GIANT DEEP WATER OIL FIELDS IN CAMPOS BASIN, BRAZIL: A GEOCHEMICAL APPROACH

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ABSTRACT—Giant hydrocarbon oil fields are located in the Northeastern portion of the Campos Basin, offshore Brazil, in water depths ranging from 250m (820 ft) to 2000m (6562 ft).
The Albacora field reservoirs are Upper Cretaceous to Tertiary turbidites whereas the Marlim field comprises Oligocene turbiditic sandstones.These reservoirs were filled with petroleum generated from lacustrine calcareous black shales, which were deposited in a closed Upper Neocomian lake system with brackish to saline alkaline water. Migration pathways are through windows in the Aptian salt layer reaching growth faults that act as conduits to turbiditic reservoirs. These hydrocarbons underwent severe bacterial alteration and are presently associated with saline waters.
Cyclic meteoric water circulation associated with changes of the rate of sea level variation, caused biodegradation. In transgressive conditions the process stopped, due to replacement of meteoric water by compaction and clay dehydration waters together with increasing reservoir temperatures and water salinity. Hydrocarbons accumulated in these fields are mainly a mixture of previously biodegraded oils with later migrated oils. The final characteristics of the oils are controlled by the efficiency of different cycles of reservoir filling. The efficiency of each migration event results from a suitable timing association between salt layer windows and fault activity related to each field. It is supposed that the migration events first contributed oil to Marlim, then to Albacora field, therefore Marlim oil is considerably heavier.

RESUMO—Campos de óleo gigante estão localizados 'a Nordeste da bacia de Campos, "offshore" Brasil, em profundidades variando de 250m à 2000m.
O campo de Albacora é constituido por reservatórios turbidíticos do Cretáceo Superior / Terciário enquanto que o Campo de Marlin é constituido por arenitos turbidíticos de idade Oligocênica. Estes reservatórios foram preenchidos por petróleo gerado a partir de folhelhos negros, depositados em um sistema lacustre fechado de idade Neocomiano Superior. Os caminhos de migração existentes são janelas na camada de sal, de idade Aptiano, que se interligam com falhas de crescimento que agem como condutos para os reservatórios turbidíticos. Esses hidrocarbonetos sofreram severa alteração devido à ação de microorganismos e estão associados com águas salinas.
A circulação cíclica de águas meteóricas associada à flutuacões do nivel do mar, causaram biodegradação. Em condições transgressivas o processo é invertido, devido à substituição das águas meteóricas por águas de compactação e de desidratação das argilas associadas ao aumento de temperatura nos reservatórios e de salinidade das águas.
Os hidrocarbonetos acumulados nestes campos são compostos por uma mistura de óleos previamente biodegradados e óleos recentemente migrados. As caracteristicas finais do óleo são controladas pela eficiência dos diferentes ciclos de preenchimento do reservatório.Estes dados levam à suposição que o reservatório de Marlin foi preenchido em fase anterior à Albacora, motivo pelo qual o óleo é consideravelmente mais pesado.

1. INTRODUCTION

The Campos Basin, offshore Rio de Janeiro (Fig. 1), is the most prolific oil province in Brazil. The intense exploratory activity in this basin in the last two decades is the result of substantial technological advances, both in geological exploration and offshore engineering. Today, PETROBRÁS is facing the challenge of producing hydrocarbons discovered in deepwater giant fields (water depths ranging from 250m (820 ft) to 2,000m (6562 ft).

The Albacora and Marlim fields are located about 100 km offshore Cape São Tomé, in the northeastern portion of the basin (Fig. 1). The Marlim complex, which encompasses the Marlim field itself, and some adjacent and proved areas, has a total surface area of 350 km2. It is the largest oil accumulation so far discovered in all of the Brazilian sedimentary basins, with a present estimate of 13.9 billion barrels of oil in place. The reservoirs are Late Oligocene Carapebus turbidite (Campos Formation; Fig. 2), composed mainly of fine to medium grained massive sandstone which forms part of a huge submarine fan system. High flow rates were obtained during formation tests

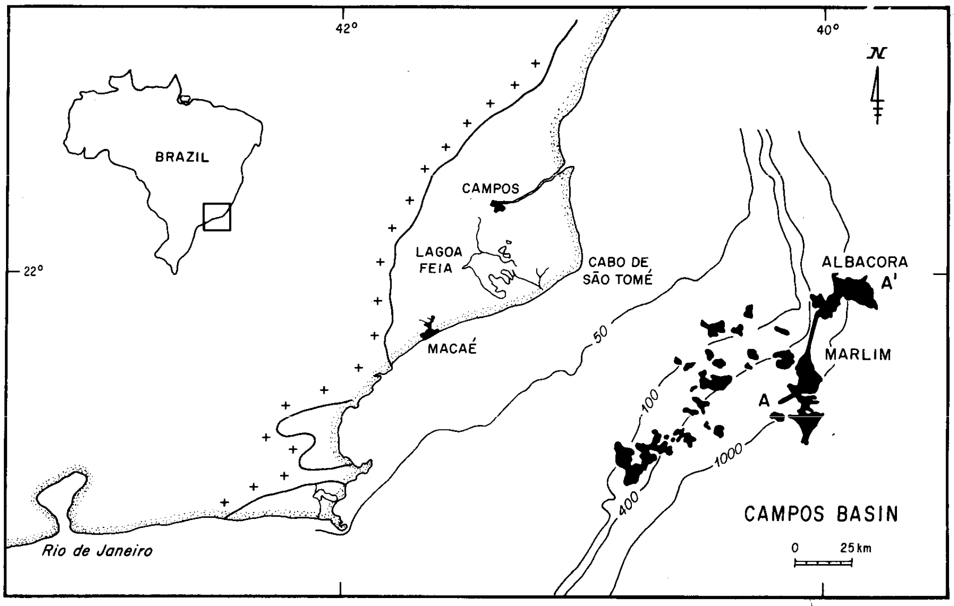

Figure 1. *Location Map: Marlim and Albacora Fields.*

(up to 1.200 m3/d) and the oil water contact has not been identified. Averages porosities are 25-30% and oils are 17-24 °API. The API values generally increase to the South of the Marlim complex.

The area of the ,Albacora field, is appropximately 235 km2, and oil in place is estimated to be 4.5 billion barrels. The main oil occurrences are found in the Albian Namorado sandstones and in the Miocene Carapebus turbiditic reservoir of the Campos formation (Figs.1 and 2).

Oil densities vary from about 30° API in Albian sandstones to less than 18 °API in Miocene reservoir. The large volume of oil accumulated in these fields together with slightly

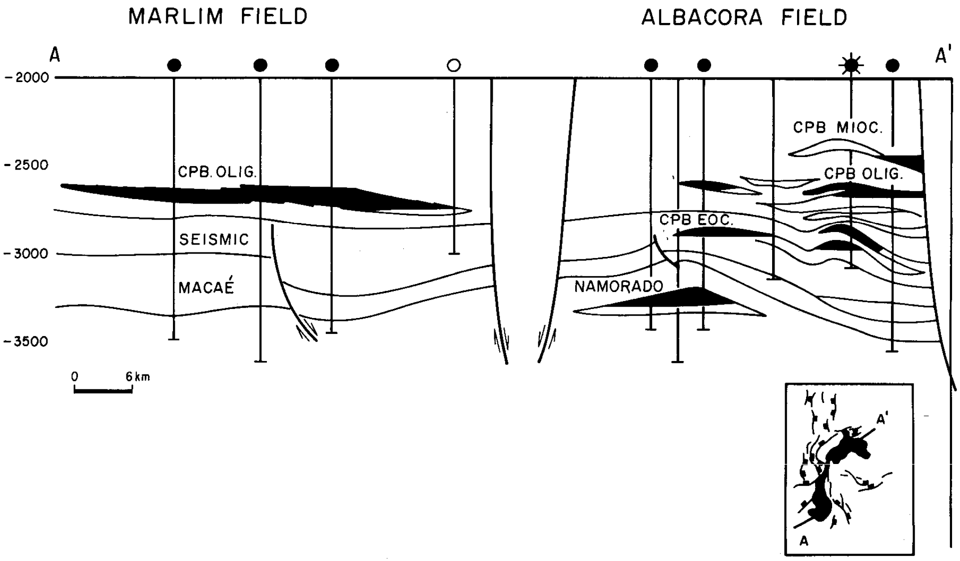

Figure 2. *Reservoirs of Marlim and Albacora oil fields.*

different geochemical features, make it necessary to conduct a detailed study of the oil composition to better understand the processes of generation, migration and accumulation in the area.

2. GEOLOGICAL SETTING

The Campos Basin is a typical passive margin basin. Its origin is associated with the rifting of the Pangea Continent. Based on distinct tectono-stratigraphic characteristics, the sedimentary section can be divided into three large units (Guardado et al., 1990). The continental sequence (Neocomian) includes volcanic rocks (basalts of the Cabiúnas Formation and terrigenous carbonate sediments of the Lagoa Feia Formation, which were affected by extensional tectonics during rifting. The transitional mega sequence (Aptian) is characterized by evaporites, halite and anhydrite of the Lagoa Feia Formation deposited in an environment of relative tectonic quiescence. The marine megasequence (Albian to Recent) is characterized by an initial phase of shallow-water carbonates that graded into deep-water siliciclastics by the end of Cretaceous.

This last unit is characterized by intense adiastrophic structures related to salt movement (Fig. 3).

Although hydrocarbon accumulations are present in reservoirs of the whole stratigraphic column (including fractured basalts of the Cabiúnas Formation, Coquinas of the Lagoa Feia Formation, and porous limestones of the Macaé Formation), the turbiditic sandstones of the Campos Formation constitute the most important reservoirs. In this context, changes of sea-level were very important parameters controlling the deposition of turbiditic fans. The Oligocene turbidites have been analyzed in detail to show this correlation.

The sismo-stratigraphic analysis of the Oligocene package has allowed the identification of at least three depositional sequences, which correspond with sedimentation of extensive turbiditic fans associated with sea-level falls (low stand fan systems). Rises in sea-level were associated with carbonate sedimentation. When transgression is at a maximum, the section is represented by zones of condensed stratigraphy that constitutes excellent stratigraphic markers, particularly in abyssal regions.

Another important element regargind oil accumulation in the basin is the occurrence of adiastrophic structures associated with halokinesis and eastward basin tilting. Faults associated with this tectonism have served as hydrocarbon migration pathways into post-evaporitic reservoirs (Meister, 1984; Guardado et al., 1990). They also played an important role in controlling the distribution of turbiditic sands in the syn-depositional troughs, formed by the salt movement, as evidence by structural inversion in Albacora Field.

3. EXPERIMENTAL AND ANALYTICAL PROCEDURES

The oil and gas samples were submited to bulk

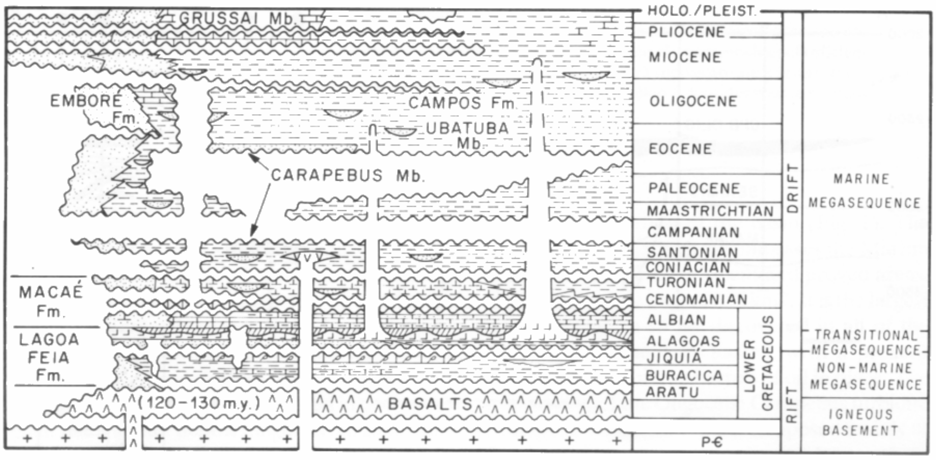

Figure 3. *Chronostratigraphy of the Campos Basin, displaying three megasequences.*

Guardado et al. 1990

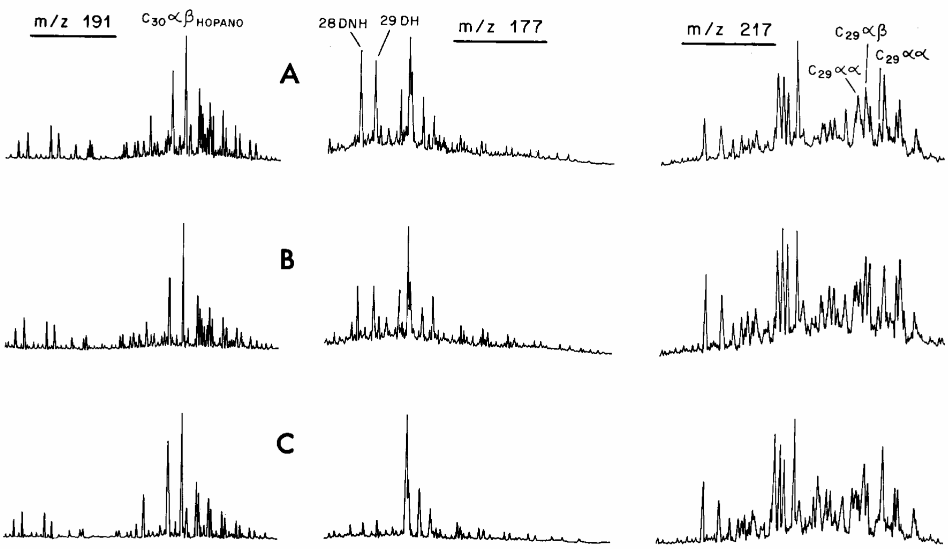

Figure 4. *Mass fragmentograms of terpanes (m/z 191), demethylated hopanes (m/z 177) and steranes (m/z 217), showing the oil source rock correlation among oils from Marlim (A) and Albacora field (B) and one organic extract of Lagoa Feia formation (Upper Neocomian) (C).*

and mass spectrometry, liquid chromatography, carbon isotope analysis according to routine methods.

Bitumen was extracted in a Soxhlet apparatus by refluxing with dichloromethane. The organic extracts were fractionated through solid-liquid chromatography (Cummings and Robinson, 1964).

The GC analyses of alkanes were carried out using a Hewlett Packard 5890A gas chromatograph equipped with a splitless injector and fitted with a 30m DB-5 column. Hydrogen was employed as carrier gas with a temperature programme of 40 to 80° C at 8°C /min and 80 to 320°C at 4°C/min, using fid detector.

The GC-MS analyses were performed using a HP-5890 spectrometer coupled to a Hewlett Packard 5890A GC equipped with on column injector, and fitted with a 25m SE-54 column. Helium was employed as a carrier gas with temperature programme of 55 to 190° at 30° C/ min, 190 to 265°C at 1.5° C/min and 265 to 300 at 2° C/min.

The mass spectrometer was operated in multiple ions detection (MID). The GCMS-MS technique was performed using a triple-quadrupole Finnigan TSQ-70 instrument and a HP 5890A gas chromatograph.

For isotope analyses, the bitumen was oxidized to CO_2 in a continuous oxygen flow preparation line. Carbon isotope ratios of bitumen were measured in a Delta E Finnigan mass spectrometer. The isotopic data were reported in the usual delta notation referenced to the PDB standard.

4. HYDROCARBON GENERATION

Geochemical analyses of source rock extracts and oil samples showed that Marlim and Albacora oils have a common origin (Fig. 4). The sediments of Lagoa Feia Formation, Upper Neocomian lake system, have been identified as the source rocks of the oils accumulated in these fields, as well as, in all the other accumulations in Campos Basin (Figueiredo et al., 1983; Meister, 1984; Pereira et al., 1984; Dias et al., 1987; Trindade et al.,1987; Mohriak et al., 1990; Guardado et al.,1990).

Calcareous black shales from the Lagoa Feia Formation were deposited in extreme anoxic conditions, in closed lacustrine environments having brackish to saline alkaline waters. The extreme anoxic conditions in this lacustrine environment resulted in the deposition of fine, well laminated organic rich black shales, with high-quality organic matter composed almost entirely type I kerogen, originated from lipid-rich algal and bacterially derived material (Bertani et al., 1984; Mohriak et al.,1990).

Detailed source rock mapping, integrated with geological and geophysical data, identified the depocenters of the best source intervals. The total thickness of the effective source rock can reach 200m in some structural lows (Dias et al.,1987).

The biomarker correlation between source rock organic extract and oils from Marlim and Albacora fields appears to establish the best link in terms of generation aspects, (Fig. 4). However, due to deep rock depocenters that have not been drilled yet, normally, oils are more mature than available organic extracts (Dias et al.,1987).

The source rocks in the area reached the oil generation window about 85 Ma (Santonian / Coniacian) and did not reach the overmature zone (Fig. 5). The low occurrence of known associated gas in the area suggests that this source rock is not in the overmature stage. This hypothesis is also substantiated by carbon isotope ratios of methane ranging from -45 to -52 parts per mil, associated with C_{2+} ranging from 10 to 15 percent, indicating that these gaseous hydrocarbons were, in general, originated within the oil window (Fig. 6).

The kinetic modeling reinforced the idea that liquid hydrocarbons are still being generated. This relatively low source rock maturation is a result of the low thermal flux, which was due to a reduced crustal thinning (Dias et al.,1987).

5. PETROLEUM MIGRATION

The Neocomian source rocks are separated from the main reservoirs by a salt layer (Fig. 3). The oil migration from the source rocks to reservoir, therefore required windows in the evaporites. These openings were formed by salt layer thinning and movement (Meister, 1984; Pereira et al., 1983) due to increasing sedimenta load.

Oil movement on the Lower Cretaceous pre-salt phase occurred through porous strata and rift-phase faults, reaching the base of the salt layer. In the post-rift phase, the oils proceeded through growth-faults associated with salt layer openings. Additional pathways were provided by erosional unconformities along canyons walls (Guardado et al., 1990).

The main path for oil migration in the Marlim Field is interpreted as the fault systems that border the field to the east (Fig. 7). The connection of the faults with an opening in the salt layer and variations on oil chromatographic composition within the field are suggested evidences for this hypothesis.

In the Albacora Field, the main hydrocarbon migratiòn pathway is the fault on the Northern Flank of the Field. Multiplicity of reservoirs in Albacora Field, compared to a single turbiditic deposit in Marlim Field is related to more intense

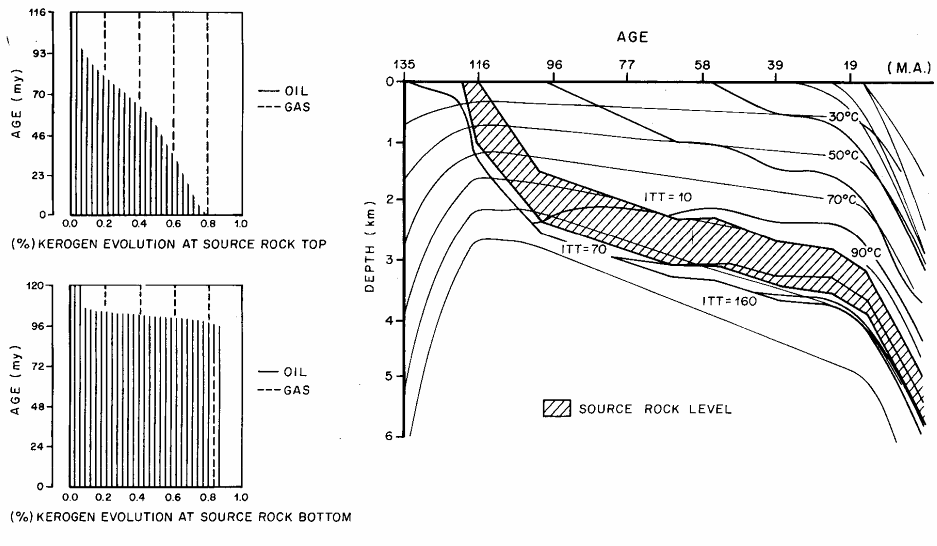

Figure 5. *Hydrocarbon Generation Modelling.*

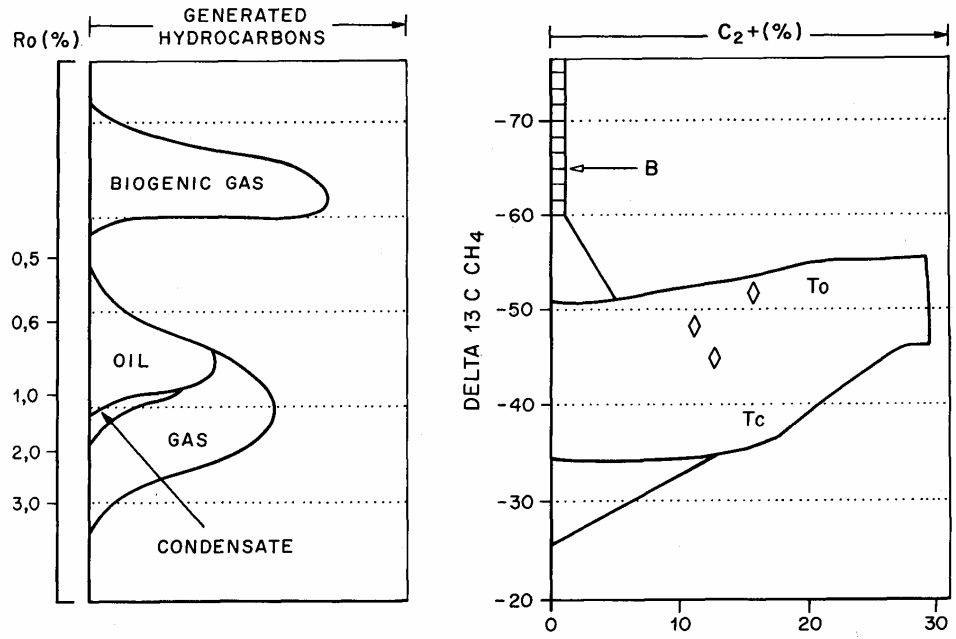

Figure 6. *Genetic characterization diagram of natural gas in Campos Basin.*
(Modified from Schoell, 1980)

fault activity in the Albacora field area due to salt movement.

6. OIL CHARACTERIZATION AND BIODEGRADATION

Data for oil samples from Campos Basin studied through a multidisciplinary geochemical approach suggest that the petroleum recovered were derived from the same source rock. These source rocks were lacustrine calcareous black shales deposited in a closed Upper Neocomian lake system and derived from type I kerogen. The oils from different areas and units have undergone different degrees of biological degradation and water-washing.

Oils of the Campos Basin are intermediate between paraffinic and naphthenic. On the average, unaltered oils have 25° API gravity whereas extremely biodegraded oils have a minimum of 10 °API gravity. Sulphur content ranges from 0.22 to 1.73% and averages about 0.5%. The acidity index is low in unaltered oils (around 0.1 to 0.3 mg KOH/g) but reaches 1.5 mg KOH in the most biodegraded oils (Guardado et al., 1990)

Carbon isotopic ratios, $\delta^{13}C$ ‰ / PDB on 59 whole oil samples, ranged from -22.7 to -26.5 parts per mil with 80% between -24.0 and -25.5 parts per mil. The oils recovered from younger reservoirs tend to have isotopic ratios slightly

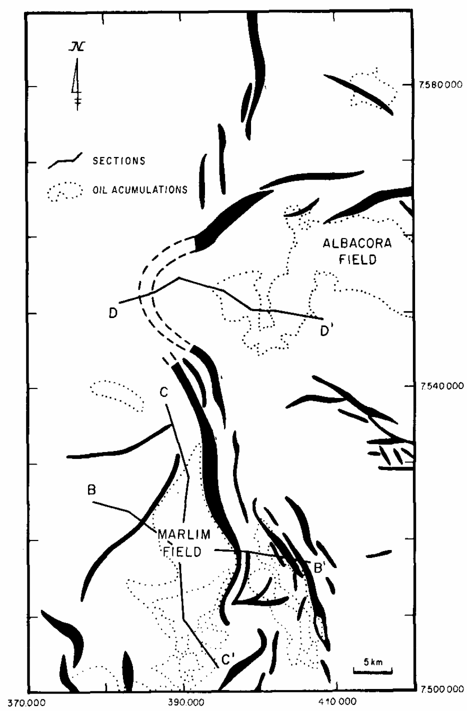

Figure 7. *Major faults in deep water area of Campos Basin.*

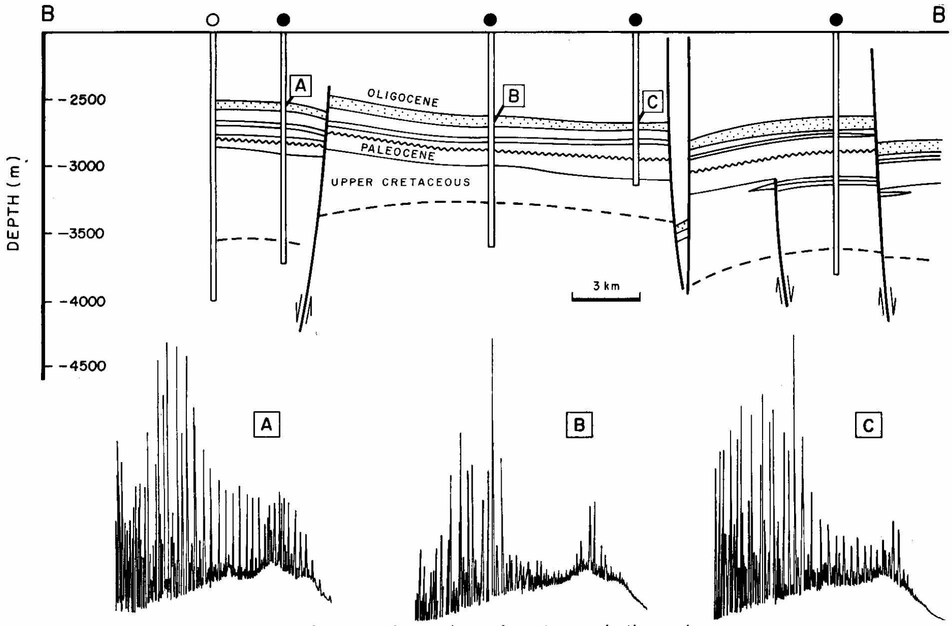

Figure 8. *Marlim complex geological section and oil gas chromatograms.*

more negative, perhaps because of isotopic fractionation during secondary migration.

Gas chromatograms of autochtonous oils recovered from the Jiquiá reservoirs are very similar to chtomatograms of nondegraded oils found in reservoir rocks above the salt section. The chromatograms show predominance of n-alkanes in C15range, a decrease in concentration of higher molecular weight components, pristane/phytane ratios of 1.5 up to 2.0 and the presence of isoprenoid compounds. Oils that accumulated in Lower Albian to Oligocene reservoirs of the marine megaseqüence have been subjected to bacterial alteration and water washing. These processes resulted in development of heavier oils, first by disappearance of n-pafaffins, branched alkanes and some naphthenes. Biodegradation has also caused a decrease in the proportion of saturated hydrocarbons and an increase in the proportion of nitrogen, sulphur and oxygen compounds. Paraffins decrease from 80% to 30%, and resins plus asphaltenes increase from 10 to 60% as a result of biodegradation (Guardado et al., 1990).

Terpanes obtained from oils of the Jiquiá to Oligocene reservoirs show similar fragmentograms, characterized by high relative abundance of triterpanes in relation to diterpanes and by low relative abundance of gammacerane. Steranes were present in very low concentrations in these oils. Demethylated hopanes thought to be a product of hopane biodegradation, occur in some heavier oils (Guardado et al., 1990)

Albacora Field oils are well correlated with the other oils recovered from the basin, but Marlim oils display an unusual n-alkane distribution. Marlim oils recovered in the main reservoir, are rich in low molecular, weight components, whilst n-C18$^+$ compounds are absent in some samples and present in small amounts in others (Fig. 8). The oils from Marlim and Albacora show °API gravity densities that very from 16 to 31 ° (Fig. 9), sulphur contents ranging betwcen 0.31 to 0.84% (Fig. 10) and saturated hydrocarbon contents from 34 to 62% (Fig. 11). N-alkanes and 25-norhopanes are observed in oils from both fields. However, Marlim Field oils display a higher proportion of 25-norhopanes (Figs.12 and 13).

Volkman et al., (1983) proposed that 25 norhopanes are not formed until an oil is severely biodegraded, when all the n-alkanes have disappeared. Among polycyclic alkanes, "demethylated hopanes" have an unclear origin. Since their first detection by Reed (1977) in a weathered oil-impregnated sandstone from Utah, their presence in an oil has been regarded as indicative of heavy biodegradation. However, another pathway with explains the origin of "demethylated hopanes", is to consider that they occur preexisting biomarkers in source rocks and are subsequently concentrated in the associated crude oils by selective biodegradation of more degradable structured (i.e. steranes, regular alfa-beta hopanes, etc. (Goodwin et al., 1983; Howell et al., 1984; Chosson et al., 1992). Blanc et Connan, 1991, supported this hypothesis using a statistical approach of numerous GC-MS data.

The presence of both n-alkanes and 25-norhopanes in an oil may be indicative of mixing between biodegraded and non degraded oils. The occurrence of demethylated hopanes at C10 (25-norhopanes) is regarded as a key indication of paleobiodegradation in an apparently non biodegraded oil containing n-alkanes (Rulikotter and Wendisch, 1982). According to several authors (Seifert and Moldowan, 1979; Volkman et al., 1983; Philp, 1983) 25-norhopanes would result from biotransformation of hopanes during the biodegradation in the reservoir of crude oils. However this hypothesis is questionable (P. Blanc and J. Connan, 1992) since biodegradation is a bioxidation process wich should generate functionalized structures. It is noticeable however, that free carboxilic acids were found in oils from Albacora field (Rebouças, L.M.C.,1993).

In Albacora and Marlim areas 25-norhopane ratios with norhopane and hopane appear to show a good correlation (Fig. 14). These ratios, plotted in maps (Figs. 12 and 13) show biodegradation tendencies for the studied area. The process seems to increase toward to the well 1-RJS-151, where the biggest fault systems in the ara are converging. These faults could have acted as conduits for oil. However, they also permitted the best conditions for biodegradation, through intensive meteoric water circulation (Trindade, 1987). Both maps, for demethylated norhopane / hopane (Fig. 13) and demethylated norhopane / norhopane (Fig. 12), show the same pattern of biodegradation. They decrease to north and south / southeastern, therefore the first ratio seems to give a better resolution.

Hydrodynamics and hydrogeochemistry studies (Figueiredo et al., 1983; Pereira et al., 1984), showed that probably, extensive meteoric freshwater incursion occurred in the past, during the Pleistocene as a result of a fall in sea level. During such events freshwater extended deeper and farther basinward (Figs. 15A and 15B). This hydrologic regime was followed by a system in which saline brines (from sediment compaction)

Figure 9. *Tendency of API^{O} densities for oligocene reservoir oils.*

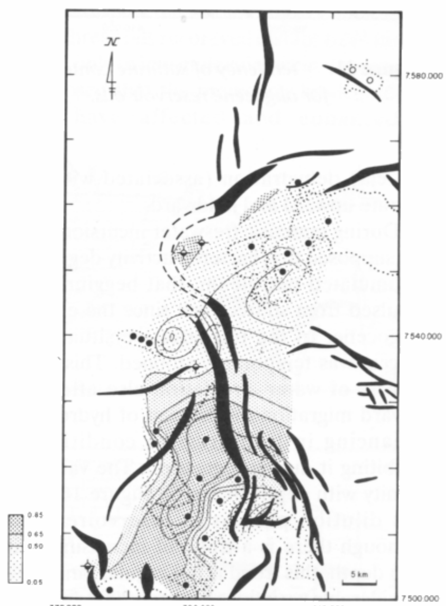

Figure 10. *Tendency of sulihur contents API^{O} densities for oligocene reservoir oils.*

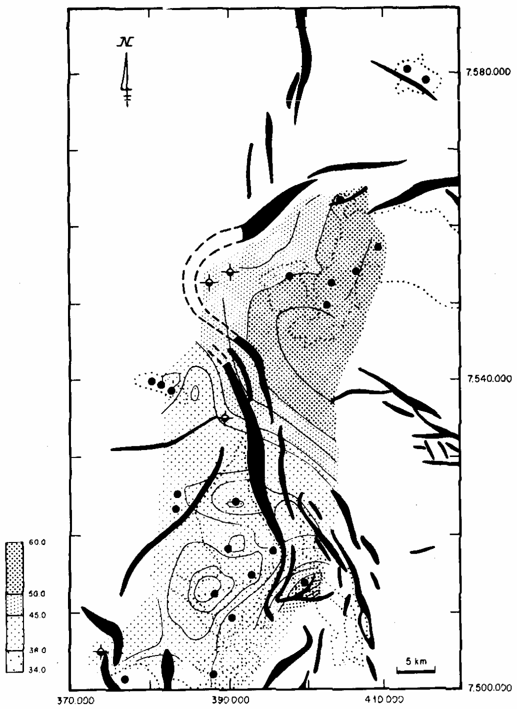

Figure 11. *Tendency of saturate contents (%) for oligocene reservoir oils.*

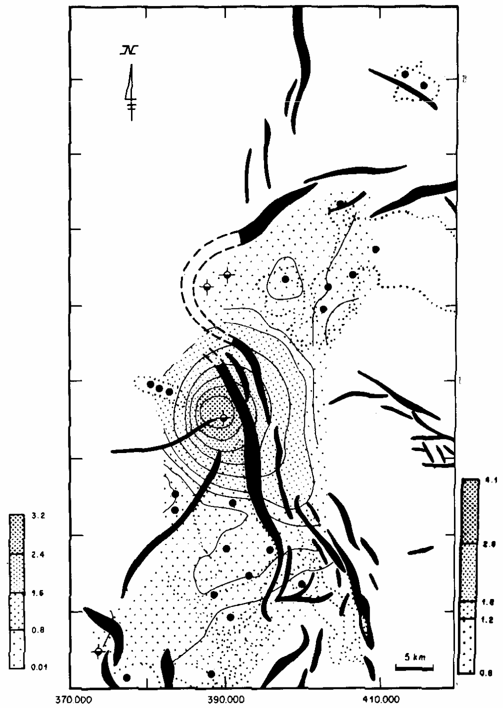

Figure 12. *Tendency of demethylated norhopane/ norhopane ratio for oligocene reservoir oils (biodegradation index).*

and clay dehydration (associated with water) migrate upward and landward.

During meteoric freswater incursion periods, it is supposed that bacterial activity degraded the accumulated petroleum, that begginned to be expulsed from source rock since the end of the Oligocene. In the transgressive situation, this process was temporarily stopped. This dynamic process of water circulation also affected the upward migration mechanism of hydrocarbons, enhancing in transgressive conditions and inhibiting it during regression. The variation of salinity with depth shown, in Figure 16, reflects this dilution process in reservoired water. Although there is a trend of increasing salinity with depth, this trend is not regular, and present considerable variations between 2000 and 3500m.

The mixture process that occurred in the successive filling stages established the fingerprint and the final characteristics of the oils. This mixture process was a function of filling efficiency during migration pulses.

The primary oil quality was established by reservoir filling conditions before biodegradation occurred. It appears that in the Marlim area the efficiency was greater than in the Albacora field, suggesting that halokinesis activity starded in Marlim area earlier than in Albacora. In the Marlim field the mixture process was incomplete and the oils are heavier than in the Albacora, with a possibility that biodegraded oil could have partially sealed the reservoir. This fact could be observed in section CC' (Fig. 7 and 17). The oils presented lower saturated hydrocarbons contents (Fig. 11), higher sulphur percentage (Fig. 10) and higher pristane/nC17 (Fig. 18), and phytane/ nC18 (Fig. 19), lower thermal evolution (Fig. 20) and lower API gravity (Fig. 9) than in the Albacora field. In the South area of the Marlim complex and Albacora Field (Figs. 9 and 21),

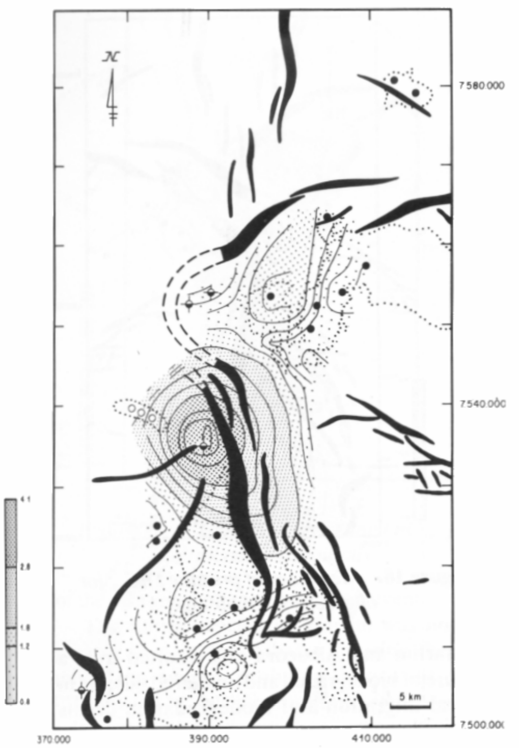

Figure 13. *Tendency of demethylated norhopane/ hopane ratio for oligocene reservoir oils (biodegradation index).*

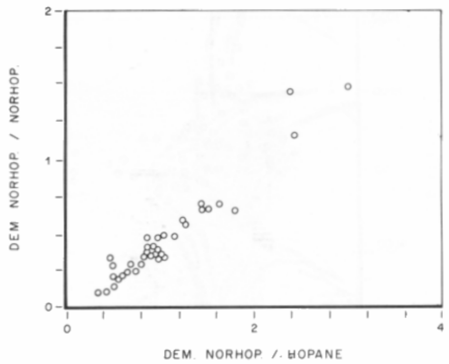

Figure 14. *23, 25 bis nor 17 α hopane / norhopane ratio versus 23, 30 bis nor 17 α hopane / hopane plot oils from the Marlim and Albacora fields.*

later oil contribution enhanced oil quality, and in this case it seems that conventional gravitational segregation was the field filling model. The lightest gas/oil ratios occur in the upper reservoirs, as shown in the gas / oil ratio map (Fig. 22).

Oil compositional variations in BB' sections through Marlim Field (Figs. 7 and 8) corroborate the model of oil migration by the fault on the east of the field. Oils recovered from wells close to the fault display the whole range of *n*-alkanes up to C_{39} whreas oils recoreved distant from the fault are rich only in low molecular weight nalkanes. It is proposed that the previously biodegraded oil could have affected and enhanced the

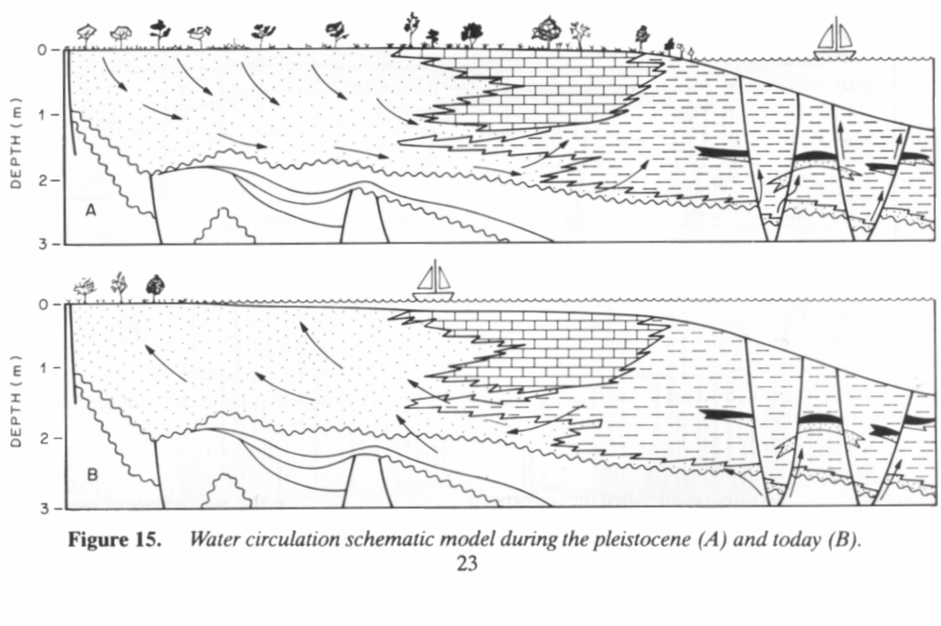

Figure 15. *Water circulation schematic model during the pleistocene (A) and today (B).*

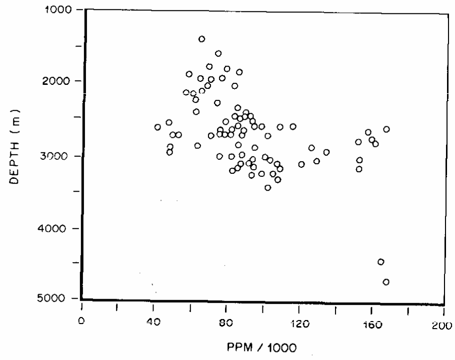

Figure 16. *Water salinity content versus depth graph from samples from Campos Basin.*

fractionation of newly migrating and more mature oil within the reservoir.

Isotope ratio distributions of oils (Fig. 23) also suggests that migration could affect these data and seems to reflect an offshore to onshore migration, with heavier oil, enriched in ^{13}C, accumulated in more offshore reservoirs and lighter oils, enriched in ^{12}C in Albacora Field.

7. CONCLUSIONS

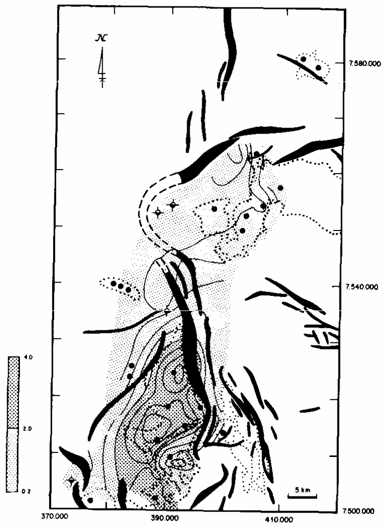

Figure 18. *Tendency of pristane / nC_{17} for oligocene reservoir oils.*

Marlim and Albacora oils resulted from a mixture of biodegraded and unaltered oils due to several migration and biodegradation events during the successive stages of reservoir filling. Final composition of these oils was the product

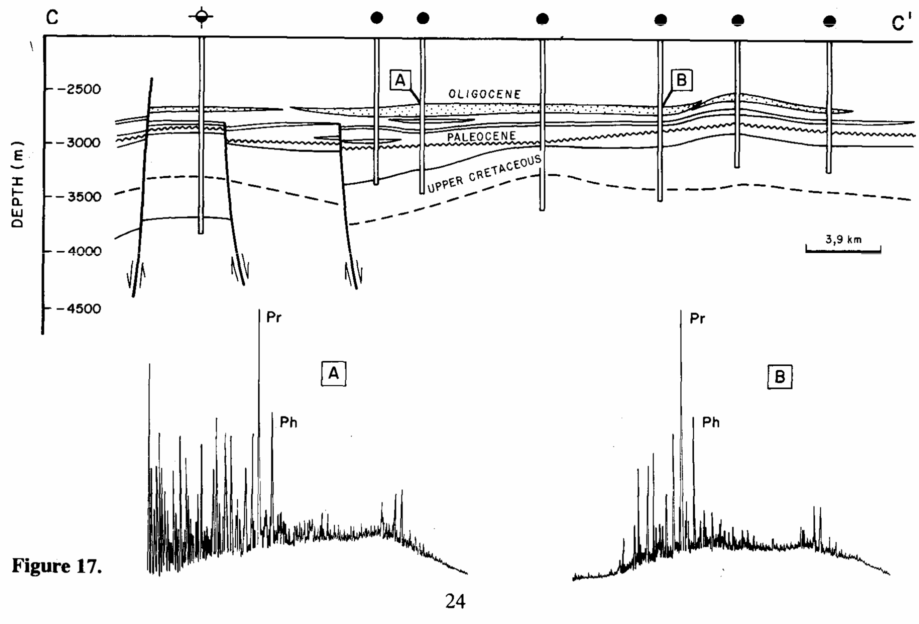

Figure 17.

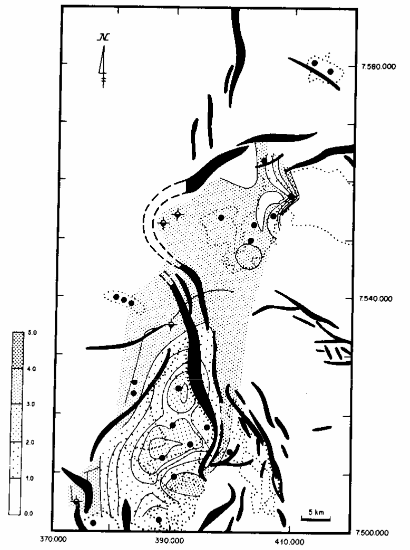

Figure 19. *Tendency of phytane / nC_{18} for oligocene reservoir oils.*

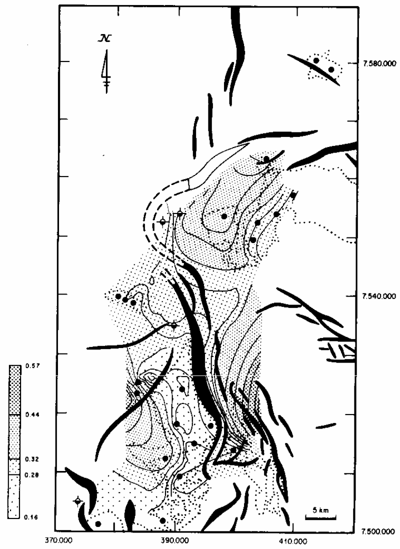

Figure 20. *Thermal evolution tendencies based on tricyclic pentaciclyc terpanes ratio.*

of the efficiency of each migration event.

The filling process in Marlim was notably greater than in the Albacora during the first migration events, probably due to different efficiencies of salt windows and fault systems related to each field.

Cyclic circulation of meteoric water associated with sea level variations created conditions for biodegradation, enhancing in regressive times and stopping in transgressive.

The greater reservoir filling efficiency in the Marlim Field, relative to Albacora, during the

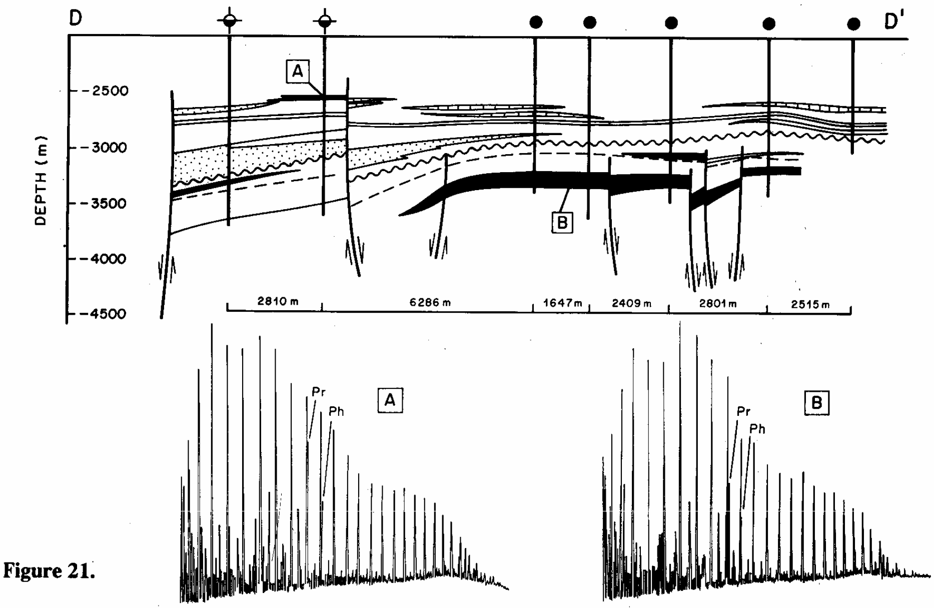

Figure 21.

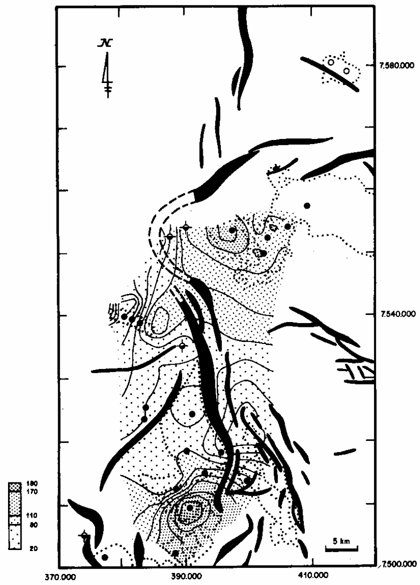

Figure 22. *Tendency of gas oil ratios for oligocene reservoir.*

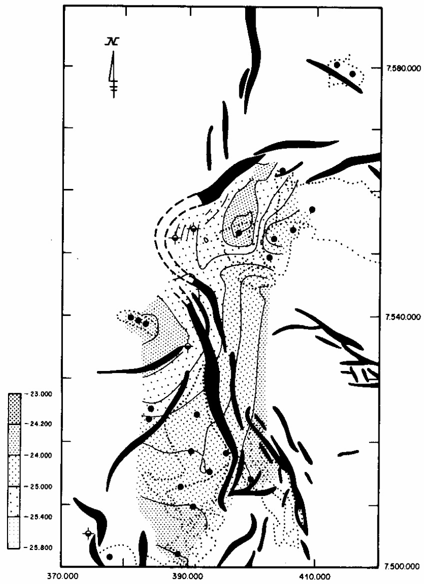

Figure 23. *Tendency of delta 13C ratios for oligocene reservoir oils.*

migration events that preceded bacterial alteration, appears to suggest that halokinetic activity began in the Marlin area (South) earlier than in Albacora area (North) .

The cementation degree in Marlim reservoir was lower than in Albacora Area, reinforcing the hypothesis that oil inhibited cementation reactions in Marlin.

While in Albacora Field a conventional gravitational segregation occurred, in Marlim Field, biodegraded oil could have acted like a partial seal of the reservoir, not allowing this process.

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