 13-20) occurs and the hydrogen index reaches values close to zero. Interesting here is the drop in the S_2 values and the inversion in the trend for some geochemical properties, such as saturates content and amount of hydrocarbon generated (% EOM; Table 1, 2; Fig. 19). Such phenomena are presumably due to the increased cracking of C-C bonds in the already formed hydrocarbons, as well as from the remaining hydrogen-depleted kerogen, and expulsion effects. At this

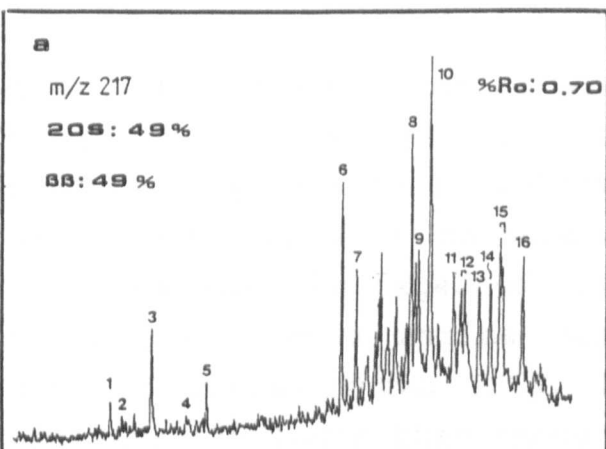
stage, the labile material is progressively thermally degraded and the aliphatic carbon chains in the kerogen are essentially destroyed (Tissot & Welte, 1984).

The recognition of a fairly precise zonation, without sharp boundaries, for the main stages of the thermal evolution of sedimentary organic matter in this well, shows the importance of a combination of optical, physical and chemical methods in the elucidation of the effects of the maturation in sedimentary organic matter.

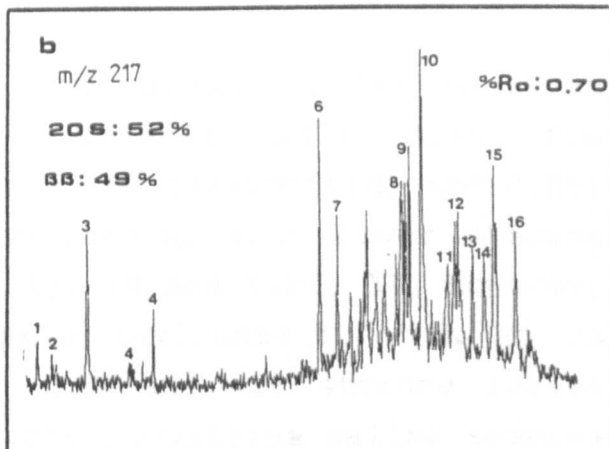
Considering the quantitative biological marker approach, it is clear that care must be exercised when assessing palaeoenvironment of deposition of mature source rocks, since at the peak of oil generation most of them are significantly reduced in concentration, and in some cases completely destroyed (Figs. 19, 20; Table 4).

The ranges of the changes in the molecular maturity ratios found in this investigation (Fig. 20; Table 3), in general compares fairly well with the results given by previous studies (e.g. Mackenzie et al., 1980; Seifert & Moldowan 1980, 1981; Mackenzie & Maxwell, 1981; Mackenzie et al., 1982; Mackenzie, 1984; Tissot & Welte, 1984; e.g. Fig. 4). They must be considered, however, as suggested by Tissot & Welte (1984), as only being a rough guide since there are other causal factors that can exert an influence on these parameters; e.g. type or quality of the organic matter having different activation energies for their transformation processes; type of geological constraints (e.g. mineral matrix, burial history, tectonic activity, heat flow, type of sedimentary basin). The difficulties which can occur are exemplified by Figs. 21-23. Figure 21 shows the m/z 217 chromatograms for the alkane fractions from sedimentary rock extracts from a number of different depositional environments with different R_o values (cf. Chapter II). In general, given the accuracy of measurement of the sterane and vitrinite maturity parameters, there is a reasonable correlation. The samples with R_o higher than or equal to 0.63% (open marine, lacustrine freshwater and saline

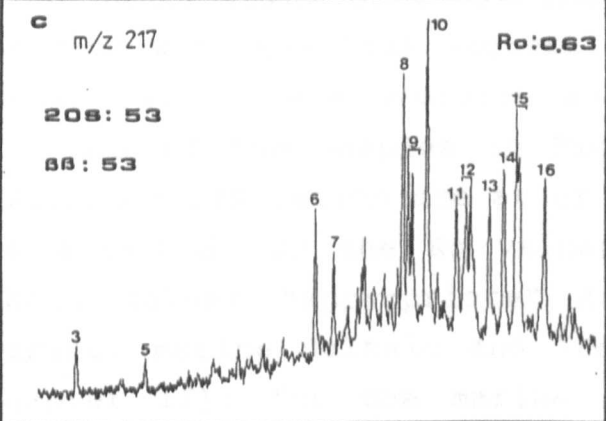
Figure 21- Partial m/z 217 chromatograms, vitrinite reflectance($R_o\%$) values and $20S/20S + 20R$ and $\alpha\beta\beta/ \alpha\beta\beta + \alpha\alpha\alpha$ sterane ratios for alkane fractions of sedimentary rock samples from different depositional environments; a: Open marine (ESS-46); b: Lacustrine freshwater (RNS-53); c and d: Lacustrine saline water (RD-1 and IP-1, respectively); e: Marine carbonate (APS-31); f and h: Evaporitic (CES-7 and RNS-10, respectively); and g: Marine deltaic (APS-36; for assessment of depositional environment and peak assignments see appendix I).



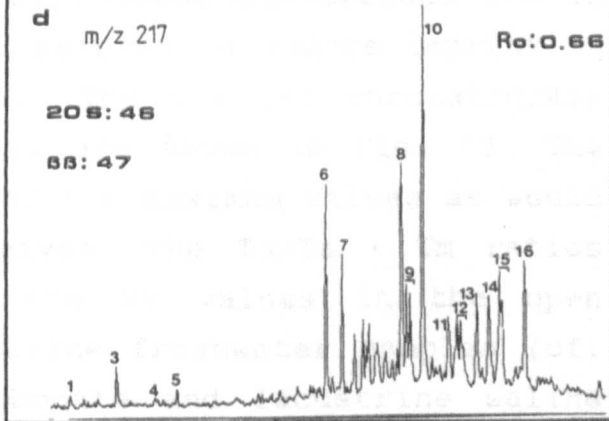
OPEN MARINE



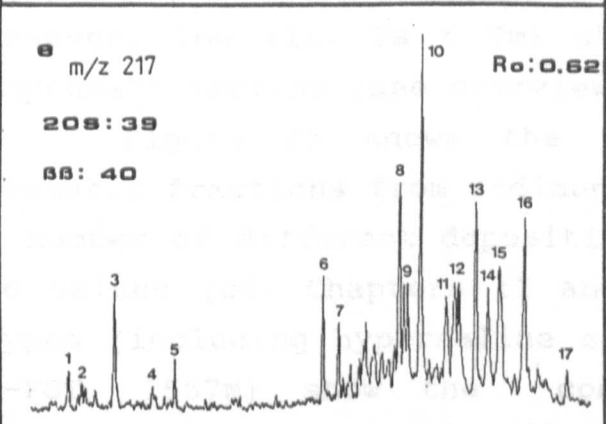
LACUSTRINE FRESHWATER



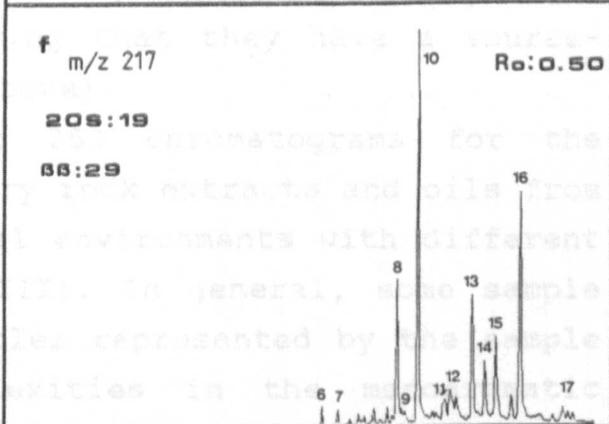
LACUSTRINE SALINE



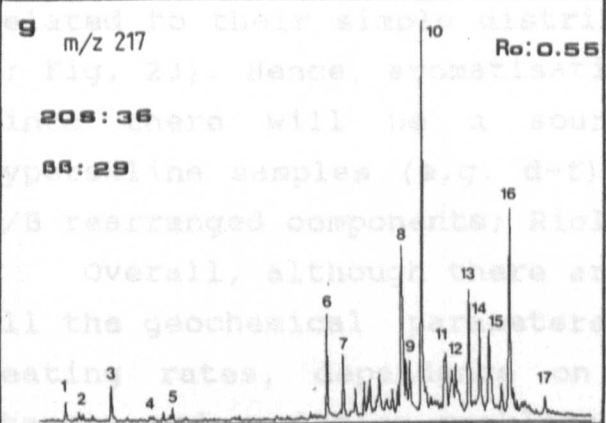
LACUSTRINE SALINE



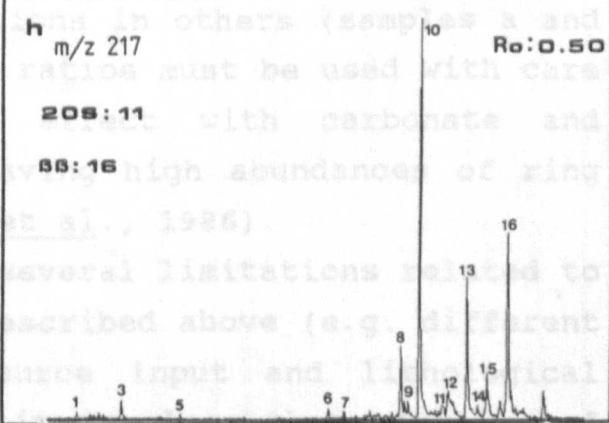
MARINE CARBONATE



EVAPORITIC



MARINE DELTAIC



EVAPORITIC

water) show sterane ratios with high values similar to those found in the samples from the 1-FGT-1-A1 well. Also, the immature samples with R_o values of 0.50% (evaporitic) and 0.55% (marine deltaic with carbonate influence) show lower sterane ratios as would be expected (cf. Fig. 18 and Table 3). However, the sample from a marine carbonate environment, with an R_o value of 0.62%, shows (Fig. 21), 20S and $\alpha\beta\beta$ sterane ratios significantly lower than those of the lacustrine saline samples with an R_o value of 0.63% (Fig. 21). These differences are in keeping with the idea suggesting, perhaps, a source imprint on these ratios (see overview above). The m/z 191 chromatograms for six of the samples in Fig. 21 are shown in Fig. 22. The 22S/22S + 22R ratios are at or near the maximum values as would be expected for the R_o values given. The Ts/Ts + Tm ratios shows values "appropriate" for the R_o values in the open marine, marine deltaic and lacustrine freshwater samples (cf. Chapter II); for the marine carbonate and lacustrine saline samples (R_o from 0.62 to 0.66%; Fig. 22) the values are, however, low (ie. Ts < Tm) showing that they have a source-dependent imprint (see overview above).

Figure 23 shows the m/z 253 chromatograms for the aromatic fractions from sedimentary rock extracts and oils from a number of different depositional environments with different R_o values (cf. Chapters II and III). In general, some sample types (including hypersaline samples represented by the sample 1-FGT, 1557m) show the complexities in the monoaromatic distributions which occur in some environments (samples c-f) related to their simple distributions in others (samples a and B; Fig. 23). Hence, aromatisation ratios must be used with care since there will be a source effect with carbonate and hypersaline samples (e.g. d-f) having high abundances of ring A/B rearranged components; Riolo et al., 1986).

Overall, although there are several limitations related to all the geochemical parameters described above (e.g. different heating rates, dependence on source input and lithological changes and coelution problems), it is clear that the use of

Figure 22- Partial m/z 191 chromatograms , vitrinite reflectance(Ro%) values and 22S/ 22S + 22R and Ts/ Ts + Tm ratios for alkane fractions of sedimentary rock samples from different depositional environments; a: Open marine (ESS-46); b: Lacustrine freshwater (RNS-53); c and d: Lacustrine saline water (RD-1 and IP-1, respectively); e: Marine carbonate (APS-31) and g: Marine deltaic (APS-36; for assessment of depositional environment and peak assignments see appendix I and Chapter II).

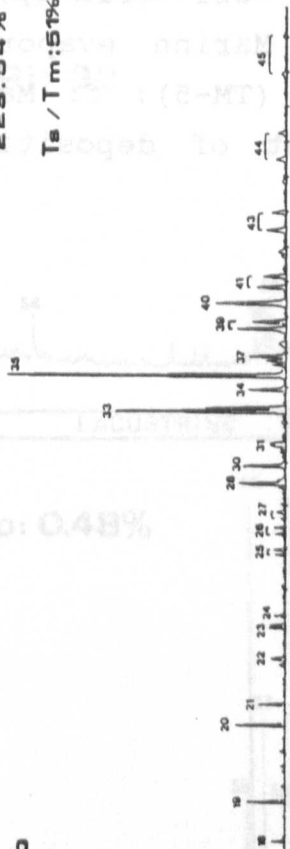
M/Z 191

M/Z 191

Ro: 0.70%

b

229:54%
Ts / Tm: 51%

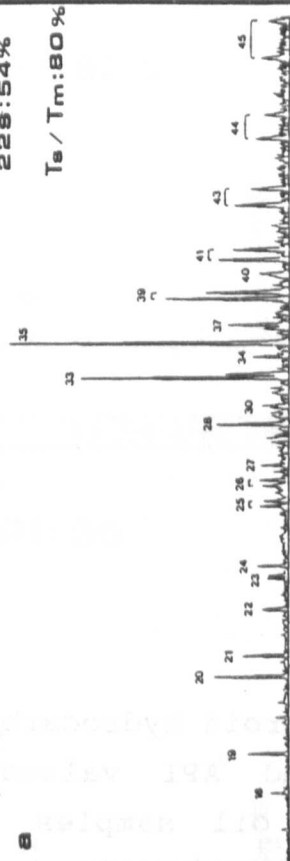


LACUSTRINE FRESHWATER

Ro: 0.70%

a

229:54%
Ts / Tm: 80%

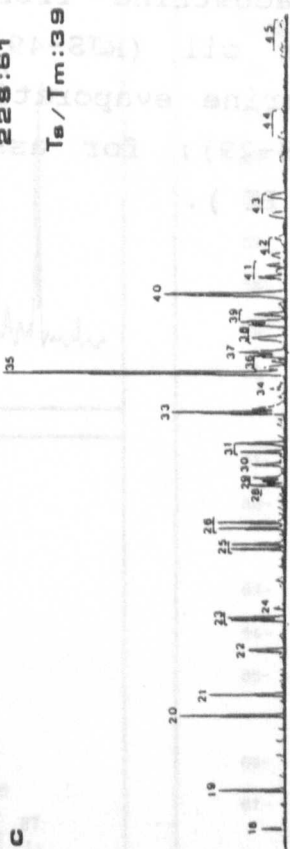


OPEN MARINE

Ro: 0.63%

c

229:61%
Ts / Tm: 39%

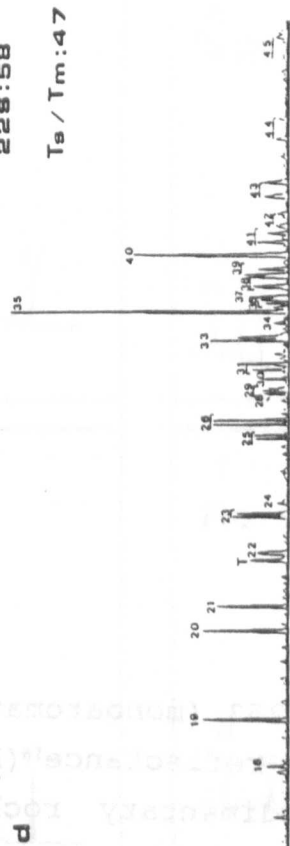


LACUSTRINE SALINE

Ro: 0.66%

d

229:58%
Ts / Tm: 47%

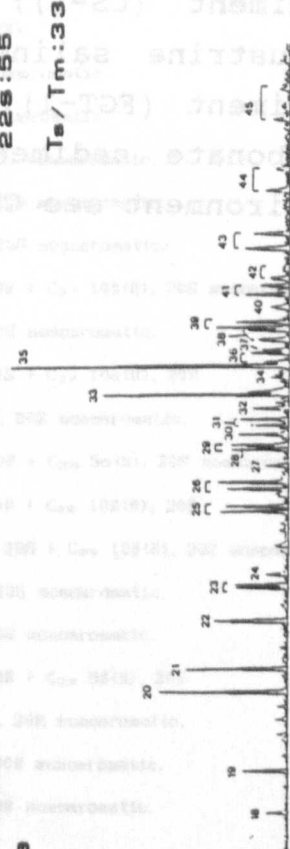


LACUSTRINE SALINE

Ro: 0.62%

e

229:55%
Ts / Tm: 33%

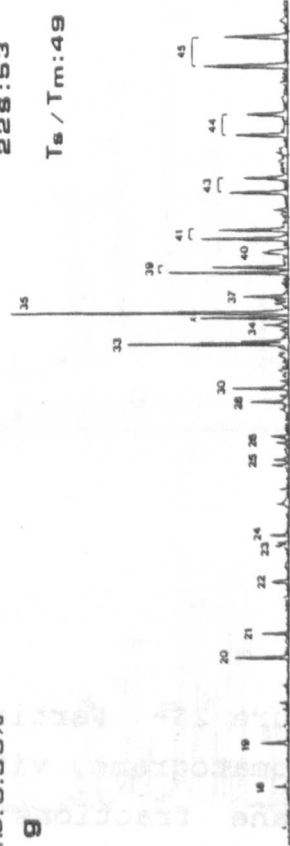


MARINE CARBONATE

Ro: 0.55%

g

229:53%
Ts / Tm: 49%



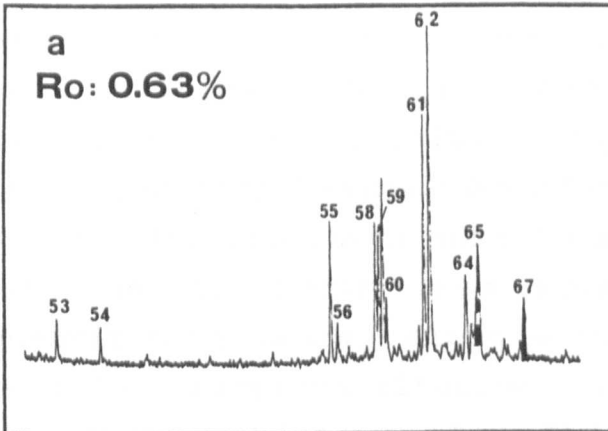
MARINE DELTAIC

RETENTION TIME →

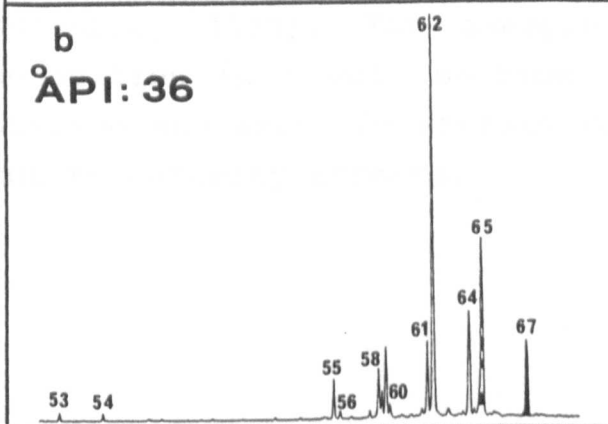
Figure 23- Partial m/z 253 (monoaromatic steroid hydrocarbons) chromatograms, vitrinite reflectance (Ro%) and °API values for alkane fractions of sedimentary rock and oil samples from different depositional environments; a: Lacustrine freshwater sediment (CS-1); b: Lacustrine freshwater oil (PIR-4); c: Lacustrine saline water oil (RJS-49); d: Marine evaporitic sediment (FGT-1); e: Marine evaporitic oil (TM-5); f: Marine carbonate sediment (APS-29); for assessment of depositional environment see Chapter II).

M/Z

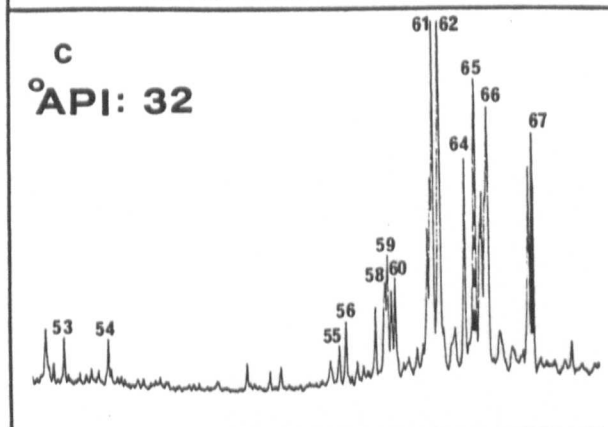
253



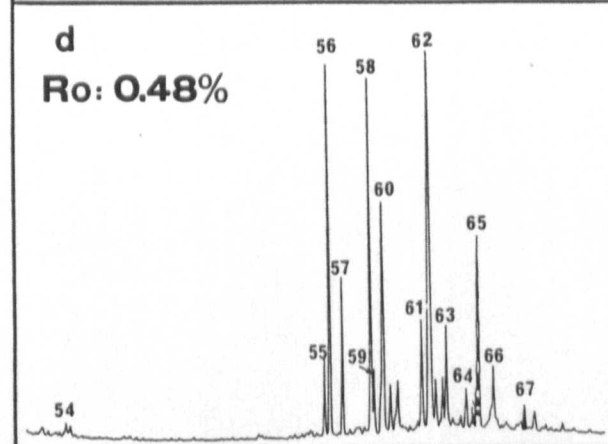
LACUSTRINE FRESHWATER



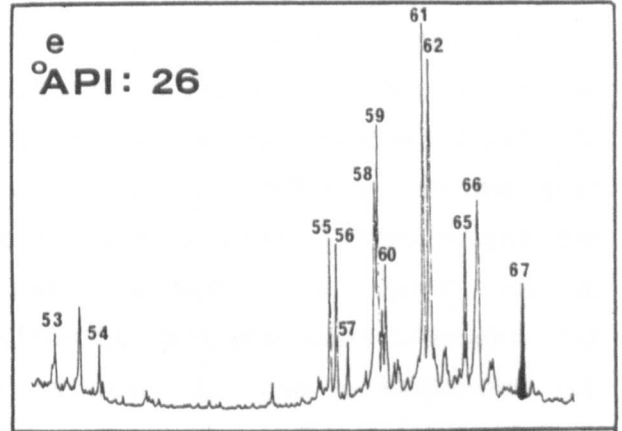
LACUSTRINE FRESHWATER



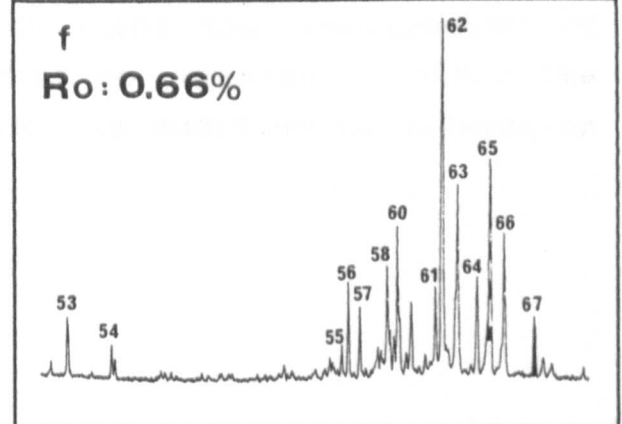
LACUSTRINE SALINE



EVAPORITIC



EVAPORITIC



MARINE CARBONATE

COMPOUND ASSIGNMENT.

- 53- C₂₁ 5β(H) monoaromatic.
- 54- C₂₂ 5β(H) monoaromatic.
- 55- C₂₇ 5β(H), 20S monoaromatic.
- 56- C₂₇ 10β(H), 20S monoaromatic.
- 57- C₂₇ 10α(H), 20S monoaromatic.
- 58- C₂₇ 5β(H), 20R + C₂₇ 10β(H), 20S monoaromatic.
- 59- C₂₇ 5α(H), 20S monoaromatic.
- 60- C₂₈ 5β(H), 20S + C₂₇ 10α(H), 20R
+ C₂₈ 10β(H), 20S monoaromatic.
- 61- C₂₇ 5α(H), 20R + C₂₈ 5α(H), 20S monoaromatic.
- 62- C₂₈ 5β(H), 20R + C₂₈ 10β(H), 20R
+ C₂₉ 5β(H), 20S + C₂₉ 10β(H), 20S monoaromatic
- 63- C₂₉ 10α(H), 20S monoaromatic.
- 64- C₂₉ 5α(H), 20S monoaromatic.
- 65- C₂₈ 5α(H), 20R + C₂₉ 5β(H), 20R
+ C₂₉ 10β(H), 20R monoaromatic.
- 66- C₂₉ 10β(H), 20R monoaromatic.
- 67- C₂₉ 5α(H), 20R monoaromatic.

RETENTION TIME →

samples from similar sedimentary facies, as exemplified above, in a multiparameter and quantitative approach, can provide results that are of value in the assessment of thermal history in sedimentary basins. Nevertheless, the literature review and the results presented herein suggest that difficulties might be expected to occur when molecular ratios are used in a quantitative sense, along with kinetic parameters thought to describe reactions altering these ratios, in the assessment of the thermal history of sedimentary basins (cf. Mackenzie & McKenzie, 1983). For example, changing the environment of deposition in a well section, would be expected to alter the sterane and aromatic steroid ratios, in addition to alteration due to maturity effects.



CHAPTER VI

CHAPTER VI

PETROPORPHYRIN CHARACTERISTICS OF ORGANIC-RICH SEDIMENTS AND
OILS FROM BRAZILIAN MARGINAL BASINS

This chapter is a preliminary study of the alkyl metalloporphyrin of a selection of organic rich sediments and oils whose geochemical features were given in Chapter II, in order to investigate the porphyrin characteristics of samples from different depositional environments .

6.1 INTRODUCTION

Petroporphyrins are widely found in oils and sedimentary rock extracts where they occur as complex mixtures, dominated by nickel and vanadyl (DPEP and ETIO) porphyrins. Knowledge of the structures of individual components and their significance as biological markers in the assessment of maturation, oil-source rock correlation and depositional environment of source rocks and oils, has increased in the last five years. This has been mainly due to the application of advanced chromatographic, spectroscopic, NMR and mass spectrometry techniques.

The assessment of thermal maturation of petroleum source rocks and oils using the relative abundance of DPEP and ETIO porphyrins (DPEP/DPEP+ETIO) has been the subject of study and practical application by several authors (e.g. Didyk, 1975; Barwise & Park, 1983; Barwise & Roberts, 1984; Mackenzie, 1980; Cassani, 1986). Others have stated that their application in maturation studies is limited and add that it is difficult to correlate mature oils with immature oils or source rock extracts (Taguchi, 1975; McKirdy & Horvath, 1976; Hajibrahim, 1978; Barker et al., 1978; Barwise & Park, 1983). Conversely, there is relatively little published data on the relationship between porphyrin distributions and depositional environment.

A survey of the literature suggests, however, that petroporphyrin distributions may provide some diagnostic criteria for the distinction of samples deposited in a variety of environments (Lewan & Maynard, 1982), such as lacustrine saline water (e.g. Green River Shale, USA (Baker & Louda, 1986), and lacustrine hypersaline (e.g. Gilsonite Bitumen, USA (Quirke et al., 1979; Eglinton et al., 1980), and sediments from Shengli oilfield and Jiangnan Basin, China (Shi Ji-Yan et al., 1982; Fu Jiamo et al., 1986), marine hypersaline (Marl Slate, England; Gafsa, Tunisia and El Lajjun, Jordan; Kaur, 1987; Quirke, 1987; Barwise & Roberts, 1984), marine carbonate (e.g. La Luna Formation, Venezuela; Toolebuc Formation, Australia and Serpiano Shale, Switzerland (Gransch & Eisma,

1966; Cassani, 1986; Kaur, 1987; Ekstrom et al., 1983; Riley & Saxby, 1982; Chicarelli, 1986; Premovic et al., 1986) and marine anoxic (e.g. Toarcian Shales, Paris Basin; Kimmeridge Shale, North Sea; Monterey Formation, California; Lower Liassic Shales, SW-Germany (e.g. Mackenzie, 1980; Farrimond et al., 1984; Kaur, 1987; Fookes & Loeh, 1983; Lewan & Maynard, 1983; Moldowan et al., 1986). Thus it is clear, for example, that the relative abundance of nickel and vanadyl species show a wide variation (see discussion below).

This study is a preliminary one, which investigates the potential application of petroporphyrins as biological markers in the characterisation of depositional environments, by way of a study of selected source rocks and oils in the major Brazilian marginal basins. For this purpose, 10 oil samples and 51 organic rich rock samples from reservoirs and sedimentary successions ranging from lower Neocomian to Oligocene in age, from most of the Brazilian marginal basins, were originally analysed (Fig. 1). The rock samples chosen belong to a succession of organic rich sediments deposited in different depositional environments within the Brazilian marginal basins as discussed in Chapters I and II (see also Mello et al., 1988a, b, c). The oil-oil and oil-source rock correlation of the samples have been discussed in Chapter III).

The sediments cover a wide range of maturity values (0.45 to 0.9% Ro) but only those with Ro values up to 0.66% are discussed because the increase in maturation resulting in thermal destruction of the porphyrins that tend to be low or absent (see below). Similarly, oils with low to medium API gravities were investigated, but no porphyrins were detected confirming the instability of these biological markers to thermal stress. Hence the oils are not discussed further.

In summary, UV-VIS data to measure porphyrin concentrations are reported for 30 rock samples with Ro up to only 0.66% (Table 1). Probe MS and HPLC data were obtained for selected samples that showed high concentrations of nickel and vanadyl porphyrins (Table 1).

TABLE - 1 Geochemical Data for Sediments from Brazilian Marginal Resins and Proposed Environment of Deposition

SAMPLE	DEPTH	EPOCH	Si/Si+V=0	Fe ppm	V=0 ppm	% Ro	% TOC	% Sulphur	$\delta^{13}C$ ‰	Org. Petrol.(%) AK, HEBB, WOODY	Depositional Environment
CES-14	2487m	Low. Neoc.	-----	traces	traces	0.47	3.0	0.3	-26.5	70 10 20	LACUSTRINE
PTA-1-SE	1731m	Low. Neoc.	-----	traces	traces	0.53	1.6	0.3	-31.0	90 5 5	FRESHWATER
CS-1-AL	1515m	Low. Neoc.	-----	traces	traces	0.62	6.4	0.5	-29.0	80 10 10	
CB-0-AL	1800m	Low. Neoc.	-----	traces	traces	0.56	1.6	0.3	-28.5	40 40 20	
BAS-32	1826m	Low. Neoc.	-----	traces	traces	0.46	1.2	0.1	-29.0	70 25 5	
☆ ESS-34	2310m	Up. Neoc.	0.97	2831	75	0.45	5.0	0.4	-26.5	90 5 5	LACUSTRINE
☆ FPD-1-ES	2095m	Up. Neoc.	0.96	1850	60	0.63	2.6	0.4	-30.0	60 30 10	SALINE
ED-1-ES	2808m	Up. Neoc.	0.94	670	40	0.66	2.9	0.6	-26.0	80 10 10	WATER
RJS-71	3060m	Up. Neoc.	----	traces	traces	0.56	3.6	0.3	-25.5	90 5 5	
RJS- 51	3320m	Up. Neoc.	----	traces	traces	0.55	2.6	0.3	-25.5	90 5 5	
☆ UPS-1-RB	1337m	Aptian	0.93	1530	95	0.50	2.5	0.4	-32.0	30 60 10	
☆ FGT-1-AL	1311m	Aptian	0.74	1870	630	0.50	3.3	0.3	-24.2	50 5 45	MARINE
☆ CES-42	3008m	Aptian	0.60	810	550	0.59	6.3	0.7	-26.0	60 30 10	EVAPORITIC
BAS-37	1650m	Aptian	0.80	360	90	0.60	2.5	0.7	-25.5	65 5 30	
BC-1-AL	411m	Aptian	0.82	360	80	0.43	3.0	0.4	-24.0	75 10 15	
CES-7	2094m	Aptian	0.84	310	60	0.55	3.1	0.9	-25.7	60 20 20	
☆ BAS-35	2313m	Albian	0.01	traces	478	0.59	3.7	0.4	-24.0	60 10 30	MARINE
☆ FRC-1-ES	1615m	Albian	0.01	traces	650	0.55	1.0	0.8	-26.6	35 15 50	CARBONATE
CAU-3-SE	1366m	Albian	0.01	Traces	180	0.59	2.6	0.4	-26.8	40 20 40	
☆ CES-46	1995m	Albian	0.12	411	2926	0.57	2.4	0.6	-27.5	75 15 10	
ABC-1-SE	1317m	Albian	0.19	75	310	0.51	4.1	0.3	-26.0	60 10 30	
APS-29	4440m	Albian	0.21	20	75	0.66	4.0	0.9	-27.9	85 10 5	
☆ CES-19	1950m	Turon.	0.75	120	40	0.54	2.5	0.3	-27.0	85 5 10	OFFE
CES-26	1911m	Turon.	0.80	140	35	0.48	2.8	0.3	-27.2	85 5 10	MARINE
CES-50	1461m	Sant.	0.68	680	120	0.47	3.2	0.4	-28.2	90 5 5	HIGHLY
☆ RFS-15	1428m	Sant.	0.92	1660	130	0.45	1.4	0.3	-26.4	90 5 5	ANOXIC
☆ APS-29	4320m	Turon.	0.93	813	55	0.63	4.0	0.4	-25.1	65 10 5	
RJS-225	1902m	Coniac.	0.88	480	60	0.55	1.7	0.4	-27.0	80 10 10	
CES-56	1710m	Sant.	0.36	945	2670	0.46	3.0	0.5	-27.8	90 5 5	
☆ CES-50	1499m	Sant.	0.30	1746	3990	0.53	3.5	0.5	-----	85 5 10	

● TOTAL EXTRACT
 ☆ Porphyrim analysed by Probe and HPLC.

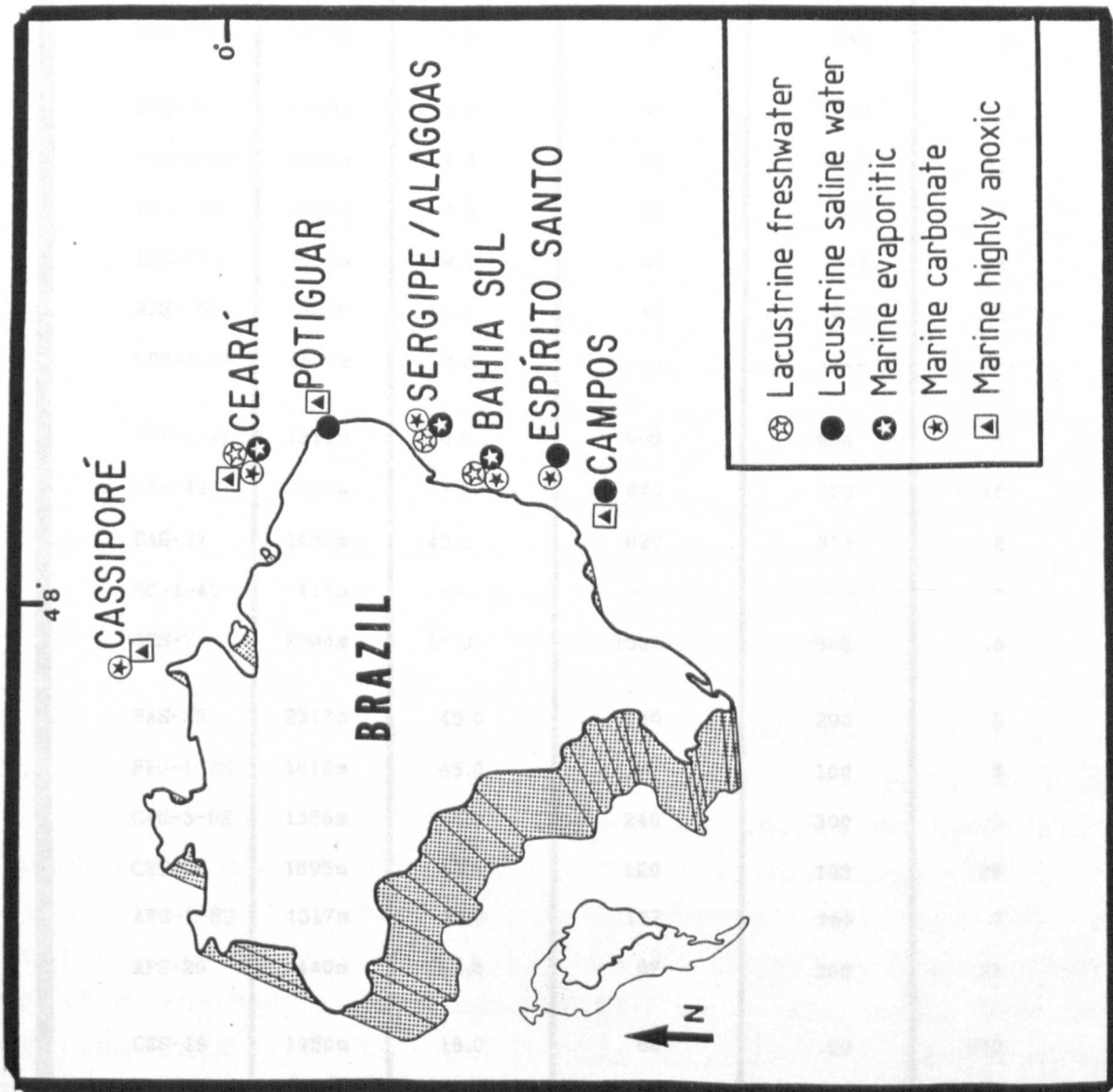
6.2 RESULTS.

The results are given below in relation to five of the depositional regimes (groups I to V) classified in Chapters I and II, with the porphyrin features of each being discussed separately in the following sections

6.2.1 Group I-lacustrine freshwater.

Only samples from Ceará, Potiguar, Sergipe/Alagoas and Bahia Sul basins in the equatorial and Eastern area of the Brazilian continental margin were investigated (Fig. 1). The sedimentological, palaeontological and geochemical data of this sedimentary succession indicates that the organic-rich sediments were deposited during the lower Neocomian to Aptian, in lacustrine freshwater environments (Ponte & Asmus, 1978; Viana, 1980; Schaller, 1969; Mello *et al.*, 1988b; Chapters I and II). The particular samples in Table 1 consist mainly of dark grey shales deposited under mild anoxic conditions (HI ranging from 133 to 576 mg Hc/ g organic carbon; TOC from 1.2 to 6.4%; sulphur content from 0.1 to 0.5%; Tables 1, 2). The organic petrology shows the presence of high amounts of higher plant debris (up to 40% herbaceous, mainly polens and spores; up to 20% woody plus coaly organic matter; Table 1). Other noteworthy features for these samples are: $\delta^{13}\text{C}$ values ranging from -28.5 to -31.0‰, absence of 25,28,30-trisnorhopane and 28, 30-bisnorhopane and very low concentration of steranes (Table 2; cf. Chapter II). The samples in Table 1 cover a relatively narrow range of maturity values (0.46-0.62% Ro), and showed only traces of porphyrins. No porphyrins were detected in three oil samples derived from source rocks deposited in this environment or in more mature sediments. Other samples within the maturity range covered by the samples in Table 1 also showed no porphyrins.

Figure 1- Location map of the Brazilian marginal basins showing the locations of the organic-rich samples investigated, along with the proposed depositional environment.



- ⊗ Lacustrine freshwater
- Lacustrine saline water
- ⊛ Marine evaporitic
- ⊙ Marine carbonate
- ◻ Marine highly anoxic

TABLE 2 - Geochemical Data for Sediments from the Brazilian Marginal Basins

SAMPLE	DEPTH	CaCO ₃ (%)	STERANE(ppm) ⁺ ☆	HOPANE(ppm) ⁺ ☆	BISNORHOPANE INDEX ☆
CES-14	2487m	5.0	20	314	ND
PTA-1-SE	1731m	18.0	35	420	ND
CS-1-AL	1515m	5.0	31	160	ND
CB-6-AL	1800m	7.0	---	---	ND
BAS-32	1826m	7.0	17	243	ND
ESS-34	2310m	4.0	95	1517	58
FRD-1-ES	2095m	4.0	76	1260	11
RD-1-ES	2808m	4.5	89	379	6
RJS-71	3060m	19.0	83	302	6
RJS- 51	3320m	11.0	45	450	3
UPN-1-RN	1337m	7.0	--	----	---
FGT-1-AL	1311m	26.0	903	960	5
CES-42	3008m	17.0	870	750	16
BAS-37	1650m	45.0	620	812	6
BC-1-AL	411m	---	---	---	---
CES-7	2094m	15.0	1531	500	16
BAS-35	2313m	45.0	230	290	6
FRG-1-ES	1615m	65.0	77	180	8
CAU-3-SE	1386m	36.0	240	300	5
CES-56	1895m	40.0	120	103	20
ANG-1-SE	1317m	39.0	112	260	7
APS-29	4440m	43.0	97	280	21
CES-19	1950m	18.0	88	29	232
CES-28	1911m	17.0	85	44	180
CES-50	1461m	15.0	37	13	1000
RNS-15	1428m	20.0	--	--	--
APS-29	4320m	48.0	110	70	29
RJS-225	1902m	22.0	58	34	27
CES-56	1710m	36.0	151	52	44
CES-50	1499m	24.0	---	---	----

☆ For Biological Marker Quantitation see appendices I and II).

± WHOLE EXTRACT

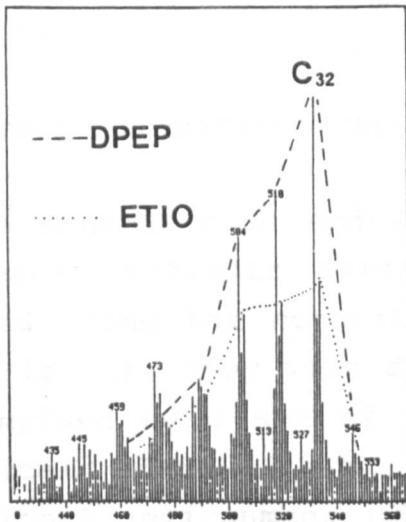
6.2.2 Group II-lacustrine saline water.

The organic-rich sediments belonging to this group are confined to Campos, Espirito Santo and Potiguar basins in the central, eastern and southern areas of the continental margin (Fig. 1). They were deposited during late Neocomian and Aptian times in a lacustrine saline alkaline environment (Chapters I and II).

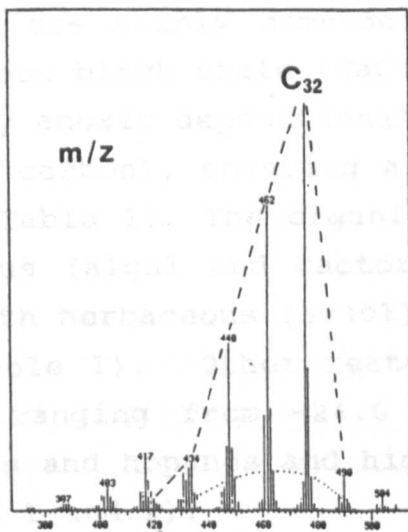
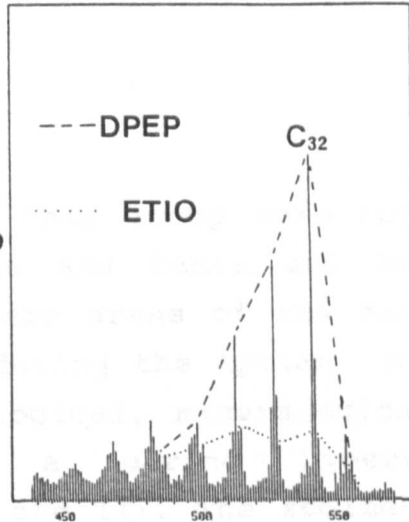
The sediments in Table I are mainly organic-rich (TOC up to 5%) calcareous black-shale (CaCO_3 up to 19%; Table 2) deposited in highly anoxic depositional environment (HI up to 970 mg Hc/ g organic carbon; Table 2), composed mainly of amorphous organic matter (algal and bacterial derived; Table 1). The samples investigated cover a wide range of maturity values (0.45 to 0.66% R_o), with sulphur content ranging from 0.3 to 0.6%; Table 1). Only samples from Espirito Santo and Potiguar basins showed significant concentrations of porphyrins. The upper Neocomian samples from Campos Basin show only traces. The samples with significant porphyrin concentrations have $\delta^{13}\text{C}$ values ranging from -26.0 to -32.0‰, high concentrations of hopanes, low concentration of steranes and significant abundances of 28, 30-bisnorhopane (Table 2; cf. Chapters II and IV). The $\delta^{13}\text{C}$ values of some of these samples are unexpectedly light for lacustrine saline derived samples, which are mainly around -25.5‰ (Table 1; cf. Chapter II).

The samples containing porphyrins showed nickel species (up to 2831 ppm of extract; Table 1) in much higher abundance than the vanadyl species (40-95 ppm; Table 1). The Ni/Ni+V=0 ratios varying from 0.93 to 0.97 (Table 1). The samples studied by Probe MS and HPLC show a series of nickel and vanadyl components ranging from C_{27} to C_{33} with the DPEP species dominant and maximising at C_{32} DPEP (Fig. 2). Five organic-rich sediments with vitrinite values ranging from 0.66% to 0.70% and four oil samples from this environment were also analysed, but showed an absence of porphyrins.

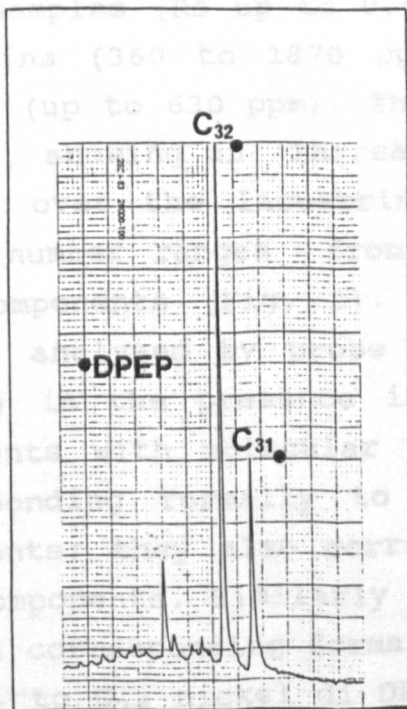
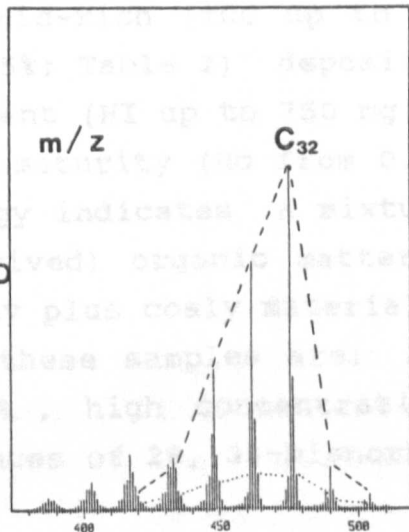
Figure 2- Probe MS of Ni and V=O metallo and demetallated porphyrin fractions, and HPLC chromatograms for an organic-rich sediment from a lacustrine saline depositional environment from Espirito Santo basin (ESS-34).



METALLATED

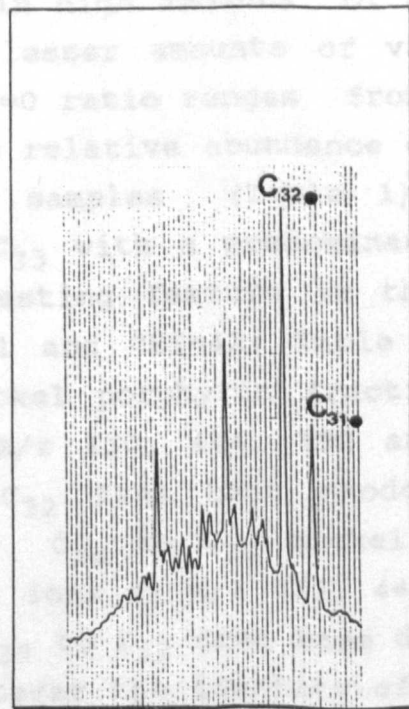


DEMETALLATED



NICKEL PORPHYRINS

HPLC



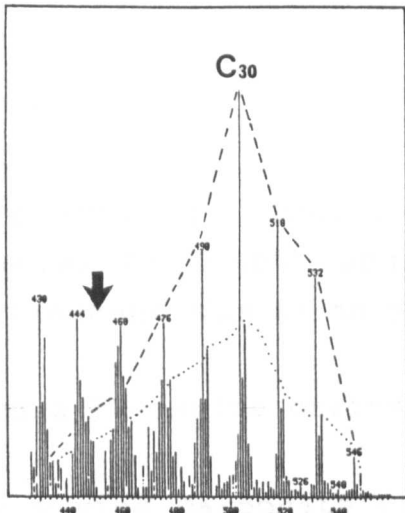
VANADYL PORPHYRINS

6.2.3 Group III-marine evaporitic.

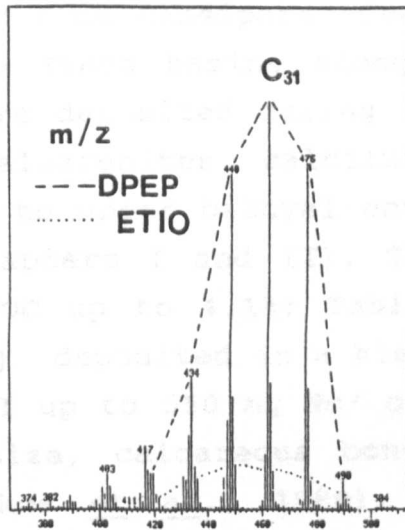
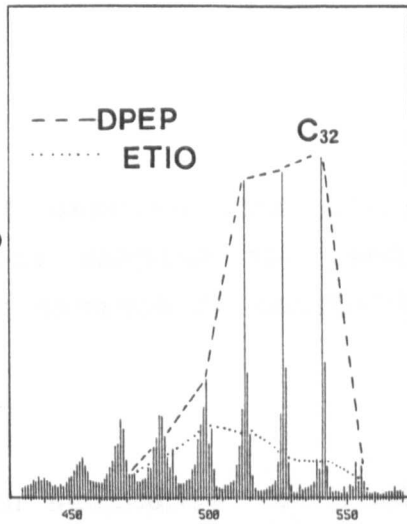
The organic-rich sediments from this group were obtained from Ceará, Potiguar Sergipe/Alagoas and Bahia sul basins, localized along the central and eastern areas of the marginal basin (Fig. 1). They were deposited during the Aptian and are characterised by a set of palaeontological, mineralogical and geochemical data that indicate a marine hypersaline depositional environment (Chapters I and II). The sediments in Table I are mainly composed of organic-rich (TOC up to 6.3%) calcareous black shale (CaCO_3 up to 45%; Table 2) deposited in a highly anoxic depositional environment (HI up to 750 mg Hc/ g organic carbon), covering a range of maturity (R_o from 0.43 to 0.60%; Table 1). The organic petrology indicates a mixture of amorphous (algal and bacterially derived) organic matter (50-75%) with herbaceous (5-30%) and woody plus coaly material (10-45%; Table 1). Other features for these samples are: $\delta^{13}\text{C}$ values ranging from -24.0 to -26.0‰, high concentration of steranes and hopanes and high abundances of 28, 30-bisnorhopane (Tables 1 and 2).

The samples (R_o up to 0.6%) contain high amounts of nickel porphyrins (360 to 1870 ppm) with lesser amounts of vanadyl species (up to 630 ppm). The $\text{Ni}/\text{Ni}+\text{V}=0$ ratio ranges from 0.60 to 0.84, showing an increase in the relative abundance of $\text{V}=0$ species over the lacustrine saline samples (Table 1). The carbon number ranges from C_{25} to C_{33} with a predominance of DPEP components (Fig. 3). An interesting feature in the two samples analysed by probe MS (FGT-1 and CES-42; Table 1 and Fig. 3) is the presence in the nickel porphyrin fraction of components with molecular ions at m/z 430, 444, 458 and 472 corresponding formally to C_{29} to C_{32} free base rhodo etio components; they also correspond to C_{25} to C_{28} nickel rhodo etio components. Similarly molecular ions at m/z 432, 446, 460 and 474 corresponding formally to C_{29} to C_{32} free base di DPEP or C_{25} to C_{28} nickel di DPEPs. Whatever the identity of these species they did not appear to survive the demetallation

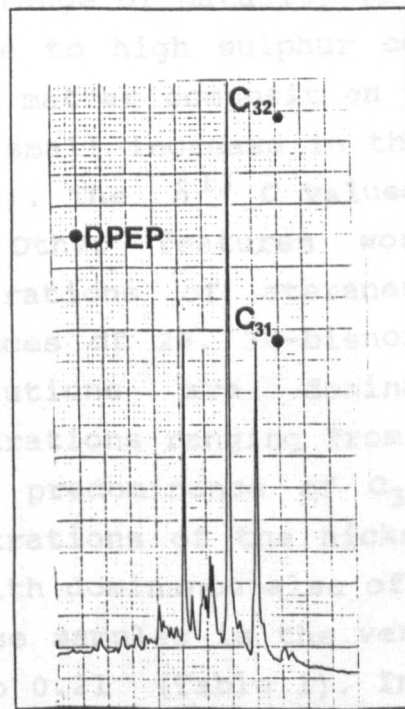
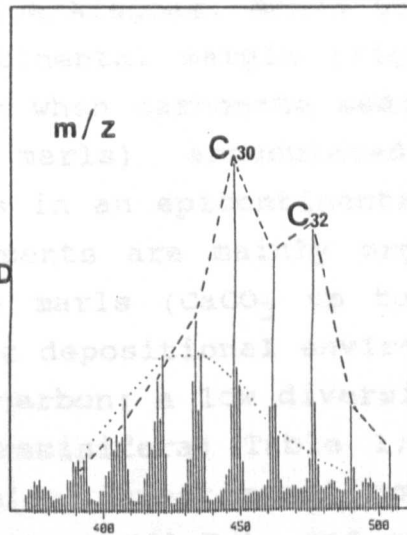
Figure 3- Probe MS of Ni and V=O metallo and demetallated porphyrin fractions, and HPLC chromatograms for an organic-rich sediment from a marine evaporitic depositional environment from Ceará basin (CES-42).



METALLATED

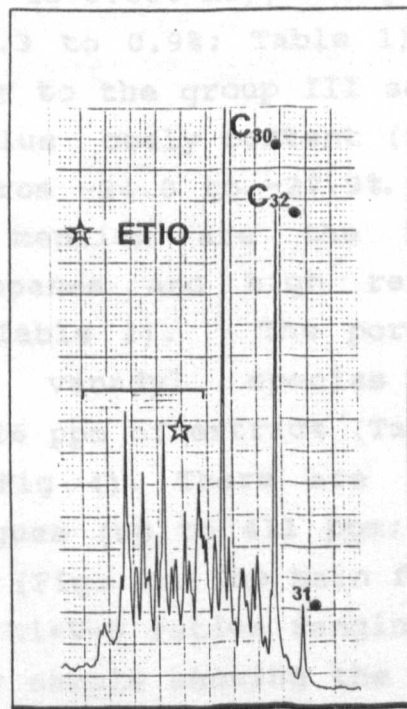


DEMETALLATED



NICKEL PORPHYRINS

HPLC



VANADYL PORPHYRINS

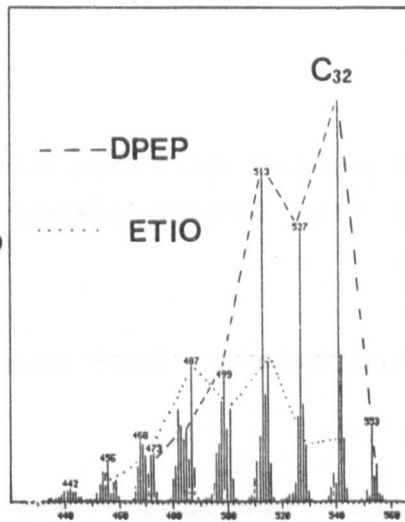
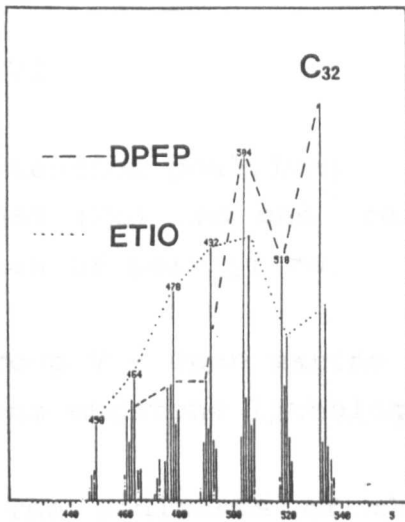
II and III samples. This is presumably a 50-50% component

procedure (Fig. 3). Four organic-rich samples with higher Ro values (0.62 to 0.68%) and three oil samples analysed from this environment showed only traces or absence of porphyrins.

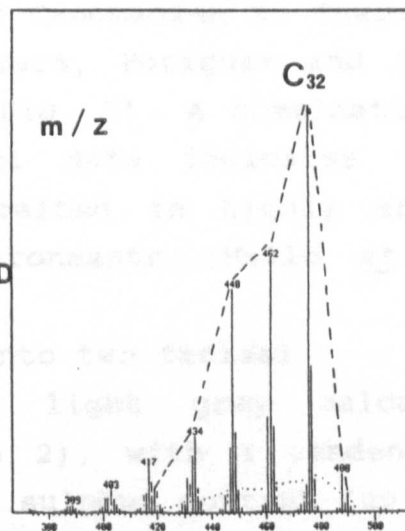
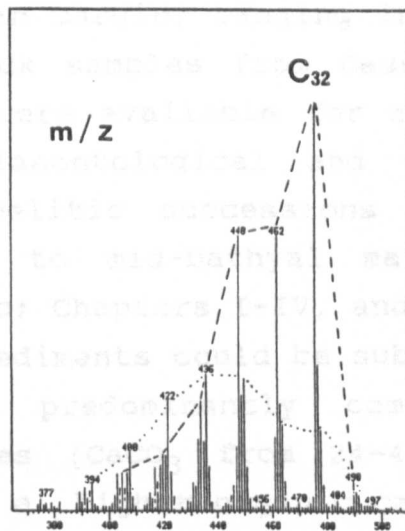
6.2.4 Group IV-marine carbonate.

The marine carbonate organic-rich sediments studied were obtained from Cassiporé, Ceará, Sergipe/Alagoas, Bahia Sul and Espirito Santo basins along the continental margin (Fig. 1). They were deposited during the Albian when carbonate sediments (e.g. calcarenites, calcilutites and marls) accumulated in a neritic to upper bathyal environments in an epicontinental sea (see Chapters I and II). These sediments are mainly organic-rich (TOC up to 4.1%; Table 1) grey marls (CaCO_3 up to 65%; Table 2) deposited in a highly anoxic depositional environment (e.g. HI up to 550 mg Hc/ g organic carbon; a low diversity of small size, calcareous benthonic foraminifera; Table 1; e.g. Koutsoukos *et al.*, 1988). The samples investigated cover a narrow range of maturity values (0.51 to 0.66% Ro), and possess moderate to high sulphur content (0.3 to 0.9%; Table 1). The organic matter composition is similar to the group III samples with a small increase in the woody plus coaly content (5-50%; Table 1). The $\delta^{13}\text{C}$ values range from -24.0 to -27.9%; Table 1). Other features worthy of mention are the medium concentrations of steranes and hopanes and high relative abundances of 28, 30-bisnorhopane (Table 2). The porphyrin distributions are dominated by vanadyl species with concentrations ranging from 75 to 2926 ppm of extract (Table 1) with a predominance of C_{32} DPEP (Fig 4). There are lower concentrations of the nickel homologues (up to 411 ppm; Table 1), with dominance also of C_{32} DPEP (Fig. 4). The main feature of these samples is the very low Ni/Ni+V=0 ratios ranging from 0.01 to 0.21 (Table 1). In the only sample showing the nickel porphyrins (see peak X, in HPLC trace of Fig. 4) there is an abundant unknown component which was not observed in the group II and III samples. This is presumably a DPEP-type component

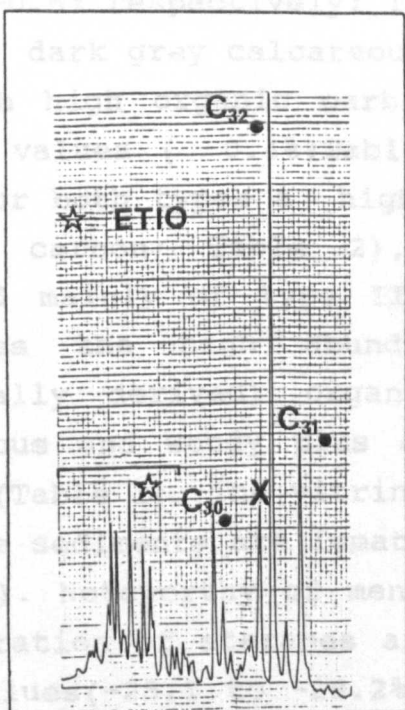
Figure 4- Probe MS of Ni and V=O metallo and demetallated porphyrin fractions, and HPLC chromatograms for an organic-rich sediment from a marine carbonate depositional environment from Ceará basin (CES-56, 1895m).



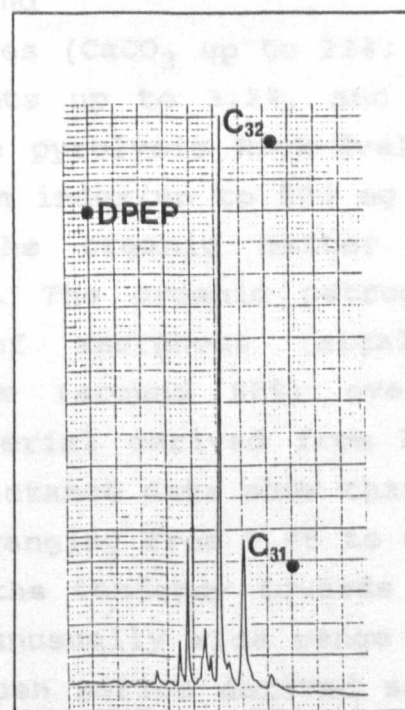
METALLATED



DEMETALLATED



NICKEL PORPHYRINS



VANADYL PORPHYRINS

HPLC

(HPLC retention position). Samples with maturity values higher than 0.66% (R_o) and one related oil sample showed only traces or absence of porphyrins.

6.2.5 Group V - Open marine highly anoxic with predominance of calcareous mudstone lithology

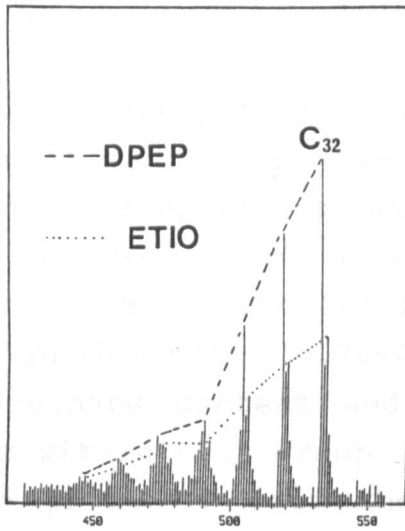
The sediments of this group are widespread along the Brazilian margin, ranging in age from Cenomanian to Campanian. Only rock samples from Cassiporé, Ceará, Potiguar and Campos basins were available for analysis (Fig. 1). A combination of micropalaeontological and geochemical data indicates that these pelitic successions were deposited in highly anoxic, neritic to mid-bathyal marine environments (Mello *et al.*, 1988b, c; Chapters I-IV, and VII).

These sediments could be subdivided into two facies:

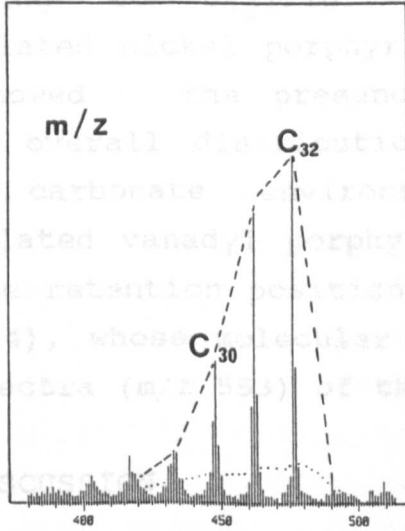
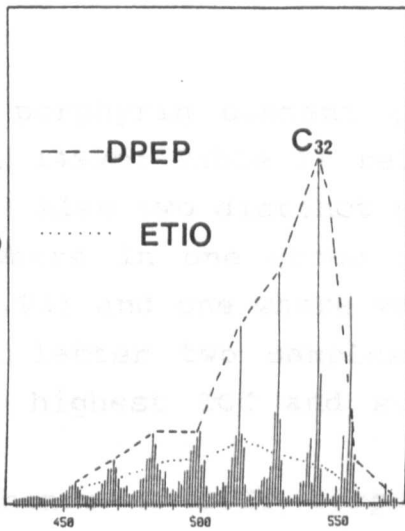
i) predominantly composed of light grey calcareous mudstones ($CaCO_3$ from 24-48%; Table 2), with a tendency to contain a higher organic carbon and sulphur content (up to 4% and 0.4-0.5% respectively; Table 1) and

ii) dark grey calcareous mudstones ($CaCO_3$ up to 22%; Table 2), with high organic carbon contents up to 3.2%, and lower sulphur values (0.4%; Table 1). The pyrolysis Rock-Eval data shows for both types a high hydrogen index (up to 500 mg Hc/g organic carbon; Table 2), with the organic matter being composed mainly of type II kerogen. The organic petrography indicates the high abundance of amorphous (algal and bacterially derived) organic matter (around 90%) over the herbaceous and woody plus coaly material derived from higher plants (Table 1). The vitrinite reflectance data show that most of these sediments are immature (R_o ranging from 0.45 to 0.63%; Table 1). Noteworthy of mention is the tendency towards a low concentration of steranes and the unusually wide range of $\delta^{13}C$ values (-25.1 to -28.2‰) for open marine derived samples (Table 1 and 2). Also the samples of this sequence showed the highest abundances of 28,30-bisnorhopane (Table 2).

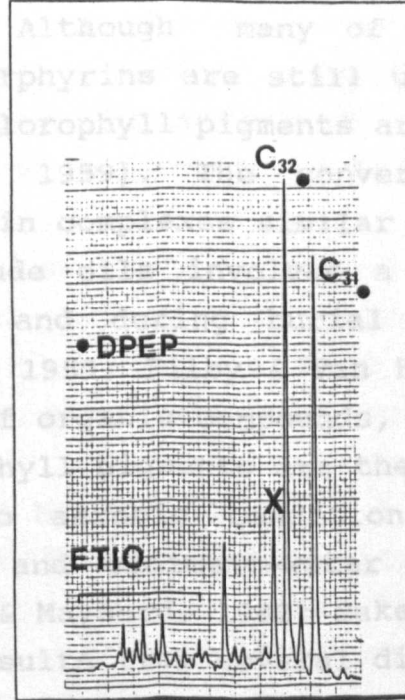
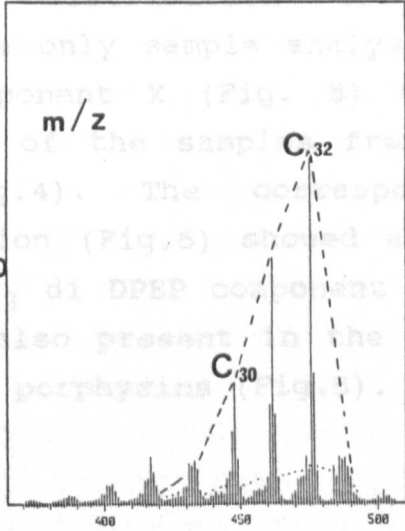
Figure 5- Probe MS of Ni and V=O metallo and demetallated porphyrin fractions, and HPLC chromatograms for an organic-rich sediment from an open marine highly anoxic depositional environment from Ceará basin (CES-50, 1461m).



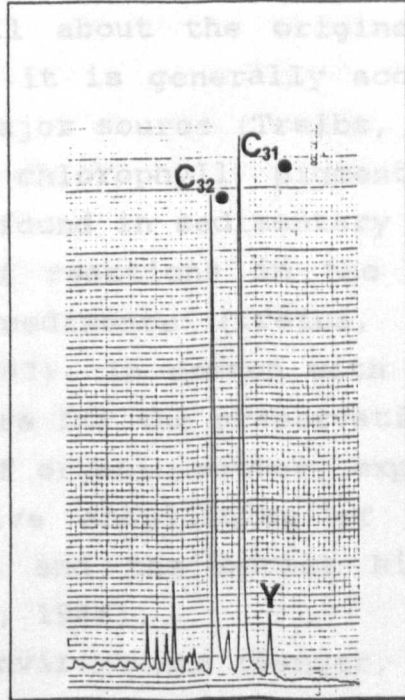
METALLATED



DEMETALLATED



HPLC



NICKEL PORPHYRINS

VANADYL PORPHYRINS

This group yielded the highest porphyrin content (up to 5736 ppm of extract in sample CES-50, 1499m; Table 1) relative to the other samples (groups I to IV). Also two distinct groups of Ni/ Ni+V=O ratios were found, where in one group nickel components predominate (ratios 0.75-0.93) and one where vanadyl species predominate (0.30-0,36). The latter two samples have high carbonate content and have the highest TOC and sulphur contents within this group.

The probe MS data show a dominance of DPEP components maximising at C₃₂ (Fig. 5). The distribution for the demetallated nickel porphyrins of the only sample analysed by HPLC showed the presence of component X (Fig. 5) and a similar overall distribution to one of the samples from the marine carbonate environment (Fig.4). The corresponding demetallated vanadyl porphyrin fraction (Fig.5) showed a peak with the retention position of a C₃₃ di DPEP component (peak Y, Fig.4), whose molecular ion was also present in the probe mass spectra (m/z 553) of the vanadyl porphyrins (Fig.5).

6.3 DISCUSSION.

Although many of the detail about the origins of petroporphyrins are still uncertain, it is generally accepted that chlorophyll pigments are their major source (Treibs, 1936; Corwin, 1959). The conversion of chlorophyll pigments to porphyrin complexes similar to those found in sedimentary rocks and crude oils involves a series of reactions in the water column and during burial in the sediments (Treibs, 1936; Corwin, 1959; Filby & Van Berkel, 1987). In common with other types of organic compounds, key factors for the preservation of chlorophyll pigments are the source of organic matter, exposure time to aerobic conditions, relative anoxicities of water column and sediment-water interface and the burial history (Lewan & Maynard, 1982; Baker & Louda, 1986).

Results from several different environments (Sanger, 1971; Koyama et al., 1973; Gagosian & Heinzer, 1979, and

experimental degradation of algae (Daley & Brown, 1973) have shown that petroporphyrin precursors decompose more readily and faster than the bulk organic matter accompanying them. This suggests that the aerobic/anaerobic conditions of the water column of a sedimentary basin would play an important role in the concentration of petroporphyrins in sedimentary rocks. Therefore, the petroporphyrin content would be expected to be low in organic matter that has settled through long aerobic water columns with a mild degree of anoxicity in the bottom waters and a low rate of sedimentation. Conversely, preservation would be expected to be high in organic matter that has encountered anaerobic conditions early in its descent through a water column with high degree of anoxicity in the bottom waters and moderate to high rates of sedimentation. Indeed, such ideas have been proposed for several sedimentary basins (e.g. Lewan & Maynard, 1982), and appear to apply to the porphyrin distribution in the Brazilian basins (see below).

The source and fate of nickel and vanadium in the organic matter of sediments and sedimentary basins are critical to understanding the variability of the pattern distribution of nickel and vanadyl porphyrins in different depositional environments. The most important source of these two metals in sedimentary basins appears to be from the water column overlaying the sediments and from interstitial waters which accompany the organic matter in a sediment (Lewan & Maynard, 1982).

In a geochemical context the process of metal insertion is not well understood. However, it has been suggested that an important factor in this process appears to be a dynamic equilibrium where the supply of metal ions from the water column is sufficient to replace those taken up on metallation (Lewan & Maynard, 1982).

Recently, some systematic studies have been performed in order to try to determine the factors that control the proportion of nickel and vanadyl porphyrins in organic-rich

sediments, oil shales and oils (Lewan, 1984; Lewan & Maynard, 1982; Baker & Louda, 1986). The studies have suggested that Eh (redox potential) and Ph conditions, and sulphide concentration in the water body of the depositional environment are important features affecting the Ni/V=0 ratios.

The very low concentrations in the samples from the lacustrine freshwater environment (Table 1), can be explained by the palaeogeographical and geological characteristics of this environment. Geological, palaeontological and geochemical evidence (Chapter I and II) suggests that such palaeolakes were deep, possessing a long aerobic water column overlaying the anaerobic layers which were localized close to the water-sediment interface. This condition might be expected to result in decomposition of the labile chlorophyll pigments before they encountered "protection" from oxidation in the anaerobic deeper waters. An analogous well-known recent environment appears to be Lake Tanganyika in the East African rift-lake system. This lake possesses a maximum water depth of about 1,500 m with anoxic conditions only apparent in deep areas of the lake (Demaison & Moore, 1980).

Unlike the freshwater lakes, the saline palaeolakes were shallow, with a few meters of well oxygenated waters overlaying a thick layer of highly anoxic reducing waters (Chapters I and II). The high phytoplankton biomass, produced within the upper well-oxygenated, nutrient-rich and light-receiving layer would spend only a very short exposure time in aerobic conditions before encountering protection, against decomposition in the anaerobic layer. With the exception of the two upper Neocomian samples from the Campos basin (Table 1), the samples from the lacustrine saline water environment show much higher porphyrins concentrations than the lacustrine freshwater samples. The porphyrins in these samples are almost entirely nickel species. An examination of available data in the literature shows that a similar proportionality of nickel and vanadyl components occurs in other lacustrine saline environments in China, and USA (e.g. Green River Shale, USA; Baker & Louda, 1986; Gilsonite

Bitumen and Rozel Point Oil, USA and sediments and oils from Shengli oilfield and Jiangnan Basin, China; Eglinton et al., 1980; Kaur, 1987; Baker & Louda, 1986; Shi Ji-Yang et al., 1982; Fu Jiamo et al., 1986; Table 3).

The relative abundance of nickel and vanadyl species is difficult to explain. If the ideas of Lewan & Maynard (1982) and Lewan (1984) are correct, then it is possible that a low availability of free hydrogen sulphide dissolved in the sediment-water interface resulted in availability of both Ni^{2+} and VO^{2+} ions in solution to compete later for chelation to free base porphyrins. Under such conditions Ni^{2+} insertion would be expected to be favoured (Lewan, 1984). Certainly, the low availability of sulphate for reduction in such alkaline saline lakes (see Chapter I) would fit in with such ideas. It is noteworthy that the two upper Neocomian samples from the Campos basin showed only traces of porphyrins (Table 1). This may relate to the geochemical evidence given in Chapter II which suggested that the samples from the upper Neocomian from Campos basin were deposited under less saline conditions than the Neocomian samples from Espirito Santo basin (cf. porphyrin concentrations for lacustrine freshwater samples in table 1).

The marine evaporitic samples also show a predominance of nickel species, although the relative abundance of vanadyl components is higher ($\text{Ni}/\text{Ni}+\text{V}$ ratios varied from 0.74-0.84; Table 1) than in the lacustrine saline water samples ($\text{V}=0$ up to 630 ppm). Similar "intermediate" ratios have been reported for samples from other marine evaporitic depositional environments, ie. Marl Slate, England; Gulf of Suez, Egypt and El Lajjun, Jordan (Kaur, 1987; Quirke, 1987; Barwise, 1987; Barwise & Roberts, 1984; Table 3). The high salinity of these environments compared with "normal" seawater, results in greater water column stability, an increased potential for stratification and the establishment of a water column with permanent anoxic conditions (oxygen solubility decrease with increasing salinity). Due to such environmental conditions, preservation of tetrapyrroles would be expected to be

TABLE 3 METALLOPORPHYRIN ABUNDANCES IN SEDIMENTARY ROCKS FROM DIFFERENT DEPOSITIONAL ENVIRONMENTS.

SAMPLE	EPOCH	$\frac{M_1}{M_1+V}=0$	M_1 ppm \odot	V=0 ppm \odot	Nature	DEPOSITIONAL ENVIRONMENT	REFERENCE
JIAGHAN Basin, China	Eocene	0.95 to 1.0	up to 77	traces	black shale	LACUSTRINE HYPERSALINE	Fu Jiama et al., 1986
SHENGLI OIL Field, China	Eocene	0.95 to 1.0	up to 100	traces	black shale	LACUSTRINE HYPERSALINE	Shi Ji-Yang et al., 1982
GREEN RIVER Shale, USA	Eocene	0.95 to 1.0	up to 150	traces	black shale	LACUSTRINE HYPERSALINE	Baker & Louda, 1986 Lewan & Maynard, 1982
GILSONITE Bitumen, USA	Eocene	0.95 to 1.0	up to 300	traces	Oil shale	LACUSTRINE HYPERSALINE	Eglinton et al., 1980 Didyk, 1975; Gill, 1984
MARL SLATE Shale, England	L. Permian	0.67 to 0.9	up to 75	up to 50	calcareous black shale	MARINE HYPERSALINE	Barwise & Park, 1983 Kaur, 1987; Gibbons, 1978
EL LAJJUN Shale, Jordan	U. Cretaceous	0.5 to 0.60	up to 1800	up to 850	calcareous black shale	MARINE HYPERSALINE	Barwise & Roberts, 1984 Kaur, 1987; Abed & Bilal, 1983
SERPIANO Shale, Switz.	M. Triassic	0.01 to 0.09	up to 101	up to 6800	dark grey marl	MARINE CARBONATE	Premovic et al., 1986 Chicorelli, 1985; Rieber, 1982
LA LUNA Shale, Venez.	U. Cretaceous	0.01 to 0.05	up to 108	up to 2300	dark grey marl	MARINE CARBONATE	Premovic et al., 1986 Cassani, 1985; Kaur, 1987
JULIA CREEK Australia	L. Cretaceous	0.2 to 0.03	up to 20	up to 245	Oil shale/marl	MARINE CARBONATE	Riley & Saxby, 1982 Ekstrom et al., 1983
WOODFORD shale Oklahoma, USA	L. Carbonif.	~0.01	up to 430	up to 8000	dark grey marl	MARINE CARBONATE	Steam et al., 1979 Lewan & Maynard, 1982
KIMMERIDGE Shale, England	Late. Jurassic	0.8 to 1.0	up to 4300	up to 100	black shale	OPEN MARINE	Farrimond et al., 1984
TOARCIAN shales Paris Basin	L. Jurassic	0.01 to 1.0	up to 230	up to 150	black shale/ dark grey marl	MARINE highly anoxic	Mackenzie, 1980 Farrimond, 1987
MONTREY Fm, California	Miocene	0.01 to 0.60	up to 700	up to 500	dark grey marl/ black shale	MARINE highly anoxic	Lewan & Maynard, 1982 Baker & Louda, 1986
IV GERMANY	L. Jurassic	0.01 to 1.0	up to 300	up to 200	dark grey marl/ bitumen shale	MARINE highly anoxic	Mackenzie, 1980 Moldovan et al., 1986

● Total soluble extract

⊙ ratios do not necessarily correspond to quantitated ppm values which

may not be for same sample.

enhanced with the immature organic-rich sediments derived from these environments possessing significant amounts of porphyrins (up to 2500 ppm in the sample FGT-1; Table 1).

The marine carbonate samples show the most distinct Ni/Ni+V=0 ratios (0.01 to 0.21; Table 1) of all the samples examined, being almost entirely dominated by vanadyl species. Again, there are similarities here with literature data for samples derived from marine carbonate environments, such as the La Luna Formation, Venezuela (Cassani, 1986; Premovic *et al.*, 1986; Kaur, 1987), Toolebuc Formation, Australia (Riley & Saxby, 1982; Ekstrom *et al.*, 1983), and and Serpiano Shale, Switzerland (Gransch & Eisma, 1966; Chicarelli, 1986; Premovic *et al.*, 1986; Table 3).

Again, if Lewan & Maynard (1982) and Lewan (1984) are correct, the drop in the ratios for the marine evaporitic and carbonate derived sediments is may be due, in part, to the presence of highly reducing conditions (low Eh), where larger amounts of free sulfide, which scavenged Ni²⁺ ions to form Ni²⁺ sulfide were present. This would leave VO²⁺ ions to complex with free base porphyrins.

The situation with respect to the open marine highly anoxic samples is complicated and different from the others in the sense that a wide range of (Ni/Ni+V=0 ratios occur (0.3-0.92). Consideration of literature examples representing this type of environment also reveals a wide range of ratios: Toarcian Shales, Paris Basin; Kimmeridge Shale, North Sea; Lower Liassic Shales, SW-Germany and Monterey Formation (Mackenzie, 1980; Kaur, 1987; Fookes & Loeh, 1983; Moldowan *et al.*, 1986; Lewan & Maynard, 1982; Table 3). It is clear that such a range reflects significant differences within this broad definition of a depositional environment. Thus, Moldowan *et al.* (1986) found markedly different (Ni/Ni+V=0 ratios among lower Toarcian samples of SW-Germany (Table 3). Very low ratios (ca. 0.2) were ascribed to more reducing conditions (black shales), favouring scavenging of Ni²⁺ ions (see above) and ratios of (> 0.9) with less reducing conditions (marls). For the Brazilian

samples it is difficult to rationalise the ratios simply on this basis. Here, the lowest Ni/Ni+V=O ratios are associated with high CaCO₃ contents but APS-29 with the highest content shows a high Ni/ Ni+ V=O ratio (Tables 1 and 2). However, it is worthy of mention that the two samples with a dominance of vanadyl porphyrins (CES-50, 1499m and CES-56, 1710m) show the higher HI values (up to 700 mg HC/ g organic carbon) and sulphur contents relative to the other samples in this group. Such characteristics could suggest more reducing conditions in the depositional environment, lending some support to the Moldowan et al. explanation. Clearly, the factors controlling the Ni/ Ni + V=O ratio are complex and more detailed studies are required to provide a detailed explanation.

It is noteworthy that the samples in this open marine group have high concentrations of porphyrins, with the highest concentrations of any of the samples analysed in this work occurring in the above two samples (Table 1). One explanation for such an abundance of porphyrins could be due to the occurrence of highly anoxic events during the Cenomanian-Campanian ages in the Brazilian marginal basins. Micropalaeontological data, indicate that during these ages, the oxygen minimum zone was expanded leaving only a few metres of well oxygenated surface waters with localized areas of high primary productivity (Mello et al., 1988c). Such a phenomenon could have provided conditions for the preservation of chlorophyll pigments, since their time of exposure to aerobic conditions during descent through the water column would be minimized. The high organic carbon content (up to 5%), hydrogen index (up to 700 mg HC/ g organic carbon), and the good preservation of organic matter (approaching 90% amorphous) support such palaeoenvironmental features (Tables 1 and 2). Since not all the samples were examined by probe MS and a few by HPLC it is difficult to tell if the distributions within the porphyrins themselves show any consistent features for a particular depositional environment. One or two features indicate, however, that the distributions should be studied in

more detail. For example, the high relative abundance of rhodochlorin components were only found in the two marine evaporitic samples examined by probe MS. Furthermore, the unknown component "X" was only found in the demetallated nickel porphyrins of samples with high CaCO_3 contents (36 and 40%). Hence careful examination of HPLC distributions, further coinjection studies and trapping of components to assign structural types would be worthwhile.

Finally, a crude comparison of porphyrin concentrations (although there will be a maturity effect on these) suggest some sort of link with the carbon isotope data and sterane concentration (tables 1 and 2). With the exception of the marine evaporitic samples, high porphyrin concentrations within a group tend to be associated with "anomalously" lighter $\delta^{13}\text{C}$ values in comparison with the "typical" value for that group (Chapter II), low sterane concentration values (low preservation of algal material probably due bacterial rework ?) and significant 28,30-bisnorhopane abundances (bacterially-derived). It is tempting to suggest, therefore, that a significant proportion of the porphyrins in these samples arises from precursor chlorophylls in bacteria and that the bacterial contribution "affects" the $\delta^{13}\text{C}$ values and the steranes preservation (see Chapter VII).

6.4 CONCLUSIONS

1-This preliminary investigation suggests that porphyrin data based on the relative abundances of nickel and vanadyl species could potentially, be of help in the assessment of depositional environments of organic-rich sediments in Brazilian marginal basins.

2-The proportionality between nickel and vanadyl porphyrins are generally in agreement with values in the literature for porphyrins from analogous depositional environments.

3-High abundances of vanadyl porphyrins tend to be associated (but not exclusively so) with higher sulphur contents within samples from a given type of depositional environment (Table 1).

4-The carbon number distributions obtained so far by probe MS do not show diagnostic features which could be linked to a specific depositional environment (except for the presence of rhodo aetio components in the two marine evaporitic samples examined), since the distributions usually showed a predominance of DPEP components generally maximising at C₃₂.

5-The very low amounts or absence of porphyrins in all the oil and most of the rock samples with vitrinite reflectance values higher than 0.60% Ro, is in keeping with their known instability to thermal stress (Barwise, 1987).

6-There is some indirect evidence that, when high concentrations of porphyrins occur, a significant proportion has arisen from bacterial sources.



CHAPTER VII

CHAPTER VII

LATE CRETACEOUS ANOXIC EVENTS IN THE
BRAZILIAN CONTINENTAL MARGIN

This chapter describes a combined geochemical and micropalaeontological study of Cenomanian to Maastrichtian pelitic sediments from the Brazilian continental margin aiming to characterize and understand the intermittent anoxic events that occurred in the Brazilian marginal basins during the Cenomanian-Santonian.

7.1 INTRODUCTION

In the last 10 years, the Deep Sea Drilling Project (DSDP) has recovered sedimentary sequences that help define the stratigraphy, geochemistry, palaeoceanographic history and palaeogeographical evolution of both the North and South Atlantic oceans (Schlanger & Jenkyns, 1976; de Graciansky et al., 1987; Bralower & Thierstein, 1987; Schlanger et al., 1987). One of the most significant discoveries of this multidisciplinary project was the recognition of the widespread occurrence of anomalously organic-rich "black shales" in major oceanic basins, in specific, short-term periods during the Cretaceous (Schlanger & Jenkyns, 1976). The episode was first observed in the Cenomanian-Turonian and was termed an "Oceanic Anoxic Event" (OAE) by Schlanger & Jenkyns (1976). Subsequently, both Ryan & Cita (1977) and Jenkyns (1980), noted that such "black shales" extended, at least in the Atlantic, through the Santonian. Recent studies (Arthur et al., 1987; Schlanger et al., 1987; de Graciansky et al., 1987, and Bralower & Thierstein, 1987) have shown that the Cenomanian-Santonian anoxic event took place in conjunction with major, intermittent and relatively brief sea level rises. They have even suggested a model that involves volcano-tectonic events, sea level rise, global warm equable climate and changes in the oceanic surface and deep water masses.

Several geochemical, biostratigraphic and palaeoenvironmental studies have been carried out in recent years using Deep Sea Drilling sites in the South Atlantic (Magniez-Jannin & Jacquin, 1986; Herbin et al., 1987; Magniez-Jannin & Muller, 1987) and from sedimentary sections of the Brazilian marginal basins (Santos basin: Koutsoukos, 1982; Viviers, 1987; ; Campos basin: Dias-Brito, 1982; Koutsoukos, 1984, 1987; Dias-Brito & Azevedo, 1986; Dias-Brito, 1987; Azevedo et al., 1987; Espirito Santo basin: Estrella et al., 1984; Azevedo, 1985; Ceará and Potiguar basins: Viviers & Regali, 1987; Pará and Maranhao basins: Beurlen & Regali,

1987). The results obtained by these investigations show the occurrence of anoxic events, favourable to the deposition of organic-rich sediments, along several mid-Cretaceous sections of the South Atlantic.

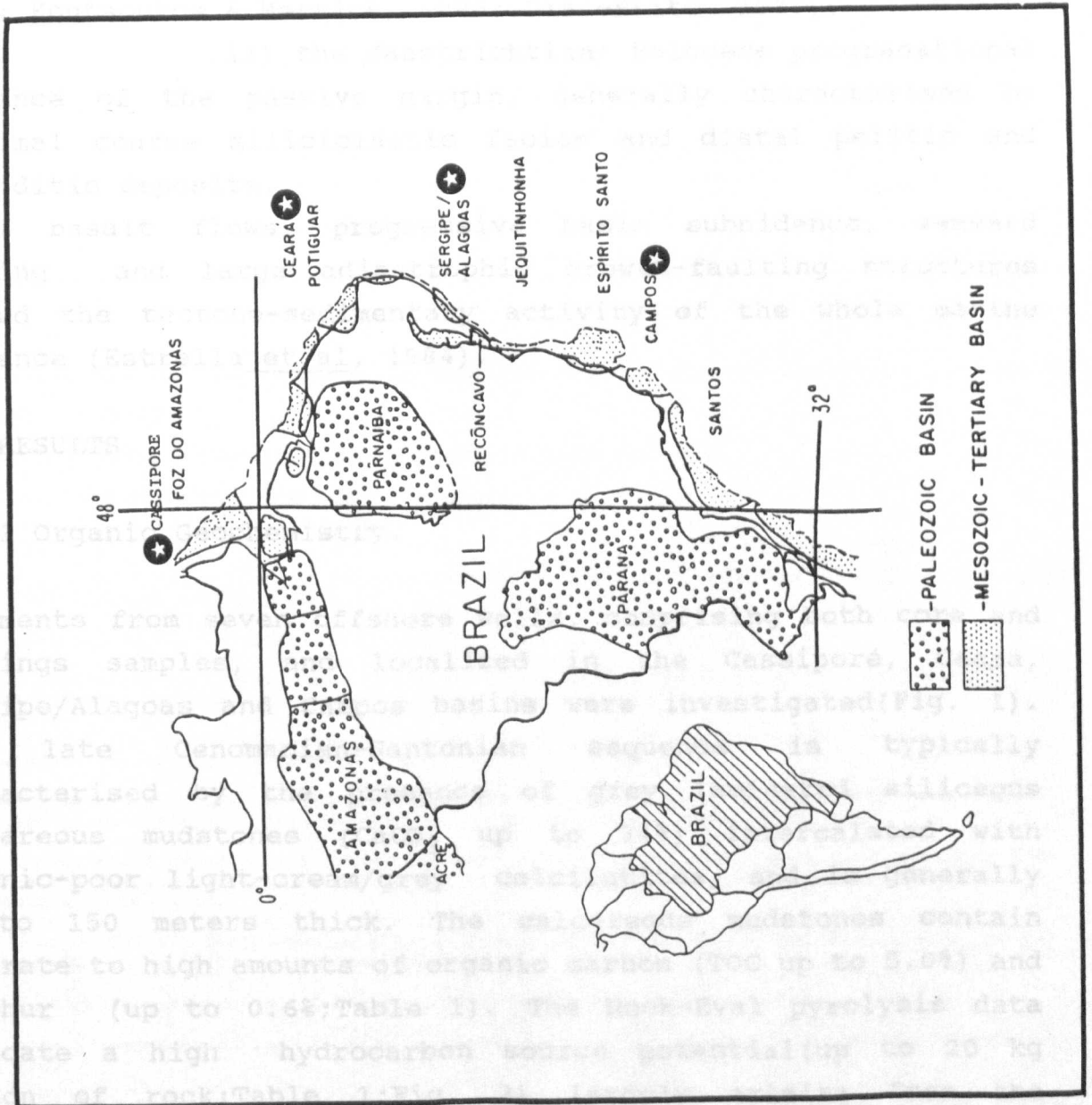
The present work describes an interdisciplinary approach, involving a combination of geochemical (elemental, bulk and biological marker) and microfossil (mainly foraminifera) studies (performed by E.A.M. Koutsoukos), to an examination of pelitic sediments from the Cenomanian to Maastrichtian successions of Brazilian marginal basins. An evaluation of the taxonomic composition, diversity, abundance and size of foraminiferal assemblages has enabled the identification of general faunal patterns associated with oxygen depletion in the water column and has allowed an estimation of the extent of the oxygen-minimum zone over the slope and shelf of the continental margin. In addition, the organic carbon contents, elemental data, porphyrin and other biological marker concentrations, and results from Rock-Eval pyrolysis and carbon isotope measurements have been used as geochemical tools in the assessment of the palaeoenvironmental conditions of deposition.

7.2 GEOLOGY

The Brazilian marginal basins (Fig. 1) are directly related to the rupture of the African-South American plates and occur in a typical divergent, rifted continental margin (Ponte & Asmus, 1978; Estrella et al., 1984). Their evolutionary geological history has been summarised previously (Mello et al., 1988a and b and references therein). In relation to the present study the open marine stage in the marginal basins can be subdivided into two sequences:

- i) the Cenomanian to Santonian marine shelf-slope sedimentary system, characterised by predominantly siliciclastic deposition in progressively deepening basins leading ultimately to bathyal conditions in the more distal

Figure 1- Location map of the Brazilian marginal basins, with the locations of the basins from which samples were investigated.



Sediments from offshore basins were investigated (Fig. 1). The late Paleozoic Amazonian sequence is typically characterized by thick beds of calcareous mudstones with organic-poor lignite, up to 150 meters thick. The mudstones contain moderate to high amounts of organic carbon (0.05 to 5.0%) and sulphur (up to 0.6%; Table I). The Rock-Eval pyrolysis data indicate a high hydrocarbon source potential (up to 20 kg HC/t of rock; Table I; Fig. 2). The presence of type-II kerogen (hydrogen index up to 55, 550 µg HC/g organic carbon and oxygen index up to 10; Table I and Fig. 2). Microscopic examination (organic petrography) of the stratigraphic sequence shows, generally, 45 to 50% amorphous organic matter, probably comprising phytoplankton and bacterial

areas. The Cenomanian succession is generally missing in some offshore areas, probably due to a widespread erosional/ non-depositional event caused by an effective oceanographic connection between the North and South Atlantic, which occurred sometime during the Cenomanian and Turonian (Koutsoukos, 1984, 1987; Koutsoukos & Merrick, 1986; Dias-Brito, 1987).

ii) the Maastrichtian/ Holocene progradational sequence of the passive margin, generally characterised by proximal coarse siliciclastic facies and distal pelitic and turbiditic deposits.

Local basalt flows, progressive basin subsidence, seaward tilting and large adiasprophic growth-faulting structures marked the tectono-sedimentary activity of the whole marine sequence (Estrella et al, 1984).

7.3 RESULTS

7.3.1 Organic Geochemistry.

Sediments from seven offshore wells, comprising both core and cuttings samples, and localized in the Cassiporé, Ceará, Sergipe/Alagoas and Campos basins were investigated (Fig. 1). The late Cenomanian-Santonian sequence is typically characterised by the presence of grey laminated siliceous calcareous mudstones (CaCO_3 up to 34%) intercalated with organic-poor light-cream/grey calcilutites, and is generally 70 to 150 meters thick. The calcareous mudstones contain moderate to high amounts of organic carbon (TOC up to 5.0%) and sulphur (up to 0.6%; Table 1). The Rock-Eval pyrolysis data indicate a high hydrocarbon source potential (up to 20 kg HC/ton of rock; Table 1; Fig. 2) largely arising from the presence of type-II kerogen (hydrogen index up to ca. 550 mg HC/ g organic carbon and oxygen index up to 100; Table 1 and Fig. 2). Microscopic examination (organic petrography) of the stratigraphic sequence shows, generally, 80 to 90% amorphous organic matter, probably comprising phytoplankton and bacterial

TABLE -1 : ELEMENTAL, BULK AND BIOLOGICAL MARKER PARAMETERS OF ROCKS AND EXTRACTS OF SAMPLES FROM SEDIMENTS DEPOSITED DURING THE CENOMANIAN-SANTONIAN ANOXIC EVENT IN THE BRAZILIAN MARGINAL BASINS.

ELEMENTAL	BULK	ALKANES	STERANES	TRITERPANES	PORPHYRINS/ TYPE ORGANIC MATTER
CARBON: 3-6%	T.O.C: 2-5%	N-ALKANES MAXIMA: ~C ₂₀	⁶ C ₂₇ STERANE: 30-200 ppm	¹¹ C ₃₀ αβ HOPANE: 30-70 ppm	NICKEL: 130-1700 ppm
HYDROGEN: 0.4-0.6%	¹ S ₂ : 8-20	SATURATES: 25-30%	⁷ C ₂₇ /C ₂₉ : 0.8-1.3	¹² GAMMACERANE INDEX: 0-25	VANADYL: 30-4000 ppm
NITROGEN: 0.05-0.1%	² HI: 300-550 mg/g	PR/PH: 0.6-0.9	⁸ DIASTERANE INDEX: 10-30	¹³ BISNORHOPANE: UP TO 110 ppm	AMORPHOUS: 80-90%
SULPHUR: 0.3-0.6%	R ₀ : 0.4-0.6%	⁴ I-C ₂₅ +I-C ₃₀ : 70-170 ppm	⁹ 4-Me STERANES INDEX: 20-40	¹⁴ TRISNORHOPANE: UP TO 130 ppm	HERBACEOUS: 5-10%
CaCO ₃ : 20-34%	³ δ ¹³ C: -27.0 TO -28.2	⁵ β-CAROTANE: 10-30 ppm	¹⁰ HOPANE/STERANES: 0.3-0.9	¹⁵ C ₃₄ /C ₃₅ HOPANE: < 1	WOODY+COALY: 5-10%

MEASUREMENT PROCEDURES

1. Hydrocarbon source potential: Kg HC/ton rock (Pyrolysis Rock-Eval).
2. Hydrogen Index (Pyrolysis Rock-Eval).
3. PDB (%)
4. Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (i-C₂₅) and squalane (i-C₃₀) peak areas in RIC trace and normalised to added sterane standard.
5. Peak area (β) in RIC trace and normalised to added sterane standard.
6. Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
7. Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethyl-cholestane (16) in m/z 217 chromatogram.
8. Sum of peak areas of C₂₇ 20R and 20S 13β,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
9. Sum of peak areas of all C₃₀ 4-methyl steranes in m/z 231 chromatogram (recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) X100.
10. Peak area of C₃₀ 17α,21β(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram.
11. Peak area of 35 measured in RIC and normalised to added sterane standard.
12. Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α(H),21β(H)-hopane (35) X100.
13. Peak area of C₂₈ 28,30-bisnorhopane (32) in RIC chromatogram over peak area of sterane standard in RIC.
14. Peak area of C₂₇ 25,28,30-trisnorhopane (T) in RIC chromatogram over peak area of sterane standard in RIC.
15. Peak areas of C₃₄ 22R and 22S 17α(H),21β(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C₃₅ counterparts (45).

* See Figs. 3 and 4.

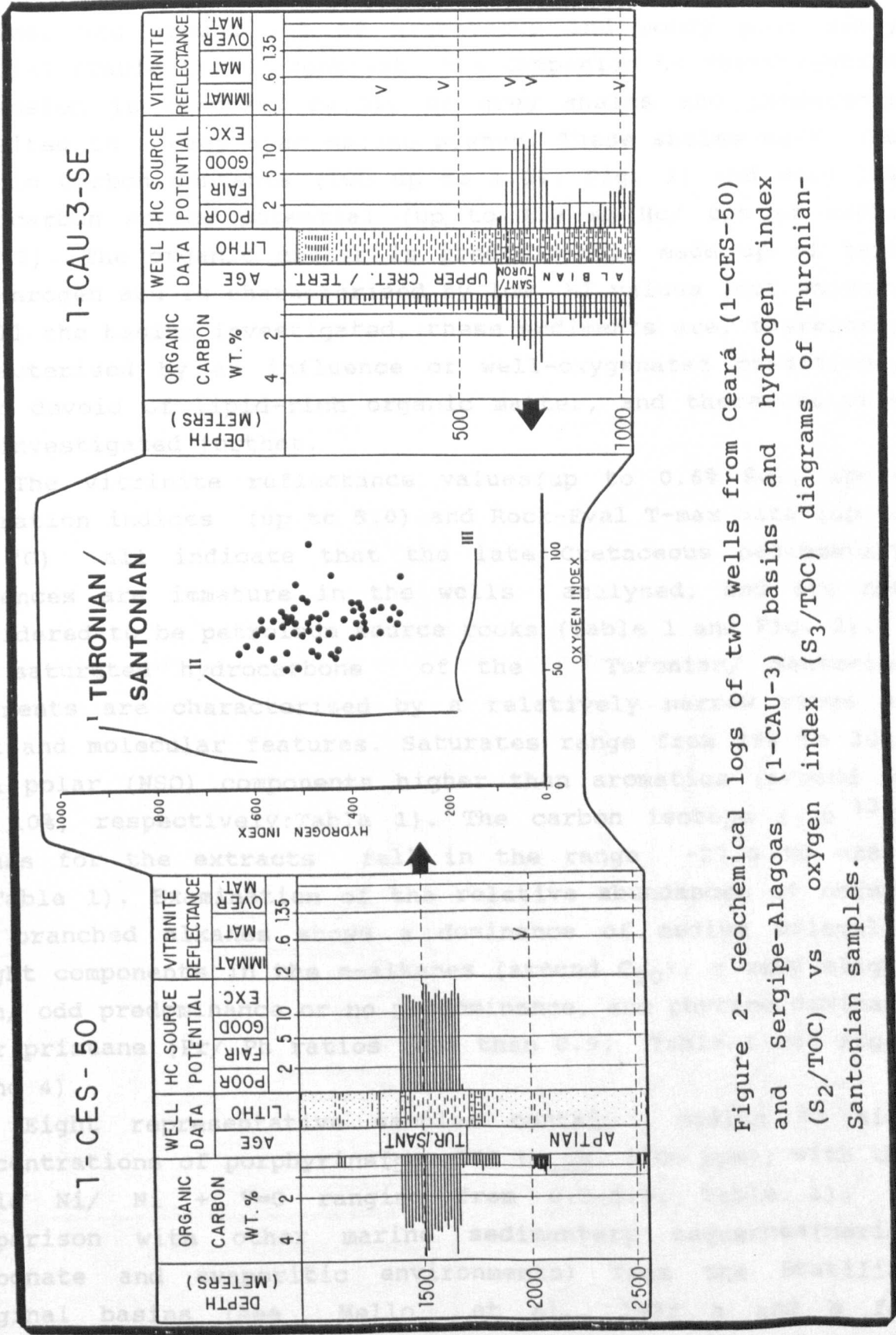


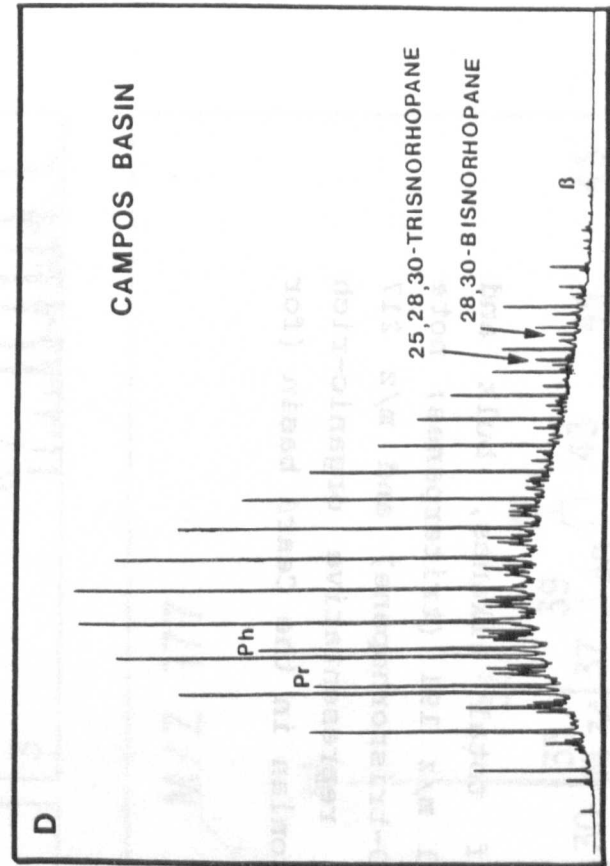
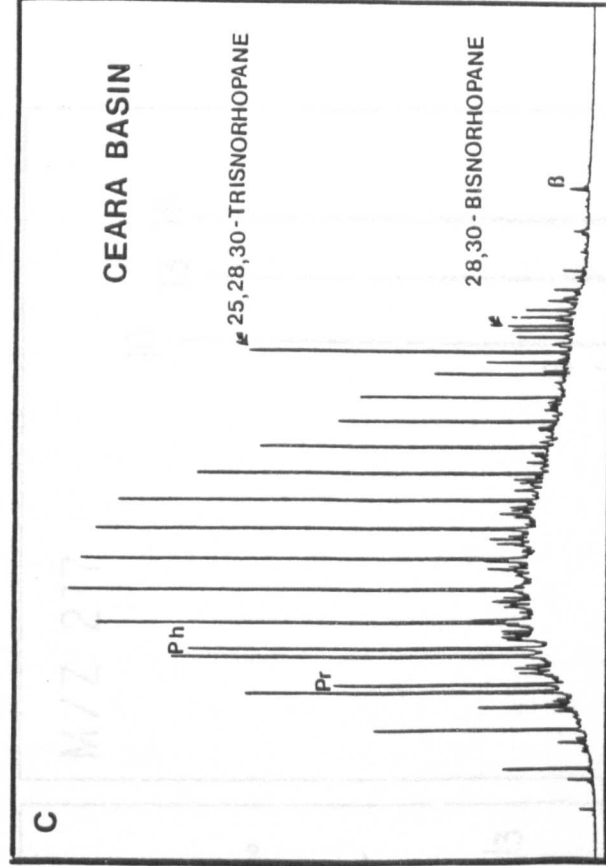
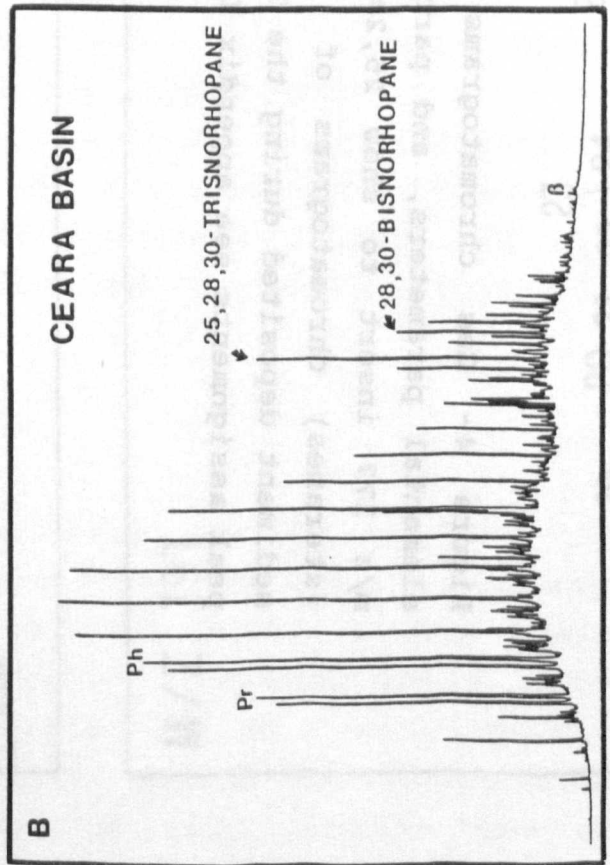
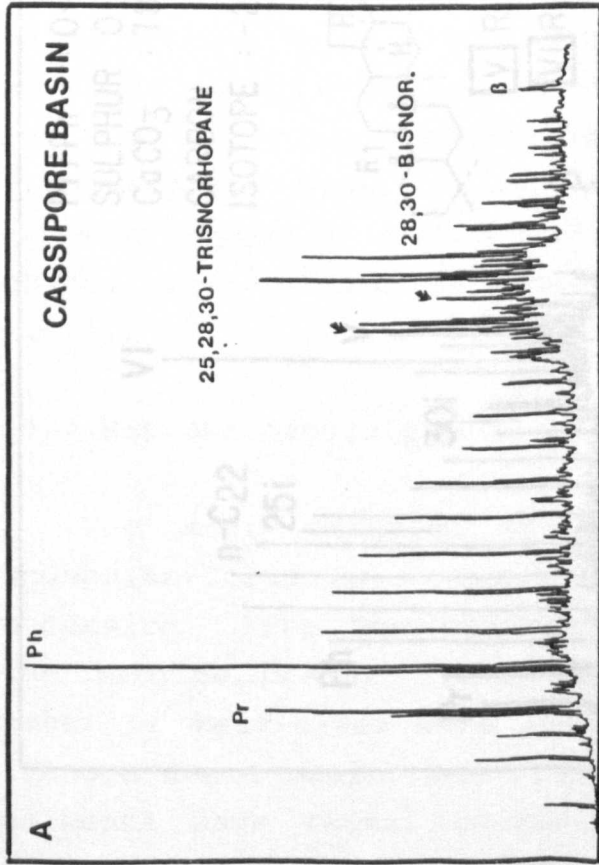
Figure 2- Geochemical logs of two wells from Ceará (1-CES-50) and Sergipe-Alagoas (1-CAU-3) basins and hydrogen index (S₂/TOC) vs oxygen index (S₃/TOC) diagrams of Turonian-Santonian samples.

remains, and around 15% of herbaceous and woody plus coaly material (Table 1). In contrast, the Campanian to Maastrichtian succession is composed mainly of grey shales and sandstones deposited in a deep open marine system. These shales have low organic carbon contents (TOC up to 1.0%; Fig. 2) and very low hydrocarbon source potential (up to 1.0 kg Hc/ ton of rock; Fig. 2). The organic matter is predominantly made up of type III kerogen and is characterised by low HI values (not shown). In all the basins investigated, these sediments are, therefore, characterised by an influence of well-oxygenated conditions, being devoid of lipid-rich organic matter, and therefore were not investigated further.

The vitrinite reflectance values (up to 0.6% Ro), spore coloration indices (up to 5.0) and Rock-Eval T-max data (up to 430 °C) all indicate that the late Cretaceous sedimentary sequences are immature in the wells analysed, and are not considered to be petroleum source rocks (Table 1 and Fig. 2). The saturated hydrocarbons of the Turonian/ Santonian sediments are characterised by a relatively narrow range of bulk and molecular features. Saturates range from 25% to 30%, with polar (NSO) components higher than aromatics (around 60 and 10%, respectively; Table 1). The carbon isotope ($\delta^{13}\text{C}$) values for the extracts fall in the range -27.0 to -28.2 ‰ (Table 1). Examination of the relative abundances of normal and branched alkanes shows a dominance of medium molecular weight components in the n-alkanes (around C₂₀), a very slight even/ odd predominance or no predominance, and phytane dominant over pristane (Pr/ Ph ratios less than 0.9; Table 1 and Figs. 3 and 4).

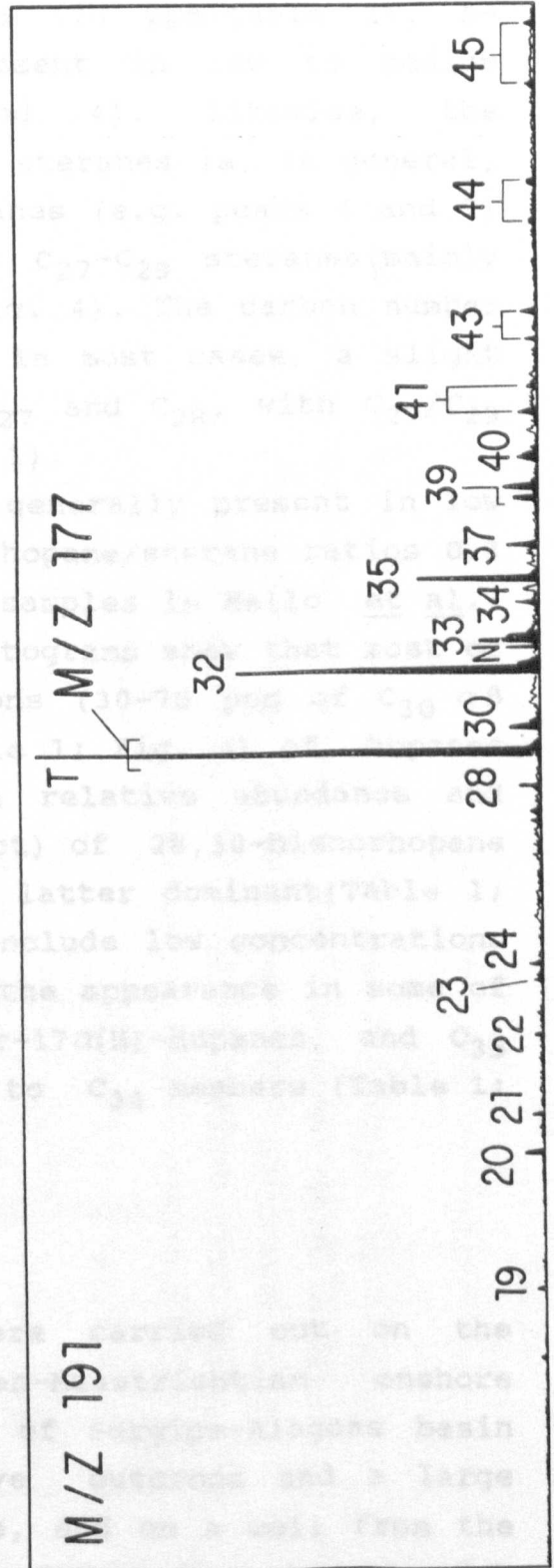
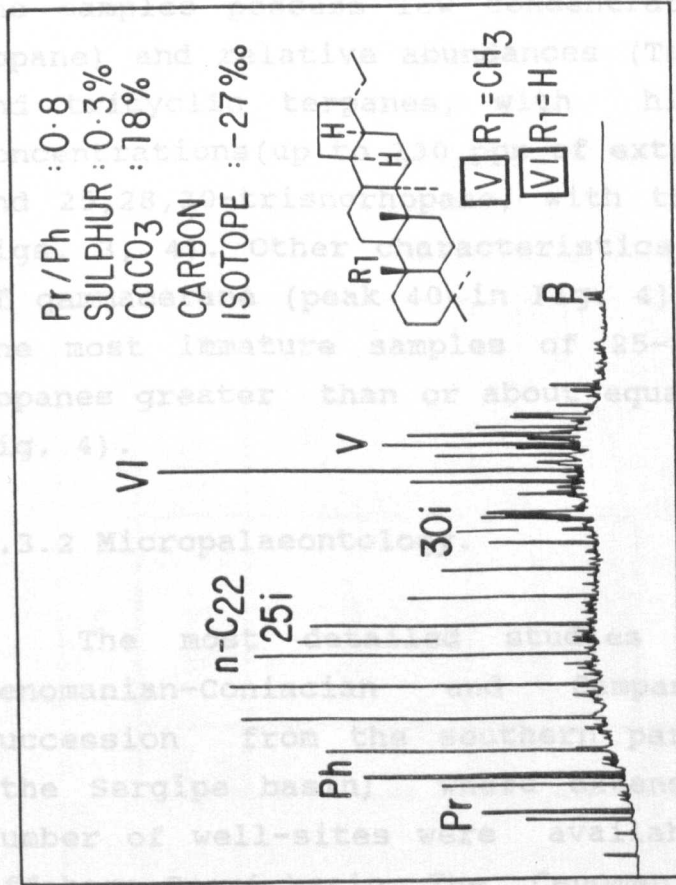
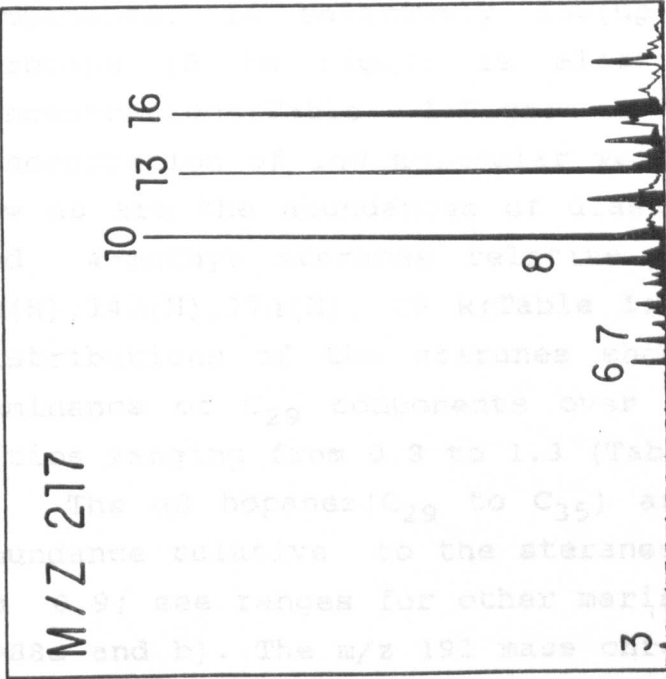
Eight representative samples contain medium to high concentrations of porphyrins (ca. 160 to ca. 5700 ppm), with the ratio Ni/ Ni + V=O ranging from 0.3-0.9: Table 1). In comparison with other marine sedimentary sequences (marine carbonate and evaporitic environments) from the Brazilian marginal basins (see Mello *et al.*, 1988 a and b for concentration ranges), the abundance of long chain

Figure 3- Gas chromatograms of alkane fraction of extracts of representative organic-rich sediments from the Turonian-Santonian sequence in wells from: Cassiporé basin (A, Turonian), Ceará basin (B and C, Santonian, Turonian respectively), Campos basin (D, Coniacian).



Retention time →

Figure 4- Gas chromatograms of total alkanes, bulk and elemental parameters, and partial m/z 191 (triterpanes; note m/z 177 insert to show 25,28,30-trisnorhopane) and m/z 217 (steranes) chromatograms of a representative organic-rich sediment deposited during the Turonian in the Ceará basin (for peak assignments see appendix I).



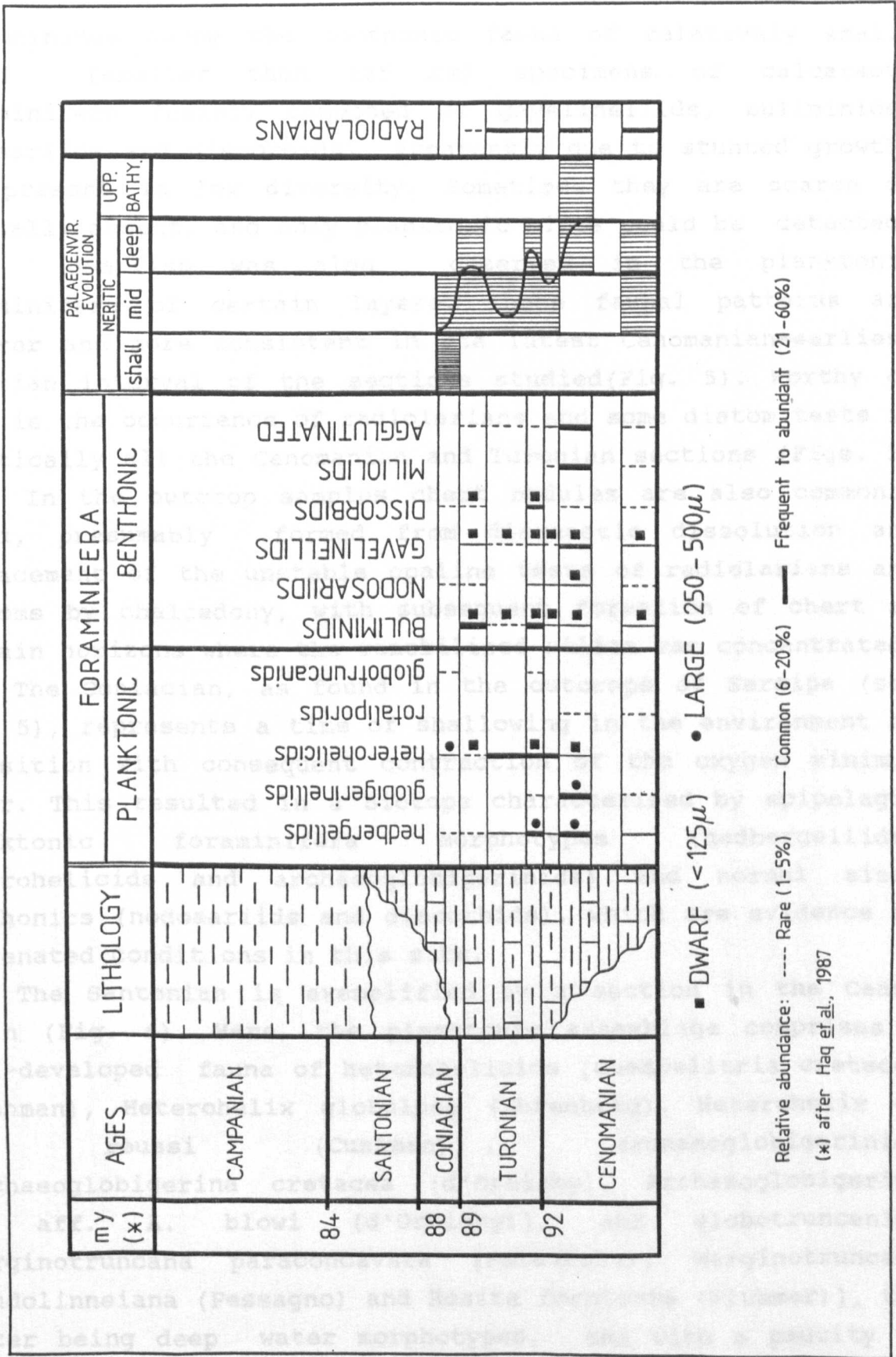
isoprenoids, mainly the C_{25} regular and C_{30} (squalane) components, is relatively low (up to 170 ppm; Table 1). β -Carotane (β in Fig. 3) is also present in low to medium concentrations (Table 1; Figs. 3 and 4). Likewise, the concentration of low molecular weight steranes is, in general, low as are the abundances of diasteranes (e.g. peaks 6 and 7) and 4-methyl steranes relative to C_{27} - C_{29} steranes (mainly $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$, 20 R; Table 1; Fig. 4). The carbon number distributions of the steranes show, in most cases, a slight dominance of C_{29} components over C_{27} and C_{28} , with C_{27}/C_{29} ratios ranging from 0.8 to 1.3 (Table 1).

The $\alpha\beta$ hopanes (C_{29} to C_{35}) are generally present in low abundance relative to the steranes (hopane/sterane ratios 0.3 to 0.9; see ranges for other marine samples in Mello *et al.*, 1988a and b). The m/z 191 mass chromatograms show that most of the samples possess low concentrations (30-70 ppm of C_{30} $\alpha\beta$ hopane) and relative abundances (Table 1; Fig. 4) of hopanes and tricyclic terpanes, with high relative abundance and concentrations (up to 130 ppm of extract) of 28,30-bisnorhopane and 25,28,30-trisnorhopane, with the latter dominant (Table 1; Figs. 3, 4). Other characteristics include low concentrations of gammacerane (peak 40 in Fig. 4), the appearance in some of the most immature samples of 25-nor- $17\alpha(H)$ -hopanes, and C_{35} hopanes greater than or about equal to C_{34} members (Table 1; Fig. 4).

7.3.2 Micropalaeontology.

The most detailed studies were carried out on the Cenomanian-Coniacian and Campanian-Maastrichtian onshore succession from the southern part of Sergipe-Alagoas basin (the Sergipe basin) where extensive outcrops and a large number of well-sites were available, and on a well from the offshore Ceará basin. The Cenomanian - Turonian organic-rich sediments have faunal characteristics (e.g. onshore area of Sergipe basin, Fig. 5 and Ceará basin, Fig. 6) showing a

Figure 5- Distribution and relative abundance of major foraminiferal taxonomic groups and associated microfossils in the Cenomanian-Coniacian onshore succession of the Sergipe basin, northeastern Brazil.



predominance among the benthonic fauna of relatively small-sized (smaller than 125 μm) specimens of calcareous foraminifera (mainly composed of gavelinellids, buliminids, nodosariids and discorbids), apparently due to stunted growth, and present in low diversity. Sometimes they are scarce or virtually absent, and only planktonic biota could be detected. This dwarfism was also observed in the planktonic foraminifera of certain layers. These faunal patterns are clearer and more consistent in the latest Cenomanian-earliest Turonian interval of the sections studied (Fig. 5). Worthy of note is the occurrence of radiolarians and some diatom tests in practically all the Cenomanian and Turonian sections (Figs. 5, 6). In the outcrop samples chert nodules are also commonly found, presumably formed from diagenetic dissolution and replacement of the unstable opaline tests of radiolarians and diatoms by chalcedony, with subsequent formation of chert at certain horizons where the remobilized silica was concentrated.

The Coniacian, as found in the outcrops of Sergipe (see Fig. 5), represents a time of shallowing in the environment of deposition with consequent contraction of the oxygen minimum layer. This resulted in a biotope characterised by epipelagic planktonic foraminifera morphotypes (hedbergellids, heterohelicids and archaeoglobigerinids) and normal sized benthonics (nodosariids and discorbids), which are evidence of oxygenated conditions in this site.

The Santonian is exemplified by a section in the Ceará Basin (Fig. 6). Here, the planktonic assemblage comprises a well-developed fauna of heterohelicids [Guembelitria cretacea (Cushman), Heterohelix globulosa (Ehrenberg), Heterohelix ex gr. reussi (Cushman)], archaeoglobigerinids [Archaeoglobigerina cretacea (d'Orbigny), Archaeoglobigerina sp. aff. A. blowi (d'Orbigny)], and globotruncanids [Marginotruncana paraconcovata (Polevault), Marginotruncana pseudolinneiana (Pessagno) and Rosita fornicata (Plummer)], the latter being deep water morphotypes, and with a paucity of dwarf benthonic specimens (Neobulimina sp. cf. N. canadensis

Figure 6- Distribution and relative abundance of major foraminiferal taxonomic groups and associated microfossils at two sections (early Turonian and Santonian) of the Ceará Basin, offshore area.

RELATIVE ABUNDANCE OF MAJOR FORAMINIFERAL TAXONOMIC GROUPS (CEARA BASIN)

AGES	LITHOLOGY	FORAM. ZONES	PLANKT.				BENTH.			MISC.	DEPOS. PALAEO-ENVIRONMENT						
			HEDBERGELLIDS	HETEROHELLIDS	GLOBOTRUNCANIDS	ARCHAEOGLOBIGERINIDS	BULMINIDS	DISCORBIDS	AGGLUTINATED		RADIOLARIANS	DEEP NERITIC	BATHYAL	UPP. MID.			
SANTONIAN	Horizontal hatched pattern	DICARINELLA CONCAVATA	Dashed line	Solid line	Thick solid line	Dashed line	Dashed line	Dashed line							Horizontal hatched pattern		
EARLY TURONIAN	Vertical hatched pattern	PRAEGLOBO. DELRIOENSIS	Dashed line	Solid line	Thick solid line	Dashed line	Dashed line	Dashed line							Horizontal hatched pattern		

Relative abundance:

- Rare (1-5%)
- Common (6-20%)
- Frequent to abundant (21-60%)

● LARGE SPECIMENS

■ DWARF

Cushman & Wickenden, *Valvulineria?* sp.).

The Campanian-Maastrichtian sediments are represented in Sergipe by an abundant and highly diversified foraminiferal microfauna, mainly made up by benthonic (calcareous and agglutinated species) and well-developed planktonic specimens (globotruncanids, rugoglobigerinids and heterohelicids). Similar microfaunal patterns have also been reported in the equatorial (Pará-Maranhão basin: Beurlen & Regali, 1987; Ceará basin: Viviers, 1982; Potiguar basin; Viviers & Regali, 1987) and eastern (Campos basin: Koutsoukos, 1984, 1987; Dias-Brito & Azevedo, 1986; Azevedo *et al.*, 1987) basins of the Brazilian continental margin.

7.4 DISCUSSION

A summary by Schlanger *et al.* (1987), shows that in many parts of the world, Cenomanian-Turonian and Coniacian-Santonian "Oceanic Anoxic Events", OAE's, occurred (Schlanger and Jenkyns, 1976; Ryan and Cita, 1977; Jenkyns, 1980) and that these cyclic events are predominantly characterised by the presence of light coloured pelagic or shelf chalks, and black shales/calcareous mudstones rich in amorphous organic matter. They are rich in sulphur, silica and phosphate, being fissile and laminated, and contain organic carbon contents up to 27%, comprising mainly lipid-rich, marine-derived type II kerogens. It is clear from the present study that such events are also associated with the Cenomanian-Santonian in the Brazilian marginal basins. This is apparent, for example, from the presence of organic-rich layers with similar lithology to the above, and containing mainly lipid-rich type II kerogen (e.g. Fig. 2). Also, in most of the Cenomanian-Turonian the microfossil assemblages are characterised by large numbers of benthonic specimens of low diversity and of varied test-sizes (Fig. 5). This is interpreted as the result of a localized and temporally variable anoxia (cf. Bernhard, 1986). Furthermore, at certain horizons (e.g. late Cenomanian-early Turonian and

Santonian times; Figs. 5, 6) the dominance of small-sized specimens of calcareous benthonic foraminifera, again low in diversity, indicates stable widespread anoxia. Some layers yielded an abundant microfauna exclusively composed of planktonic foraminifera with no benthonic specimens and, would, therefore, represent deposition under anaerobic bottom conditions.

Similar faunal patterns to those found here have also been found in Cenomanian to Santonian sections from North West Europe (Hart & Bigg, 1981), Trinidad, West Indies (Koutsoukos & Merrick, 1986), Mancos Shale of New Mexico and Arizona (Bernhard, 1986), the Benue trough and Calabar flank, Nigeria (Petters, 1983; Petters & Ekweozor, 1982 a,b; Nyong & Ramanathan (1985) and other areas of the South Atlantic (Magniez-Jannin & Jacquin, 1986). Similarities have also been reported for the Cenomanian-Turonian succession of the several basins in the Brazilian continental margin (Santos basin: Koutsoukos, 1982; Viviers, 1986, 1987; ; Viviers et al., 1986; Campos basin: Dias-Brito, 1982; Koutsoukos, 1984, 1987; Dias-Brito & Azevedo, 1986; Azevedo et al, 1987 a, b; Ceará and Potiguar basins: Viviers & Regali, 1987; Pará and Maranhão basins: Beurlen & Regali, 1987). In all of these cases the benthonic faunal patterns were attributed to the prevalence of anoxic conditions in the depositional environment. The present study, also reveals relative uniformity in the bulk geochemical and biological marker features (Table 1 and Figs. 2-4), and therefore, emphasises the widespread occurrence of anoxic events in the Brazilian marginal basins during Cenomanian-Santonian times.

The most marked feature in the hydrocarbon biological marker distributions is the presence of high concentrations (up to 130 ppm of extract; Table 1) of 28,30-bisnorhopane and 25,28,30-trisnorhopane (Figs. 3, 4). Both compounds have been identified in sediment extracts and oils from many parts of the world, varying in age from Pliocene to Pre-Devonian (Anders et al ., 1978; Fowler & Douglas, 1984). It has been inferred from

kerogen pyrolysis studies that they occur in sediments as free hydrocarbons and are not present as part of the kerogen (Noble et al., 1984). It was also suggested by Katz and Elrod (1983) that they arise from a precursor or precursors in anaerobic bacteria living in strongly reducing conditions. This suggestion arose from the fact that anaerobic bacteria are known to form mat structures (up to 80% of the biomass) within anoxic zones in areas of intense upwelling (e.g. offshore Peru; Gallardo, 1978). Certainly, where they occur in sediments as major components, this occurrence is interpreted to indicate deposition under severely oxygen deficient conditions (Seifert et al., 1978; Anders et al., 1978; Cornford et al., 1979; Grantham et al., 1980; Rullkötter et al., 1982; Katz & Elrod, 1983; Volkman et al., 1983; Curiale et al., 1985). The high abundances found in the present study (occasionally the C₂₇ component is the major hydrocarbon) provide, therefore, independent evidence for the presence of extensive severe oxygen deficient conditions in the bottom waters in the Turonian-Santonian along the marginal basins.

Both the relative position of the anoxic layer and the degree of oxygen depletion have had a differential effect on the selection, abundance and diversity of the foraminifera in the water column and on the sea floor. Thus the taxonomic composition, diversity, abundance and specimen sizes recorded permit an estimation of the extent of the oxygen-minimum zone over the shelf and slope, and an evaluation of the degree of oxygen depletion in the water column.

The oxygen minimum zone generally creates a stratification in the degree of oxygen depletion, which tends to increase with depth and varies proportionally with the thickness and intensity of anoxia. Usually two layers can be broadly distinguished: An upper dysaerobic layer (> 0.1 - 1.0 ml oxygen/ L water) and a lower, thicker, anaerobic layer (from 0 - 0.1ml/ L). Table 2 summarizes the characteristics of the foraminifera found in the organic-rich sediments of the latest Cenomanian-earliest Turonian sections studied in the Sergipe/

TABLE - 2. PROPOSED RELATIONSHIP BETWEEN EXTENT OF OXYGEN DEPLETION AND EFFECT ON FORAMINIFERAL ASSEMBLAGE IN THE LATEST CENOMANIAN-EARLIEST TURONIAN (ONSHORE SERGIPE, SERGIPE ALAGOAS BASIN, BRAZIL).

<p>WELL OXYGENATED</p> <p>LOW/MODERATE DEGREE OF OXYGEN DEPLETION</p>	<p style="text-align: center;">SURFACE WATERS</p> <p>("aerobic" conditions, > 1.0 ml oxygen/L water): juvenile and abundant fully developed planktonic fauna (<i>Whiteinella</i>, <i>Hedbergella</i>, <i>Globigerinelloides</i>, <i>Heterohelix</i>), without or with a few keeled forms (<i>Dicarinella</i>, <i>Rotalipora</i>)</p> <p>("dysaerobic" conditions, > 0.1 - 1.0 ml/L; oxygen minimum zone near the wave base) :dwarf and/ or juvenile planktonic fauna (<i>Heterohelix</i>, <i>Guembelitria</i>, <i>Hedbergella</i>, <i>Globigerinelloides</i>) with practically no keeled forms</p>
<p>LOW DEGREE OF OXYGEN DEPLETION</p> <p>MODERATE DEGREE OF OXYGEN DEPLETION</p> <p>HIGH DEGREE OF OXYGEN DEPLETION</p>	<p style="text-align: center;">BOTTOM WATERS</p> <p>("dysaerobic" conditions, >0.5 - 1.0 ml/L) : specialized benthic fauna, mainly composed of calcareous hyaline foraminifera (gavelinellids: <i>Gavelinella</i>, <i>Lingulogavelinella</i>; bulliminids: <i>Gabonella</i>, <i>Praebulimina</i>, <i>Buliminella</i>; nodosariids: <i>Globulina</i>, <i>Dentalina</i>, <i>Nodosaria</i>; and discorbids: <i>Valvulinera</i>, <i>Gavelinopsis</i>. Many dwarf specimens occur.</p> <p>("dysaerobic" conditions, > 0.1 - ≤ 0.5 ml/L) : predominance of a dwarf benthic fauna, mainly composed of calcareous hyaline foraminifera (bulliminids, nodosariids, discorbids and gavelinellids - except for the morphotypes with a spiral boss of the <i>Gavelinella reussi-berthelini plexus</i>) a specialized monospecific fauna of miliolids (<i>Spiroloculina</i>) and simple agglutinated forms (<i>Trochammina</i>, <i>Textularia</i>, <i>Ammobaculites</i>, <i>Tritaxilina</i>, <i>Dorothia</i>, <i>Marssonella</i>)</p> <p>("anaerobic" conditions, 0-0.1 ml/L) : varies between virtually no benthic fauna and that shown for bottom waters with a moderate degree of oxygen depletion.</p>

Remarks : The genera are listed in a decreasing order of abundance from left to right.

Alagoas basin (onshore Sergipe), along with the proposed extents of oxygen depletion in the water column. The basic foraminiferal morphotypes and general characteristics observed can be used as an example of similar faunal patterns to be found in anoxic sediments along the Cenomanian-Santonian of the Brazilian margin. Therefore, from the comparison of Table 2 and Figs. 5 and 6, it can be seen from the assemblages of benthonic foraminifera that lived in the bottom waters during the Cenomanian-Santonian, that conditions varied from moderate oxygen depletion (dysaerobic) to truly anaerobic (virtually no benthonic foraminifera present). The presence of a well developed planktonic foraminiferal assemblage in some layers of the Cenomanian-Turonian sequence (Figs. 5, 6) indicates well oxygenated surface waters (cf. Table 2). On the other hand, the dwarfism observed in the benthic species was also observed in the planktonic species in certain layers of the Cenomanian-Turonian (Fig. 6), suggesting periodic dysaerobic conditions (oxygen depletion) in the surface waters and extension of the oxygen minimum zone upwards (Table 2). In the Santonian succession the presence of an abundant and fully developed planktonic fauna indicates the existence of a well oxygenated epipelagic layer (Table 2 and Fig. 6).

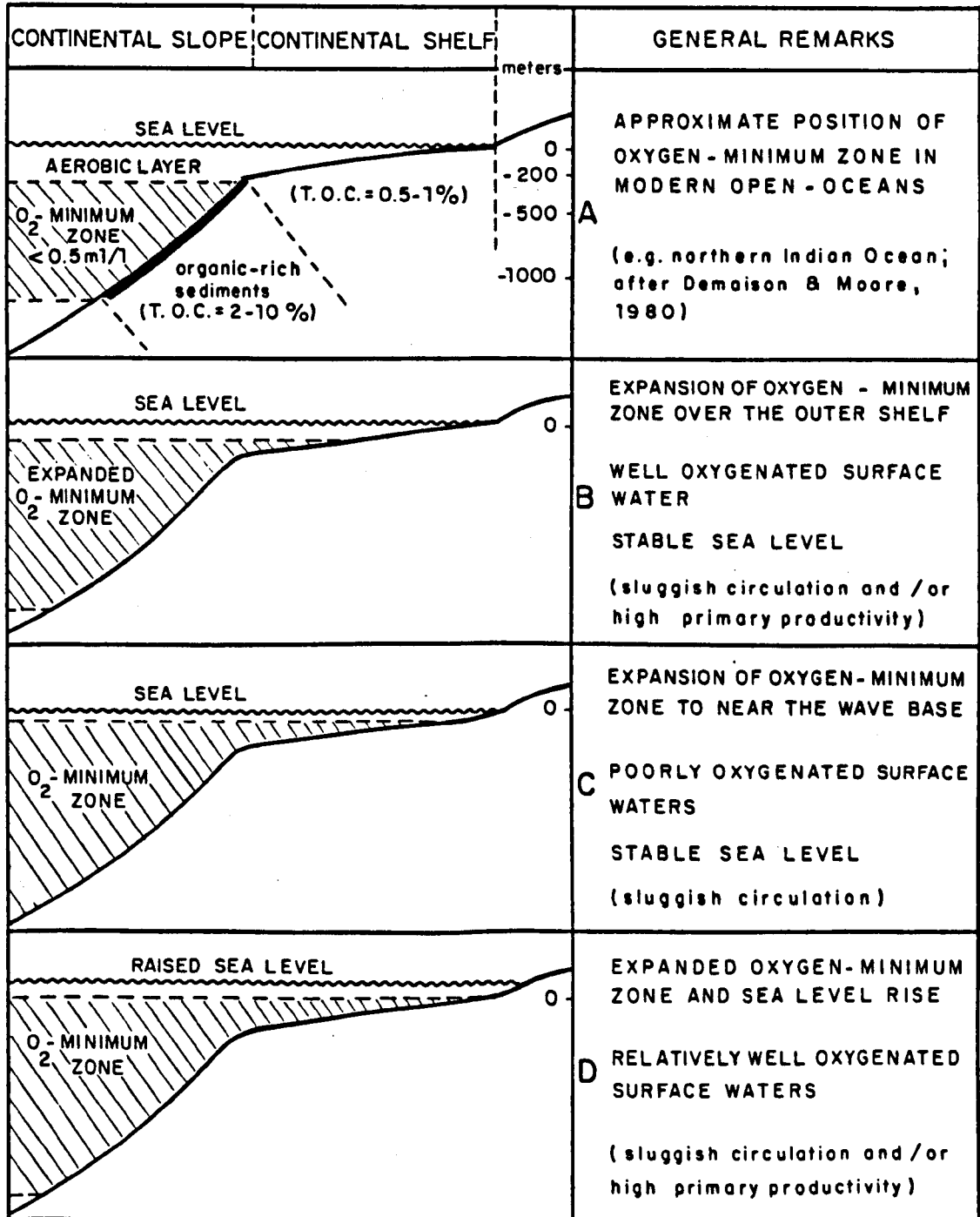
Radiolarian and some diatom tests were found consistently in most of the Cenomanian-Turonian sections (Figs. 5, 6). These assemblages are a clear indication of open water conditions, with peak abundances in the deep neritic (outer shelf) and upper bathyal (slope) environments. In most Recent sediments radiolarians and diatoms are absent through post-mortem dissolution of their tests, which are composed of relatively unstable amorphous biogenic silica. They are relatively common, however, only in certain areas of vigorous upwelling, such as the peri-equatorial Pacific and part of the northwestern African slope (Jenkyns & Winterer, 1982). In the geological record of Tethyan regions "Radiolarians are often preserved where organic matter is abundant, generally in highly reducing environments . Such an anaerobic environment preserves silica

from dissolution (de Wever, 1983). The presence of radiolarians and diatom tests in most of the Cenomanian-Turonian is not only in keeping with high epipelagic primary productivity and that the sea water apparently contained a high level of dissolved silica, but also suggests that the bottom waters were depleted in oxygen, had a low pH and were enriched in carbon dioxide, permitting, therefore, their preservation. Similar features have been reported for sediments from many areas of the world, deposited during OAE's (Schlanger *et al.*, 1987) and during older upwelling events (e.g. Monterey formation, California: Katz & Elrod, 1983).

The Santonian (Fig. 6) appears to be characterised by an upper to middle bathyal environment of deposition, with the occurrence of deep water, well developed, planktonic morphotypes (globotruncanids).

From the application of previous palaeobathymetric models of benthonic foraminifera (see references above) to the Cenomanian-Coniacian onshore succession of the Sergipe-Alagoas basin, it appears that the water depth fluctuated considerably, varying from neritic to upper bathyal conditions, suggesting that cyclic sea level changes occurred over the shelf and slope (Fig. 5). The proposed periods of maximum water depths (latest Cenomanian and earliest Turonian) are associated with an abundance in the planktonic foraminifera of non-keeled forms with large test size (250-500 μ m) and a predominance of small-sized benthonic specimens. This indicates the development of aerobic conditions in the epipelagic layers and an expansion of the oxygen minimum zone over the shelf. Sporadic levels containing small-sized planktonic and benthonic foraminifera occur (as in the latest Turonian) attesting to dysaerobic conditions affecting the surface waters as a consequence of a further expansion of the anoxic layer. Figure 7 compares the approximate position of the oxygen minimum zone in modern open oceans (Demaison & Moore, 1980) with different palaeoceanographic settings for an expanded oxygen minimum zone over the shelf. The expansion is associated with higher

Figure 7- Generalized scheme showing possible oceanographic settings of an anoxic layer in the open ocean and its effect on the continental shelf and slope: (A) approximate position of the oxygen minimum zone (o.m.z.) on modern "anoxic open oceans" (e.g., northern Indian Ocean; after Demaison & Moore, 1980); (B-C) expansion of the o.m.z. due to sluggish circulation and/or high primary productivity, middle and/or outer shelf affected; (D) expansion of the o.m.z. and sea level rise, extreme situation, most of the shelf affected.



biological productivity and/or sluggish circulation, with (model D) or without (models B/C) sea level rises. From the depth fluctuations proposed in Fig. 5 for the Sergipe-Alagoas basin it appears that the setting represented by model D occurred, probably during the latest Cenomanian-earliest Turonian. However, the situation represented by models B/C seem to have also played an extensive role in the deposition of organic-rich sediments over the shelf during polytaxic periods (period of high sea level, warm climate, sluggish ocean circulation and well stratified water masses), which were probably fairly constant in the northern South Atlantic.

Within the biological marker distributions of the organic-rich sediments there is some evidence of salinity enhancement in the water column over "normal marine" conditions. The C₄₀ alkane β -carotane has been widely reported in sediments and oils, and its presence in significant abundance appears to be associated with anoxic depositional environments having such enhanced salinity (Murphy et al., 1967; Hall & Douglas, 1983; Moldowan et al., 1985; Jiang & Fowler, 1986; Mello et al., 1988a and b). It has also been reported in high concentrations in Albian marine carbonates and Aptian evaporitic sediments and derived oils from the Brazilian marginal basins (Mello et al., 1988a, b). The triterpenoid gammacerane frequently co-occurs with β -carotane (Hills et al., 1966; Rohrback, 1983; Mello et al., 1984; Moldowan et al., 1985; ten Haven et al., 1985, 1988; Fu Jiamo et al., 1987; Mello et al., 1988a, b). Although these compounds are not major components of the Brazilian Cenomanian-Santonian organic-rich sediments, they are almost always present and often in significant concentrations (Table 1, Figs. 3, 4). This feature suggests, perhaps, a salinity enhancement over "normal marine" conditions in the water column, but not to the extent associated with hypersaline environments, which contain high concentrations of both compounds (e.g. Mello et al., 1988a, b).

The dominance of phytane over pristane in the samples (Pr/ Ph from 0.6 to 0.9) are also in keeping with the idea of

enhanced water column salinity. Recently, it has been shown that low ratios are associated with hypersaline depositional conditions, and it has been suggested that such ratios reflect differences in source input rather than simply anoxic conditions of deposition (Mello et al., 1988; ten Haven et al., 1987; Wang Tieguan et al., 1988). A further feature is the occurrence of C₃₅ αβ hopanes in similar abundance to, or in higher abundance than, their C₃₄ counterparts (Table 1, Fig. 4). This feature has also been suggested as being diagnostic of enhanced salinity (ten Haven et al., 1985; Fu Jiamo et al., 1986; Mello et al., 1988a, b).

The samples tend to contain higher concentrations of metalloporphyrins (up to ca. 5700 of extract in the least mature sediments) in comparison with other samples from the Brazilian marginal basins (Mello et al., 1988b). These high concentrations are again in keeping with anoxic depositional conditions and an extended oxygen minimum zone (cf. Lewan & Maynard, 1982).

The abundances of nickel to vanadyl species vary within the sequence. In the samples with the higher carbonate and sulphur contents (see results) the vanadyl species tend to dominate, whereas the nickel species tend to dominate in the samples with lower carbonate and sulphur contents. Similar variations with sulphur content have been reported for sediments from the Monterey formation (Baker & Louda, 1987, and references therein; Lewan & Maynard, 1982), and the Toarcian of SW Germany (Moldowan et al., 1986). The sterane concentrations are relatively low (30-200 ppm) in comparison with samples of similar maturity from other marine depositional environments in the Brazilian basins (Mello et al., 1988a, b). It is generally accepted that sedimentary steranes arise mainly from the sterols of algae. These sterane contents perhaps suggest, therefore, a relatively low preservation of algal derived organic matter as a result of bacteria reworking. The porphyrins could arise, therefore, partly from precursor chlorophylls in bacteria in the water column. Such an idea may

help to explain the $\delta^{13}\text{C}$ values of the extracts, which occur in the range -27.0 to -28.2‰ (Table 1). These values are lighter than those reported as typical of extracts from sediments from Cretaceous marine environments (eg. Galimov, 1973; Tissot & Welte, 1984; Sofer, 1984; Moldowan et al., 1985; Mello et al., 1988a, b). It appears, therefore, that they may reflect a bacterial component in the organic matter (cf. Hayes et al., 1987).

7.5 CONCLUSIONS

This investigation indicates the value of an interdisciplinary approach, using a combination of geochemical and microfossil studies of pelitic sediments in the assessment and characterisation of the depositional environment of the Cenomanian-Maastrichtian sedimentary succession of the Brazilian continental margin.

1. Integration of the data classifies this section into two distinct depositional regimes, namely:

i) marine with intermittent anoxia of variable intensity, increased bottom water salinity, and with a predominance of siliceous calcareous mudstone lithology (Cenomanian to Santonian); and,

ii) marine oxygenated, with a predominance of siliciclastic lithology (Campanian-Maastrichtian).

2. Most of the Cenomanian and Turonian appears to be characterised by an oxygen-minimum zone, occasionally depressed to deeper waters and variable in intensity. During this time-interval intermittent upward expansion of the oxygen minimum zone (due to high productivity and/ or sluggish circulation - polytaxic episodes) appear to have occurred, probably accompanied by rises in sea-level, leading to widespread deposition of highly anoxic organic-rich layers over the slope and continental shelf. The sediments laid down during these events typically possess the following features: high

hydrocarbon potential yields and hydrogen indices, medium to high concentrations of metalloporphyrins, 28,30-bisnorhopane and 25,28,30-trisnorhopane, plus large numbers of calcareous benthonic foraminifera (mainly composed of gavelinellids, buliminids, nodosariids and discorbids) of low diversity and predominantly of small-sized tests, together with agglutinated specimens and an abundant planktonic microfauna of well-developed non-keeled foraminifera (hedbergellids and globigerinellids), radiolarians and diatoms.

3. During the Santonian, layers with similar geochemical features, coupled with a paucity of dwarf benthonic specimens and a fully-developed planktonic fauna with deep water morphotypes (globotruncanids), indicates a thicker well-oxygenated epipelagic layer, severely anoxic bottom conditions and a contracted oxygen minimum zone to bathypelagic depths.

4. This investigation extends the works of Schlanger & Jenkins (1976), Ryan and Citta (1977), and Jenkins (1980), and also suggests that anoxic conditions prevailed during most of the Cenomanian-Santonian interval in the Brazilian continental margin. The anoxic events are only recorded where the oxygen-minimum zone, apparently ubiquitous in the South Atlantic at that time, came into contact with the continental margin at intermediate or shallower water depths, as a consequence of an expansion of the anoxic layer (e.g., during the latest Cenomanian/ earliest Turonian time interval).

5. The anoxic events in the Brazilian basins were intermittent, rather than continuous, covering relatively short periods of time, most of them associated with sea level rises. Also, there is evidence from the biological markers that salinity stratification played a role in the establishment of oxygen-deficient conditions in the bottom waters.

6. In general, during the Campanian to Maastrichtian interval, oxic conditions became widespread along the Brazilian continental margin. The low organic carbon content, poor potential yield and high oxygen index (Rock-Eval pyrolysis), together with an abundant and highly diversified microfauna indicate generally well-oxygenated conditions.

7. The high concentration of 28,30-bisnorhopane and 25,28,30-trisnorhopane, coupled with a relatively low preservation of algal organic matter suggested by the sterane concentrations, and evidence from $\delta^{13}\text{C}$ data, suggest a bacterial origin for a significant proportion of the organic matter, including the tetrapyrrole pigments, deposited during the Turonian-Santonian anoxic events in the Cassiporé, Ceará, Sergipe/Alagoas and Campos basins.



CHAPTER VIII

CHAPTER VIII

EXPERIMENTAL AND ANALYTICAL PROCEDURES

This chapter describe the analytical procedures which were employed in this study.

8.1 INTRODUCTION

Each of the different analytical techniques, which were employed in this work, is discussed separately in the following sections.

8.2 GENERAL

All solvents were distilled in order to avoid contamination. Glassware was cleaned by soaking in "Lipsol" solution in de-ionized water for about 24 hours. It was then rinsed with de-ionized water and oven dried at about 65 °C, and rinsed with dichloromethane before use. Thin-layer chromatography plates (TLC) were pre-developed in ethyl acetate for 24 hours and re-activated (120 °C, 1 hour) immediately prior to use. Silica gel and alumina for column liquid chromatography were pre-eluted with dichloromethane-methanol (3:1), dried and re-activated overnight (silica gel, 120 °C and alumina, 300 °C respectively). Cotton wool and Soxhlet thimbles were pre-extracted with dichloromethane for 24 hours before use. The disc and ball mill, employed to grind the rock samples, were similarly treated.

8.3 SOURCE ROCK SELECTION

Source rock samples were in the form of cuttings or cores. The cuttings samples were carefully selected using a series of techniques (e.g. well log) to ensure that each sample was representative of the drill depth. They were hand-picked in order to remove contaminants from depths above the depth being drilled (e.g. cavings or recirculated fragments). Also, care was taken to ensure that the samples (cuttings and cores) were not contaminated by drilling mud or corer lubricant (screened by Rock Eval pyrolysis). The samples were then ground using a

disc mill (Tema) and/ or mortar and pestle, in order to achieve a typical particle size of about 5 to 100 μm .

8.4 ELEMENTAL ANALYSIS

Rock samples were extracted with dichloromethane/methanol (see 8.10) to remove soluble organic material and dried under vacuum before analysis. Elemental analyses were performed using a Perkin-Elmer 240 °C Elemental Analyzer. The C, H, N, and S values were calculated on an ash-free (ie. sample weight minus ash weight) basis. The $\text{CaCO}_3\%$ values were measured from the carbonate carbon using a multiplication factor of 8.3 . All measurements were performed twice, and the average values used. These services were performed by the Microanalytical Laboratory, School of Chemistry, University of Bristol.

The sulphur, nickel and vanadium contents and the API gravities of the oil samples were performed according to procedures described previously (Gaglianone & Mello, 1984; Petrobrás internal report), by courtesy of the Chemistry Division of Petrobrás Research Centre (CENPES), Brazil.

8.5 TOTAL ORGANIC CARBON

The pulverized rock (0.5g) was treated with warm hydrochloric acid . After filtration, washing and drying, the residue was analysed using a WR-12 LECO carbon analyzer. The carbon is measured using a thermal conductivity detector, the result being reported as weight (%) carbon of the original rock sample. Most of the samples were analysed twice in order to ensure reproducible results. These analyses were performed by the Organic Geochemistry Section of Petrobrás Research Centre (CENPES), Brazil.

8.6 ROCK-EVAL PYROLYSIS

About 100 mg of pulverized rock sample was analysed on a Rock-Eval pyrolyser. This technique involves the heating of the sample from 300 °C to 550 °C for about 15 minutes (25 °C/ min) in a helium plus hydrogen atmosphere (carrier gas). The results are expressed as mg/g of rock, and include three parameters: i) S_2 represents the quantity of hydrocarbons released by the thermal breakdown of the kerogen; ii) S_3 corresponds to the amount of oxygen present; and iii) T-max (°C) is the temperature at which the maximum rate of generation (S_2 peak) occurs. The S_2 / TOC and S_3 / TOC ratios furnish the hydrogen and oxygen index, respectively, in mg of hydrocarbons (S_2 peak) or carbon dioxide (S_3 peak) per gram of organic carbon. When plotted against each other they provide the so-called van Krevelen-type diagram. Most of the samples were analysed twice to ensure reproducible results. These analyses were performed on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES), Brazil.

8.7 VISUAL KEROGEN ANALYSIS

The ground rock samples were treated successively with hydrochloric and hydrofluoric acids in order to concentrate the kerogen, which was mounted on a thin plate. The types and percentage of organic matter were determined by visual examination under a transmitted light microscope.

Amorphous organic matter represents lipid-rich unstructured material. Herbaceous type organic matter includes lipid-rich structured material such as spores, pollens and cuticles. Woody and coaly types represent hydrogen-lean organic matter, typically derived from land plants. These analyses were performed on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES) and IPT, Brazil.

8.8 SPORE COLOUR INDEX (SCI)

The same thin plates and microscope used for visual

kerogen analysis were employed in these analyses. The values were estimated by a visual technique, comparing the samples examined with known standards. The results are given as an index and may be interpreted as follows:

- < 5 - immature;
- 5 - 8.5 mature; and
- > 8.5 - overmature

These analyses were performed on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES) and IPT, Brazil.

8.9 VITRINITE REFLECTANCE ANALYSIS

Around 20g of ground rock were treated successively with hydrochloric and hydrofluoric acids to remove the inorganic content and concentrate the kerogen. The organic matter is separated from the remaining residue by heavy liquid separation, dried, mounted on a epoxy plug and polished. The analyses were performed using a Zeiss Universal reflecting microscope. The results are given in R_o (%) values (vitrinite reflectance mean in immersion oil) that are related to a known standard. These analyses were performed on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES) and IPT, Brazil. Several samples were repeated twice in order to ensure quality control.

8.10 CARBON ISOTOPIC ANALYSIS

Carbon isotope analyses of whole oil, whole extract and of n-alkane and aromatic fractions were undertaken using a vacuum combustion line linked to a Varian MAT-230 instrument. The data are presented in delta-notation ($\delta^{13}C$ ‰) relative to Pee Dee Belemnite (PDB). These analyses were performed on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES), Brazil.

8.11 SOLVENT EXTRACTION

Typically, 60 grams (weighed exactly) of pulverized rock sample were Soxhlet extracted with 400 ml of dichloromethane-methanol (3:1) for 48 hours. Copper was employed in the Soxhlet apparatus to remove elemental sulphur. After filtration the solvent was removed in a rotary evaporator, the extract was transferred in solvent to a weighed vial and the solvent removed under a stream of dry nitrogen.

8.12 LIQUID CHROMATOGRAPHY

Rock extracts and oil samples were fractionated into three main fractions (alkanes, aromatics and polar compounds. Two methods were employed in order to have better results; i) thin layer chromatography (TLC); and ii) column chromatography. Column chromatography analyses were performed in Bristol and on the Organic Geochemistry Section of Petrobrás Research Centre (CENPES), Brazil in order to check the reproducibility of the method and compare results. Columns were packed with a mixture (1:1, 100g) silica gel (BDH) and alumina (BDH; grade II neutral) in a hexane slurry under a constant flow rate. Samples (100mg of extract or oil) were diluted in a minimum volume of dichloromethane and added to the column. Gradient elution, using solvents with successively increasing polarity (e.g. hexane to methanol) was employed. To ensure recovery of the polar compounds, the column was washed twice with 20ml of methanol. After filtration, solvent was removed in a rotary evaporator, the fraction was transferred to a weighed vial and the solvent was removed under a stream of dry nitrogen.

As a check, thin layer chromatography (TLC) analyses were performed on glass plates coated with silica gel G (Merck; 0.4 mm). The sample (30mg of oil or extract), diluted in 300 μ l of dichloromethane was loaded onto the plate. Two reference standards (C₂₄ n-alkane and phenantrene) were used. The plate was developed (hexane developer) until the solvent front was

nearly at the top of the plate. After drying, Rhodamine 6G was sprayed over the standards, and the elution position of each fraction was visualized using U.V light. Each fraction was recovered from the plate and eluted with dichloromethane or dichloromethane-methanol through elution tubes containing a short alumina column. The solvent, after filtration was removed in a rotary evaporator, the fraction transferred in solvent to a weighed vial, and the solvent removed under a stream of dry nitrogen.

8.13 MOLECULAR SIEVING

This method was used with a few highly mature source rocks and oils in order to concentrate the isoprenoids, terpenoids and steroids. The molecular sieves (5 Å) were initially Soxhlet-extracted with dichloromethane for 48 hours, activated at 330 °C for 3 days and left to cool under vacuum. For sieving, 1-11 mg of alkane fraction was dissolved in 2-24 ml of iso-octane (spectroanalytical grade, Aldrich) and added to a vial containing 200 mg of molecular sieves. The vial was heated in an oven at 80 °C for two days with occasional shaking. The solution was transferred to a flask and the sieves washed twice with iso-octane. The washings were combined and the solvent removed in a rotary evaporator. Then the fraction was transferred in solvent to a weighed vial, and the solvent removed under a stream of dry nitrogen.

8.14 GAS CHROMATOGRAPHY

Alkanes were analysed by gas chromatography (GC) employing two different systems; i) a Carlo Erba Mega series 5160 gas chromatograph, equipped with an on-column injector and a 50m OV-1 column (cross-linked methyl silicone; Hewlett Packard). Hydrogen was employed as the carrier gas with a temperature programme of 60-300 °C at 5 °C/ min. Peak areas for compound quantitation (e.g. pristane/ phytane ratio) were

measured by a computing integrator (minichrom system; Laboratory Data Control) ; ii) the GC traces displayed in the figures were obtained employing an HP 5880 chromatograph instrument (Norsk-Hydro, Norway) equipped with a split/splitless injection HP5673 autosampler. The GC was fitted with a 30m, 0.25mm i.d fused silica DB-1 (Durabond) column. Helium was employed as carrier gas with a temperature programme of 30-310 °C at 6 °C/ min.

8.15 GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

GC-MS analyses of alkanes were carried out using a Finnigan 4000 spectrometer coupled to a Carlo Erba 5160 gas chromatograph equipped with on-column injector, and fitted with a 60m DB-1701 column. Helium was employed as carrier gas with a temperature programme of 50-90 °C at 6 °C/ min and 90-310 °C at 4 °C/ min. The aromatic hydrocarbon analyses were performed using a fused silica SE-54 WCOT coated (25m x 0.30mm) column. Either column was led directly into the ion source (ioniser temperature around 250 °C; electron energy 35 eV; emission current 350 μ A; voltage 2 kV). The scan range was typically m/z 50-550 with total scan time of 1.0 second. The spectrometer was operated in two different modes for each sample; i) full data collection (FDC) for routine analyses, and multiple ion detection (MID), monitoring only selected ions, for biological marker quantitation. Data were acquired and processed using an Incos 2300 data system, comprising of a Data General Corporation Nova/ 4 computer with 96 Mbyte capacity. Relative quantitation and ratios measured for hydrocarbons were performed using peak areas in appropriate mass chromatograms (cf. appendix II). In order to ensure comparative results, the analyses of all the samples were repeated by GC-MS at Norsk-Hydro, Norway, using different instruments, columns and conditions. The GC-MS analyses were performed using a HP 5880 gas chromatograph interfaced to a HP 5970 mass selective detector (MSD) in the single ion monitoring mode. The

chromatograph was fitted with a 30 m, 0.25mm i.d. fused silica DB-1(Durabond) column. Helium was employed as the carrier gas with a temperature programme of 30-310°C at 6°C/min.

To ensure comparable results the analyses were performed as far as possible sequentially, under similar conditions using large batches in each laboratory. All the quantitative data on biological marker concentrations, reported as ppm of extract or oil, were performed in Bristol. They were obtained for selected samples (Tables 1 and 2 in Introduction) by adding a fixed amount of synthesised deuteriated sterane internal standard (2,2,4,4-d₄ 5 α (H),14 α (H),17 α (H)-cholestane) to each alkane fraction; 20R + 20S 5 α (H), 14 α (H), 17 α (H) cholestanes were quantified by comparing peak areas in m/z 217 chromatograms with the peak area of the standard in m/z 221 chromatograms (cf. appendix II. Although response factors for m/z 217 in the low molecular weight steranes are expected to be different, the ppm concentrations of these components were measured in the same way. Other components were quantified by comparison of peak areas with that of the standard in the Reconstituted Ion Chromatogram (RIC) traces (cf. appendix II). To confirm the order of concentrations of specific biological markers, quantitation was also carried out using mass chromatograms (e.g. by comparison of m/z 221 for the standard with m/z 191 to obtain relative concentrations of C₃₀ $\alpha\beta$ hopane). In cases where concentrations were too low to be measured using RIC traces, quantitation was obtained by comparing mass chromatograms for the standard (m/z 221) with mass chromatograms for the components in question (e.g. m/z 125 for β -carotane) and then making a correction using a derived factor obtained from analyses of samples where the components could be observed in the RIC traces. Peak identities were established by mass spectral examination, GC retention time and, in a number of cases coinjection of standards (18 α (H)-oleanane, gammacerane, C₂₉ $\alpha\beta$ and $\beta\alpha$ norhopanes, C₃₀ $\alpha\beta$ and $\beta\alpha$ hopanes, C₂₇ to C₂₉ 20R 5 α (H), 14 α (H), 17 α (H) steranes, ,

C_{21} $\beta\alpha$ diapregnane, C_{22} $\alpha\alpha\alpha$ 4-methylhomopregnane, C_{21} $\alpha\alpha\alpha$ pregnane, C_{24} des-E tetracyclic terpane, C_{25} regular isoprenoid and C_{25} irregular isoprenoid).

In the steranes the ratio % 20S/ 20S + 20R was measured using peak areas in m/z 217 chromatograms for the C_{29} $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ compounds. The ratio % $\alpha\beta\beta$ / $\alpha\beta\beta$ + $\alpha\alpha\alpha$ was measured using m/z 217 for the C_{29} $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ compounds, and m/z 218 for C_{29} $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$ compounds (see Mackenzie, 1980). The relative abundances of the $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ 20S + 20R components for different carbon numbers (C_{27} to C_{29}) were measured from m/z 217 (more details are present in the relevant sections and appendix II). In the aromatic fraction the ratio " C_{28} 20R triaromatic/ C_{28} 20R triaromatic + C_{29} 20R monoaromatic" (but see text) was calculated using the ratio A/ D-C (B/ A-1) + A where A- represents C_{28} 20R triaromatic; and B- C_{27} 20R triaromatic measured in m/z 231 mass chromatograms. C- represents $5\alpha(H)$ C_{29} 20 R monoaromatic; and D- $5\beta(H)$ C_{29} 20R + $5\alpha(H)$ C_{28} 20R monoaromatics in the m/z 253 mass chromatogram(for more details see Mackenzie et al., 1981 and Chapter V).

8.16 SELECTED METASTABLE ION MONITORING (SMIM)

The metastable linked scan technique was performed by computerised GC-MS using a VG-7070E instrument, coupled to a HP 5790 Split/ Splitless gas chromatograph fitted with a Ultra 1 HP crosslinked methyl silicone fused silica column (25m, 0.2mm, 0.33 μ m). Helium was employed as the carrier gas with a temperature programme of 70-150 °C at 25 °C/ min and 150-310 °C at 1.5 °C/ min. Metastable ions, formed in the first field free region of the mass spectrometer, were monitored using a fixed accelerating voltage (6 kV) and pre selected changes in the electrostatic analyser/ magnet values. These analyses were carried out at Norsk Hydro Research centre, Norway.

The presence and absence of C_{30} regular steranes was

checked by monitoring the transition m/z 414-217 (cf. Moldowan et al., 1985).

8.17 GAS CHROMATOGRAPHY-MASS SPECTROMETRY/ MASS SPECTROMETRY (GC-MS/MS)

Four selected rock samples were analysed by GC-MS/ MS employing a VG 70-250SEQ MS-MS instrument, coupled to a HP 5890A Split/ Splitless gas chromatograph fitted with a 50m DB-01 fused silica column. Helium was employed as the carrier gas with a temperature programme of 50-120 °C at 6 °C/ min and 120-320 °C at 5 °C/ min. The presence of dinosterane and 4-methyl 24-ethylcholestane was checked by monitoring the transitions m/z 231-95 and 231-98 respectively. These analyses were kindly performed at VG analytical research centre, Manchester, England.

8.18 PORPHYRINS.

This work was carried out in collaboration with Mr John Waring.

Typically, metalloporphyrins were obtained by column chromatography of an aliquot (250mg) of the solvent extract on alumina (Grade 2 neutral) using hexane/dichloromethane (90/10) to obtain the saturated and aromatic hydrocarbons, hexane/dichloromethane (75/25) to obtain the nickel porphyrin fraction, and hexane/dichloromethane (70/30) followed by dichloromethane/methanol (90/10) to obtain the vanadyl fraction. Further purification of the nickel and vanadyl porphyrin fractions was performed using thin layer chromatography (Silica gel 60G: toluene/acetone 95/5 as developer).

Demetallation was carried out essentially according to the procedure used by Chicarelli (1985). Typically, the metalloporphyrin concentrate was heated (90 °C, 4h for nickel;

80 °C, 3h for vanadyl) under nitrogen with excess methanesulphonic acid (MSA 98%, 4-5 drops). The mixture was allowed to cool to ambient temperature (and allowed to stand for a further 2h in the case of the vanadyl fraction), and the reaction quenched by diluting with 25% aqueous MSA (ca 15ml). The coagulated organic matter was finally removed by filtration under gravity, and washed with aqueous MSA (ca 25ml).

The aqueous filtrate, containing the porphyrins as dications, was extracted with dichloromethane (3 x 5ml) and neutralised with a saturated aqueous solution of NaHCO_3 .

The metalloporphyrins were quantified using ultraviolet/visible spectrophotometry on a Perkin Elmer 555 spectrophotometer, spectra being recorded under the following conditions: scan range from 700 to 350nm, scan speed 120nm/min., and cell path length of 1cm (for quantitation details, cf. Chicarelli, 1985). Dichloromethane was used as solvent and reference.

High performance liquid chromatography (HPLC) was performed using a Spectra Physics SP8700 tertiary solvent delivery system and Rheodyne 7125 injector valve with a 20 μl injection loop. Detection (400nm) was obtained using an LDC Spectromonitor III with variable wavelength detector. The analyses was performed using three Spherisorb S3W (150 x 4.6mm) columns connected serially and using a solvent program described previously (Barwise et al ., 1986)

Probe mass spectrometry was obtained using a Finnigan 4000 quadrupole spectrometer with heated probe inlet system. The conditions employed were: probe temperature from 90 to 350 °C, electron energy of 40eV, emission current 350 μA , ionizer temperature of 250 °C and scan range from 50-650 AMU, total scan time of 3 seconds. The probe temperature programme was from ambient to 250 °C at 32 °C/min., then 250-350 °C at 16 °C/min. Data acquisition and processing were performed using a Finnigan INCOS 2300 data system. Spectra were summed over the range of evaporation of porphyrins as estimated from the total ion

current (>ca 220 °C for metalloporphyrins and >ca 180 °C for free bases).

8.19 MICROPALAEONTOLOGICAL ANALYTICAL PROCEDURES USED IN CHAPTER VII

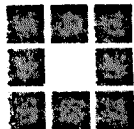
This work was performed by Mr E. A.M. Koutsoukos at Plymouth Polytechnic, Plymouth.

The biostratigraphy of the Cenomanian-Coniacian section of the Sergipe-Alagoas basin was based mainly on the integration of the ammonite zonation for the basin (Bengtson, 1983) and microfossil assemblage zones, chiefly based on foraminifera. Sample preparation for the Cretaceous outcrops involved crushing of indurated samples ca. 120g per sample) and immersion (8h) in a hydrogen peroxide solution (120 v/v), washing and decanting through a fine-mesh sieve (63 μ m), drying (8h at 60 °C), picking of the microfauna from the dried residues on a gridded tray, and collection into one-hole slides.

Sediments from the Cassipore, Ceará and Campos basins were selected from horizons with high-organic contents in five offshore wells, and were processed in a standard manner as follows. Dried samples were soaked in 'White Spirit' overnight. Excess solvent was decanted off and distilled water added (1h) until breakdown. After normal washing procedures and picking the samples were submitted to microfossil analysis.

8.20 MULTIVARIATE ANALYSIS

The multivariate statistical evaluation of total biological marker elution profiles was undertaken using SIMCA(Wold.,1976), after variable reduction with a maximum entropy technique (Telnaes and Dahl, 1986; details are presented in Chapter IV).



CONCLUSIONS

GENERAL CONCLUSIONS

Although most of the findings related to this work were described in detail in the conclusions at the end of each chapter, a summary of the more important contributions related to assessment of palaeoenvironment of deposition and thermal history using biological markers from oils and organic-rich sediments from the major Brazilian marginal basins are summarised here.

1- The biological marker data revealed significant differences among the organic-rich sediments allowing them to be classified into seven different depositional regimes, namely I-lacustrine freshwater; II-lacustrine saline water; III-marine evaporitic; IV-marine carbonate; V-marine deltaic with carbonate influence; VI-open marine highly anoxic with dominance of calcareous lithology, and VII-open marine anoxic with dominance of siliciclastic lithology.

2- The distribution pattern and concentrations of biological markers of a selection of oils allowed their correlation with source rocks laid down in five of the seven depositional regimes identified above, namely I-lacustrine freshwater; II-lacustrine saline water; III-marine evaporitic; IV-marine carbonate and V-marine deltaic with carbonate influence.

3- Although the open marine sedimentary succession in some areas of the continental margin contain organic-rich sediments, they are generally immature, due to a combination of low geothermal gradient with shallow burial, and are not considered source rocks in the Brazilian continental margin. The fact that no open marine oil type was identified lends support to this.

4- The use of oil-oil, oil-source rock and rock-rock correlations based on biological marker distributions and concentrations has been shown to be valid and should be a powerful tool in the petroleum exploration strategy for the Brazilian sedimentary basins.

5- One of the major findings of the use of biological marker distributions and concentrations in palaeoenvironment assessment is in helping to ascertain the type of depositional environment of source rocks in the Brazilian marginal basins using only oil samples.

6- It is clear that, in most cases, no single biological marker property is sufficient to assess a specific environment of deposition. Nevertheless, consideration of various properties in a multiparameter approach can provide diagnostic criteria. On the other hand, the presence of specific compounds such as $18\alpha(H)$ -oleanane can be diagnostic of particular depositional environment (associated here with a deltaic environment).

7- In attempting to assess palaeoenvironment of deposition of sedimentary rocks, the absence of diagnostic biological marker compounds can be as important as their presence. For example, the absence of C_{30} steranes and dinosterane isomers appears to be diagnostic of non-marine depositional environments.

8- One key point of this study was the use of a deuteriated sterane as internal standard to allow a quantitative (ppm of extract or oil) approach. This technique, together with distribution pattern, proved to be useful and adds a new dimension to the use of biological markers in assessment of palaeoenvironment of deposition.

9- The use of metastable ion GC-MS and GC-MS/MS techniques has proved to be valuable in both the assessment of depositional environments and in oil-source rock correlation, and must be considered a promising geochemical technique for the future.

10- Based on the results of this investigation, and as an extension of previous studies, it is proposed that some biological marker properties such as low pristane/ phytane ratio, and high concentrations of regular C₂₅ isoprenoid, squalane, β -carotane and gammacerane may be considered useful indicators of enhanced salinity of the water column in the depositional environment.

11- Hypersaline depositional conditions tend to result in the highest concentrations of biological markers derived from bacterial and algal precursors. This appears to be due to the availability of nutrients in such an extreme environment, associated with a selective number of adapted species. These well adapted organisms with little or no competition for the nutrients available are then able to bloom, producing a high input of organic matter.

12- Although the "end members" of specific depositional environments possess a diagnostic group of characteristics, overlaps of a number of biological marker features do occur. Such features were mainly observed for environments thought to represent enhanced salinity conditions and environmental transitions (e.g. lacustrine hypersaline/ marine evaporitic and lacustrine fresh/ brackish/ to saline water). These "overlaps" show the difficulties that can occur when trying to characterise and distinguish depositional environments in a single geological evolutionary realm such as the Brazilian continental margin.

13- A preliminary study did not reveal any environmental specificity in the aromatic hydrocarbons. This, together with the fact that the complex mixtures are poorly separated by typical GC columns, restricted their use herein as palaeoenvironmental indicators. Hence, further studies need to be undertaken to examine these compounds as possible indicators of depositional environments in the Brazilian marginal basins.

14- Although only preliminary studies were carried out, multivariate analyses using the principal component technique, appears to be a promising tool for assisting in the interpretation, classification and discrimination of a complex biological marker data set with the aims of assessment of palaeoenvironment of deposition and of oil-source rock correlation.

15- Integration of the findings from Chapters I to IV provides a framework of biological marker characteristics for prolific oil-prone depositional environments which can be compared with samples from other parts of the world.

16- The use of biological marker parameters in the assessment of thermal maturity of sedimentary rocks must be exercised with care, since source input, mineral matrix and contamination by migration may play an important role. Examples worth to mention are the variation in relative abundance of rearranged monoaromatic steroid hydrocarbons and the T_s/T_m ratio.

17- It is clear that no single geochemical parameter is sufficient to determine maturity level with certainty. Nevertheless, consideration of several parameters together in a multidisciplinary approach (optical, bulk, chemical and molecular) can provide a precise assessment of the thermal evolution of a specific sedimentary succession.

18- In relation to the quantitative biological marker approach, it is clear that care must be taken when attempting to assess palaeoenvironment of deposition using mature sediments and oils, since the concentration of biological markers decreases considerably, and in some cases the components are completely degraded, around and after the peak of oil generation.

19- The ranges of the changes in the molecular ratios according to maturity arising from this investigation indicate that such molecular parameters must be considered only as a rough guide, as suggested by Tissot & Welte (1984), since there are several factors that can exert an influence on them (e.g. depositional environment/ source imprint).

20- The results from the sterane concentrations and distributions suggest that isomerisation may only be responsible for part of the changes that occur in the biological markers properties during thermal evolution. A concentration effect, as less stable components are degraded, appears to be a major factor. These findings together with others herein suggest that difficulties might be expected when molecular ratios are used in a quantitative sense with kinetic parameters thought to describe reactions altering these ratios, in the assessment of the thermal history of sedimentary basins.

21- The preliminary investigation reveals that porphyrin data based on concentration and the proportionality of nickel to vanadyl components obtained from immature organic-rich sediments, could be of potential help in the assessment of characterization of different palaeoenvironments of deposition.

22- The low concentration or absence of porphyrins found in mature organic-rich sediments and oils are in keeping with previous findings that these biological markers are readily degraded when submitted to increasing thermal stress in the sedimentary column.

23- High concentrations of 28,30-bisnorhopane and 25,28,30-trisnorhopane, coupled with a relatively low preservation of algal organic matter suggested by the sterane concentrations, and the evidence of carbon isotope data, suggest that a significant proportion of the porphyrins present in the samples investigated could arise from chlorophyll precursors in photosynthetic bacteria.

24- A combination of geochemical and microfossil studies of pelitic sediments of the Cenomanian-Maastrichtian sedimentary succession from the continental margin showed that much of the Cenomanian to Santonian sedimentary succession was deposited in an environment characterized by an oxygen-minimum zone, occasionally depressed to deeper waters and variable in intensity. Intermittent upward expansion of this zone (due to high productivity and/ or sluggish circulation) appears to have occurred, probably accompanied by rises in sea-level, leading to widespread deposition of highly anoxic organic-rich layers over the slope and continental shelf. This finding extends the occurrence of the Cenomanian to Santonian "global oceanic anoxic events", and also suggests that anoxic conditions prevailed during the Coniacian interval in the Brazilian continental margin. The anoxic events are only recorded where the oxygen-minimum zone, apparently ubiquitous in the South Atlantic at that time, came into contact with the continental margin at intermediate or shallower water depths, as a consequence of an expansion of the anoxic layer.

25- In general, during the Campanian to Maastrichtian interval, oxic conditions became widespread along the continental margin. The low organic carbon content, poor hydrocarbon source potential and high oxygen index (Rock-Eval pyrolysis), together with an abundant and highly diversified microfauna indicate generally well-oxygenated conditions.

26- The sediments laid down during these events can be traced in several sedimentary basins around the world and typically possess the following features: high hydrocarbon potential yields and hydrogen indices, medium to high concentrations of metalloporphyrins, 28,30-bisnorhopane and 25,28,30-trisnorhopane, plus large numbers of calcareous benthonic foraminifera (mainly composed of gavelinellids, buliminids, nodosariids and discorbids) of low diversity and predominantly of small-sized tests, together with agglutinated specimens and an abundant planktonic microfauna of well-developed non-keeled foraminifera (hedbergellids and globigerinellids), radiolarians and diatoms.

27- The use of a particular fused silica capillary column (60m, DB 1701) in the GC-MS analyses proved to be of value since it allowed the resolution of most of the alkane biological markers applied in this study (e.g. gammacerane eluting alone).

28- The results show examples of the value of biological markers for correlation in both a horizontal and vertical sense. For example, samples from a lacustrine saline depositional environment collected from > 2000 miles apart show very similar features (Fig. 22, Chapter II); also, evaporitic samples from well FGT-1-AL show features similar to each other over 2000 m depth, until the effects of maturity alters them significantly (Figs. 12 to 16, Chapter V).

29- Finally, Table 1 summarizes the ranges of bulk and biological marker data for both oils and organic-rich sediments discussed in Chapters II and III. This summary provide a framework of biological marker and geochemical characteristics which can be used with samples from other parts of the world.

Table 1- BULK AND MOLECULAR DATA FOR BRAZILIAN OILS AND SEDIMENTS

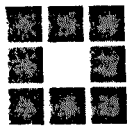
ENVIRONMENT OF DEPOSITION	LACUSTRINE FRESHWATER	LACUSTRINE SALINE	MARINE EVAPORITIC	MARINE CARBONATE	MARINE DELTAIC	MARINE CALC.LITH.	MARINE SILIC.LITH.
*API (oils)	30-39	24-32	20-30	25-30	42-44	-	-
% SATURATES (oils)	60-73	45-65	30-59	20-60	60-70	-	-
% SULPHUR (oils)	<0.1	0.2-0.4	0.3-1.5	0.4-0.7	0.3-0.4	-	-
V/Ni (oils)	<0.05	0.3-0.4	0.2-0.3	0.4-0.5	0.8-1.0	-	-
% Ro (rocks)	0.4-0.7	0.4-0.8	0.5-0.7	0.4-0.6	0.5-0.6	0.4-0.6	0.5-0.7
% SATURATES(rocks)	40-60	25-55	25-40	20-45	27-30	22-34	25-44
% SULPHUR(rock)	0.2-0.3	0.1-0.5	0.3-2.5	0.2-0.6	0.6-0.7	0.4-0.5	0.3-0.7
% CaCO ₃	<7	2-30	5-25	15-65	50-70	15-48	6-20
δ ¹³ C(PDB,‰)	<-28	-23:-27	-25:-27	-26:-28	-21:-26	-26:-28	-26:-27
n-ALKANE MAX.	~C ₂₃	~C ₁₉	~C ₁₈	C ₂₀ -C ₂₂	C ₂₀ -C ₂₂	~C ₂₀	~C ₁₇
ODD/EVEN	≥1	≥1	≤1	≤1	≤1	<1	>1
Pr/Ph	>1.3	>1.1	<1.0	<1	≤1	<1	>1
*1-C ₂₅ +i-C ₂₆ (ppm)	<370	70-700	300-1500	100-500	150-300	10-100	40-180
2 β-CAROTANE (ppm)	ND	10-200	100-400	20-60	5-10	10-30	ND
3 C ₂₁ +C ₂₂ STERANES(ppm)	tr	10-30	10-60	10-60	30-50	10-30	25-35
4 C ₂₇ STERANES (ppm)	10-50	50-160	500-4000	50-300	50-350	30-200	20-400
5 C ₂₇ /C ₂₉ STERANES	1.5-4.0	1.5-2.5	1.0-2.2	1.1-2.5	1.3-1.8	0.8-1.2	1.5-2.5
6 DIASTERANE INDEX	20-40	10-50	6-20	20-30	30-60	10-30	30-80
7 C ₃₀ STERANE (MS-MS)	ND	ND	LOW	HIGH	HIGH	HIGH	HIGH
8 4-Me-STERANE INDEX	10-50	30-150	30-80	30-80	<10	20-40	10-20
9 HOPANE/STERANES	5-15	5-15	0.4-2.0	0.9-3.0	0.5-3.0	0.3-0.9	1.5-3.0
10 TRICYCLIC INDEX	30-100	100-200	10-60	60-200	60-180	50-100	70-100
11 C ₃₄ /C ₃₃ αβ HOPANES	>1	>1	<1	≤1	<1	≤1	>1
12 BISONORHOPANE INDEX	0	3-15	10-40	10-30	0	20-1000	1-5
13 18α(H)OLEANANE INDEX	0	0	0	0	20-40	0	0
14 Ts/Tm	>1	<1	≤1	<1	>1	<1	>1
15 C ₃₀ αβ HOPANE (ppm)	200-500	200-1600	300-2000	80-300	100-250	10-70	50-800
16 GAMMACERANE INDEX	20-40	20-70	70-120	10-20	0-5	0-25	1-5
Ni-PORPHYRINS (ppm)	tr	0-2800	0-1900	0-400	tr	0-1700	0-800
V-O-PORPHYRINS (ppm)	tr	0-150	0-600	0-3000	tr	0-4000	0-130
** Ni/Ni + V-O PORPHYRINS	-	0.9-1.0	0.6-0.9	0.1-0.3	-	0.3-0.9	0.8-1.0
% AMORPHOUS	55-65	85-90	45-60	50-60	60-70	60-70	85-95
% HERBACEOUS	25-35	5-10	15-25	10-15	10-15	5-10	5-10
% WOODY + COALY	5-10	5-10	10-25	20-30	15-25	20-25	0-5

* For measurement see Appendices.

** Ratios range given only when V=O Porphyrins>trace quantities.

tr:trace

ND:not detected



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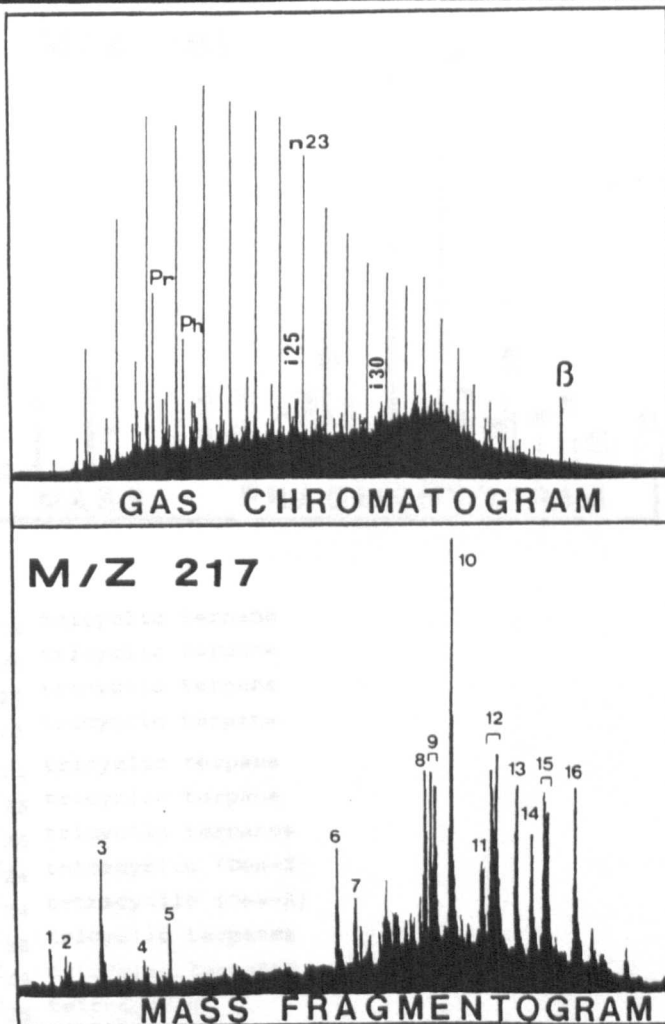
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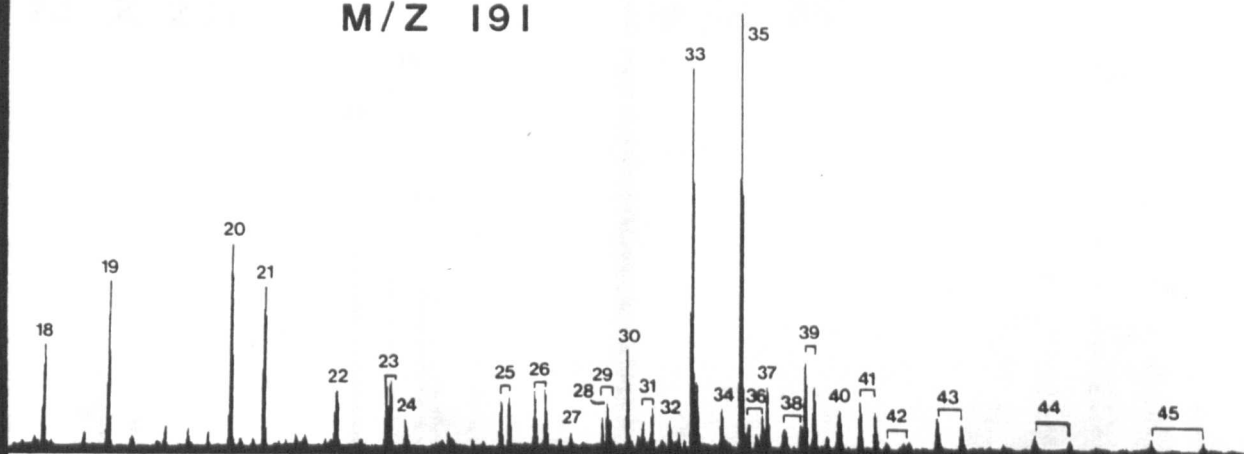
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APPENDIX I



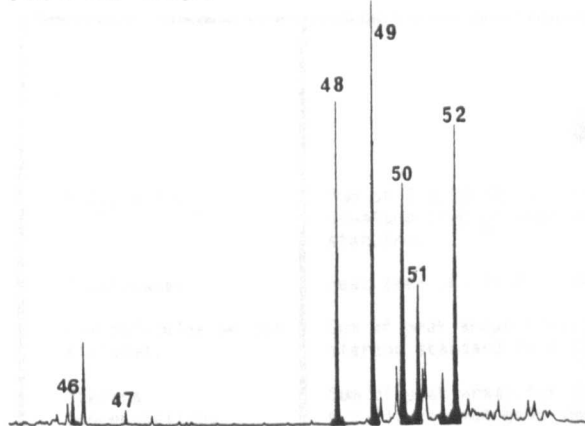
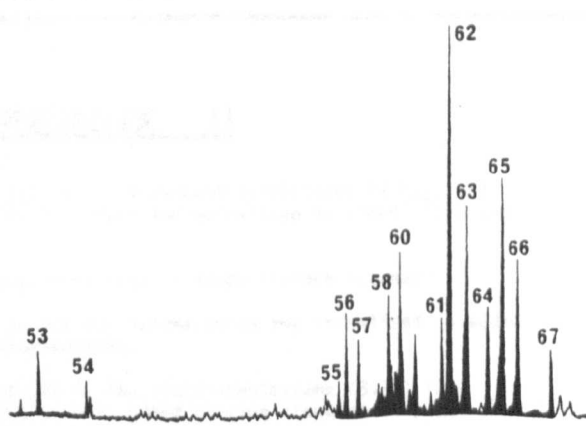
- Pr- 2,6,10,14-tetramethylpentadecane (pristane).
 Ph- 2,6,10,14-tetramethylhexadecane (phytane).
 i-C₂₅ 2,6,10,14,18-pentamethyleicosane (regular).
 i-C₂₅ 2,6,10,15,19-pentamethyleicosane (irregular).
 i-C₃₀ squalane.
 β- β-Carotane.
 1- 13β(H), 17α(H)-diapregnane (C₂₁)
 2- 5α(H), 14β(H), 17α(H)-pregnane (C₂₁)
 3- 5α(H), 14β(H), 17β(H) + 5α(H), 14α(H), 17α(H)-pregnane (C₂₁)
 4- 4α-methyl-5α(H), 14β(H), 17β(H) +
 4α-methyl-5α(H), 14α(H), 17α(H) homopregnane (C₂₂)
 5- 5α(H), 14β(H), 17β(H) + 5α(H), 14α(H), 17α(H)-
 homopregnane (C₂₂)
 6- 13β(H), 17α(H)-diacholestane, 20S (C₂₇-diasterane).
 7- 13β(H), 17α(H)-diacholestane, 20R (C₂₇-diasterane).
 8- 5α(H), 14α(H), 17α(H), 20S (C₂₇-cholestane).
 9- 5α(H), 14β(H), 17β(H), 20R + 20S (C₂₇-cholestane).
 10- 5α(H), 14α(H), 17α(H), 20R (C₂₇-cholestane).
 11- 5α(H), 14α(H), 17α(H), 20S (C₂₈-methylcholestane).
 12- 5α(H), 14β(H), 17β(H), 20R + 20S (C₂₈-methylcholestane).
 13- 5α(H), 14α(H), 17α(H), 20R (C₂₈-methylcholestane).
 14- 5α(H), 14α(H), 17α(H), 20S (C₂₉-ethylcholestane).
 15- 5α(H), 14β(H), 17β(H), 20R + 20S (C₂₉-ethylcholestane).
 16- 5α(H), 14α(H), 17α(H), 20S (C₂₉-ethylcholestane).

M/Z 191



MASS FRAGMENTOGRAM

- 17- C₁₉ tricyclic terpane
- 18- C₂₀ tricyclic terpane
- 19- C₂₁ tricyclic terpane
- 20- C₂₃ tricyclic terpane
- 21- C₂₄ tricyclic terpane
- 22- C₂₅ tricyclic terpane
- 23- C₂₆ tricyclic terpanes
- 24- C₂₄ tetracyclic (Des-E)
- Te- C₂₄ tetracyclic (Des-A)
- 25- C₂₈ tricyclic terpanes
- 26- C₂₉ tricyclic terpanes
- 27- C₂₅ tetracyclic
- 28- C₂₇ 18 α (H)-trisinorneohopane (Ts).
- 29- C₃₀ tricyclic terpanes
- T- C₂₇ 25,28,30-trisnorhopane
- 30- C₂₇ 17 α (H)-trisnorhopane (Tm).
- 31- C₃₁ tricyclic terpanes
- 32- 17 α (H), 18 α (H), 21 β (H)-28,30-bisnorhopane (C₂₈).
- N - 25-norhopane (C₂₉)
- 33- C₂₉ 17 α (H), 21 β (H)-norhopane.
- 34- C₂₉ 17 β (H), 21 α (H)-norhopane.
- 35- C₃₀ 17 α (H), 21 β (H)-hopane.
- 36- C₃₃ tricyclic terpanes
- 37- C₃₀ 17 β (H), 21 α (H)-hopane.
- 38- C₃₄ tricyclic terpanes
- 39- C₃₁ 17 α (H), 21 β (H)-homohopane (22S + 22R).
- 40- C₃₀ gammacerane.
- 41- C₃₂ 17 α (H), 21 β (H)-bishomohopane (22S + 22R).
- 42- C₃₅ tricyclic terpanes
- 43- C₃₃ 17 α (H), 21 β (H)-trishomohopane (22S + 22R).
- 44- C₃₄ 17 α (H), 21 β (H)-tetrakishomohopane (22S + 22R).
- 45- C₃₅ 17 α (H), 21 β (H)-pentakishomohopane (22S + 22R).

M/Z 231**M/Z 253****MASS FRAGMENTOGRAM**

- 46- C₂₀ triaromatic.
 47- C₂₁ triaromatic.
 48- C₂₆ (20S + 20R) triaromatic.
 49- C₂₆ 20R + C₂₇ 20S triaromatic.
 50- C₂₈ 20S triaromatic.
 51- C₂₇ 20R triaromatic.
 52- C₂₈ 20R triaromatic.
 53- C₂₁ 5β(H) monoaromatic.
 54- C₂₂ 5β(H) monoaromatic.
 55- C₂₇ 5β(H), 20S monoaromatic.
 56- C₂₇ 10β(H), 20S monoaromatic.
 57- C₂₇ 10α(H), 20S monoaromatic.
 58- C₂₇ 5β(H), 20R + C₂₇ 10β(H), 20S monoaromatic.
 59- C₂₇ 5α(H), 20S monoaromatic.
 60- C₂₈ 5β(H), 20S + C₂₇ 10α(H), 20R + C₂₈ 10β(H), 20S monoaromatic.
 61- C₂₇ 5α(H), 20R + C₂₈ 5α(H), 20S monoaromatic.
 62- C₂₈ 5β(H), 20R + C₂₈ 10β(H), 20R + C₂₉ 5β(H), 20S + C₂₉ 10β(H), 20S monoaromatic.
 63- C₂₉ 10α(H), 20S monoaromatic.
 64- C₂₉ 5α(H), 20S monoaromatic.
 65- C₂₈ 5α(H), 20R + C₂₉ 5β(H), 20R + C₂₉ 10β(H), 20R monoaromatic.
 66- C₂₉ 10β(H), 20R monoaromatic.
 67- C₂₉ 5α(H), 20R monoaromatic.

APPENDIX II

I-C ₂₅ + I-C ₃₀ :	Sum of 2,6,10,14,18- and/or 2,6,10,15,19-pentamethyleicosane (I-C ₂₅) and squalane (I-C ₃₀) peak areas in RIC trace and normalised to added sterane standard.
β-carotane:	Peak area (β) in RIC trace and normalised to added sterane standard.
Low molecular weight steranes:	Sum of peak areas (1+2+3+5) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
Sterane concentration:	Sum of peak areas for 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram and normalised to added sterane standard (m/z 221 chromatogram).
C ₂₇ /C ₂₉ sterane:	Peak area of 20R 5α,14α,17α(H)-cholestane (10) over peak area of 20R 5α,14α,17α(H)-ethylcholestane (16) in m/z 217 chromatogram.
Diasterane index:	Sum of peak areas of C ₂₇ 20R and 20S 13B,17α(H)-diasteranes (6+7) in m/z 217 chromatogram over sum of peak areas of C ₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) x 100. Low < 30, Medium 30-100, High > 100.
4-Methyl sterane index:	Sum of peak areas of all C ₃₀ 4-methyl steranes in m/z 231 chromatogram recognised using mass spectra and m/z 414 chromatogram) over sum of peak areas of C ₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) x 100. Low < 60, Medium 60-80, High > 80.
Hopane/sterane:	Peak area of C ₃₀ 17α,21B(H)-hopane (35) in m/z 191 chromatogram over sum of peak areas of C ₂₇ 20R and 20S 5α,14α,17α(H)-cholestane (8+10) in m/z 217 chromatogram. Low < 4, Medium 4-7, High > 7.
Tricyclic index:	Sum of peak areas of C ₁₉ to C ₂₉ (excluding C ₂₂ , C ₂₇) tricyclic terpanes (18-23, 25, 26) in m/z 191 chromatogram over peak area of C ₃₀ 17α,21B(H)-hopane (35) x 100. Low < 50, Medium 50-100, High > 100.
C ₃₄ /C ₃₅ Hopane:	Peak areas of C ₃₄ 22R and 22S 17α,21B(H)-hopanes (44) in m/z 191 chromatogram over peak areas of C ₃₅ counterparts (45). Low < 1, High > 1.
Bisnorhopane index:	Peak area of C ₂₈ 28,30-bisnorhopane (32) over peak area of C ₃₀ 17α,21B(H)-hopane (35) x 100 in m/z 191 chromatogram. Low < 10, Medium 10-50, High > 50.
Oleanane index:	Peak area of 18α(H)-oleanane (X) in m/z 191 chromatogram over peak area of C ₃₀ 17α,21B(H)-hopane (35) x 100 in m/z 191 chromatogram.
Ts/Tm:	Peak area of 18α(H)-trisnorhopane (Ts) (28) over peak area of 17α(H)-trisnorhopane (Tm) (30) in m/z 191 chromatogram.
Hopane concentration:	Peak area of 35 measured in RIC and normalised to added sterane standard.
Gammacerane index:	Peak area of gammacerane (40) in m/z 191 chromatogram over peak area of 17α,21B(H)-hopane (35) x 100. Low < 50, Medium 50-60, High > 60.
Bisnorhopane concentration:	Peak area of 32 measured in RIC and normalised to added sterane.
Trisnorhopane concentration:	Peak area of "T" measured in RIC and normalised to added sterane.
Tetracyclic index:	Peak area of C ₂₄ tetracyclic (24) over peak area of C ₃₀ 17α,21B(H)-hopane (35) x 100 in m/z 191 chromatogram.

STRUCTURES

