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1.14 Palaeoenvironmental changes in an Aptian restricted marine basin: the Machiques Formation of Western Venezuela

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Although the La Luna Formation is the best known and most important petroleum source rock of the Maracaibo Basin in Western Venezuela, several other organic-rich units have been described in the area (Gonzalez de Juana *et al.*, 1980). These include the Machiques Formation which formed during partial drowning of the Venezuelan carbonate platform in the latest Aptian-earliest Albian (Martinez and Hernandez, 1992). The distribution of the Machiques Formation coincides with an area of increased subsidence called the Machiques-Perija Trough which formed part of a graben system on the Proto-Caribbean Plate (Mendez, 1989). The boundaries of this trough are difficult to define because they have been masked by further orogenic episodes and movement of the Caribbean Plate, but its original extent was probably between 10,000 and 70,000 km^2.

This work presents a geochemical evaluation of the Machiques Formation which shows a strong heterogeneity at the sequence scale. Over 60 samples were collected from Quebrada Maraca, in the central area of the Perija Foothills at the Western boundary of the Maracaibo Basin, where the Machiques Formation is approximately 160 metres thick. They were evaluated using bulk geochemical and stable isotopic analysis, molecular geochemistry and optical methods.

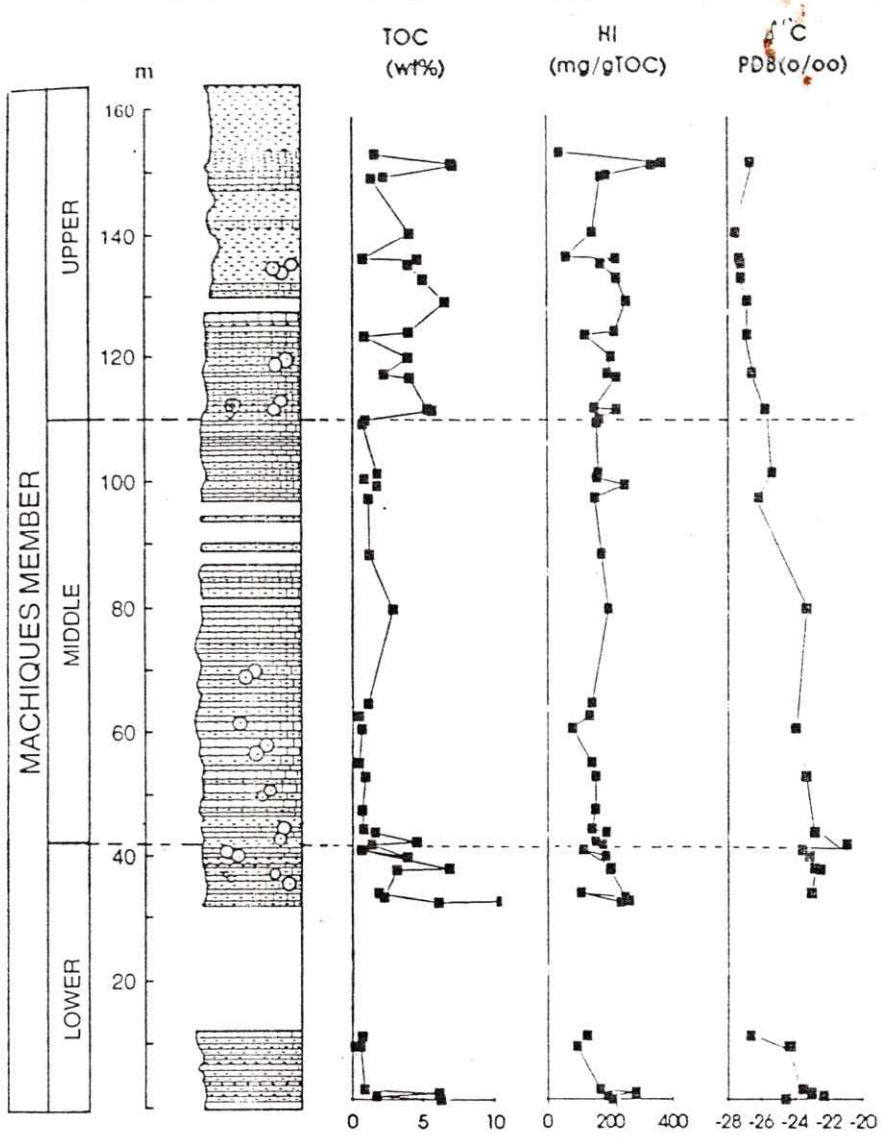


Figure 1: Lithology, %TOC, Hydrogen Index and $\delta^{13}C$ of the Machiques Formation in Quebrada Maraca.

Variations in Bulk Geochemistry

Variations in lithology, organic carbon (TOC), hydrogen index (HI) and isotopic signature of the organic carbon allow the division of Machiques Fm. into three different units (Fig. 3):

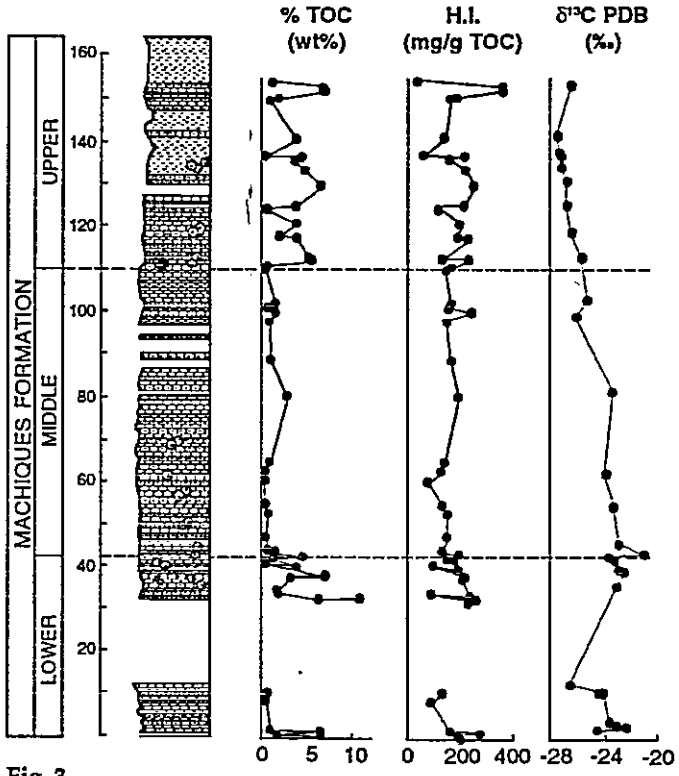


Fig. 3

Upper Unit:

- Marls with laminated shales at the top of the unit
- Ratio marl: shale is approximately 2:1
- Thickness: marls 20-40cm, shales: 10cm-10m
- TOC values of up to 7% (carbonate-poor layers), down to 1% in uppermost shale (10m thick)

Middle Unit:

- Mainly limestones and marls
- Ratio limestone: marl is about 4:1
- Thickness: marls 1-25cm, limestone 30-100cm (progressively thicker to the top of the unit)
- TOC values are less than 30%

Lower Unit

- Rhythmically interbedded marls and shales with a few limestones
- Ratio marl: shale is approximately 3:1
- Thickness: shales <15cm, marls 10-15cm
- TOC values of shale up to 10%, varies strongly with carbonate content, often less than 1% in marls

Organic matter variation

The organic matter is mature with respect to hydrocarbon generation (vitrinite reflectance 0.8 to 1.0% Ro; Tmax. 442 to 446 °C; complete side-chain isomerisation of hopanes and steranes).

In spite of the lithological variation, microscopic analysis of the kerogen shows that the organic matter is mainly amorphous with only minor contribution of structured organic matter (pollen, spores) in the uppermost shale. GM-MS analysis displays few differences in biomarker composition in the two lower units (Fig. 4a,b,c). However, the upper unit has several biomarker features which make it more similar to the black shales of the La Luna Fm. (deposited in a moderately deep, open carbonate platform), including a relatively lower tricyclics/hopanes ratio, lower amounts of 18α(H)-trisnorneohopane (Ts), presence of methylhopanes and a higher ratio of steranes/diasteranes.

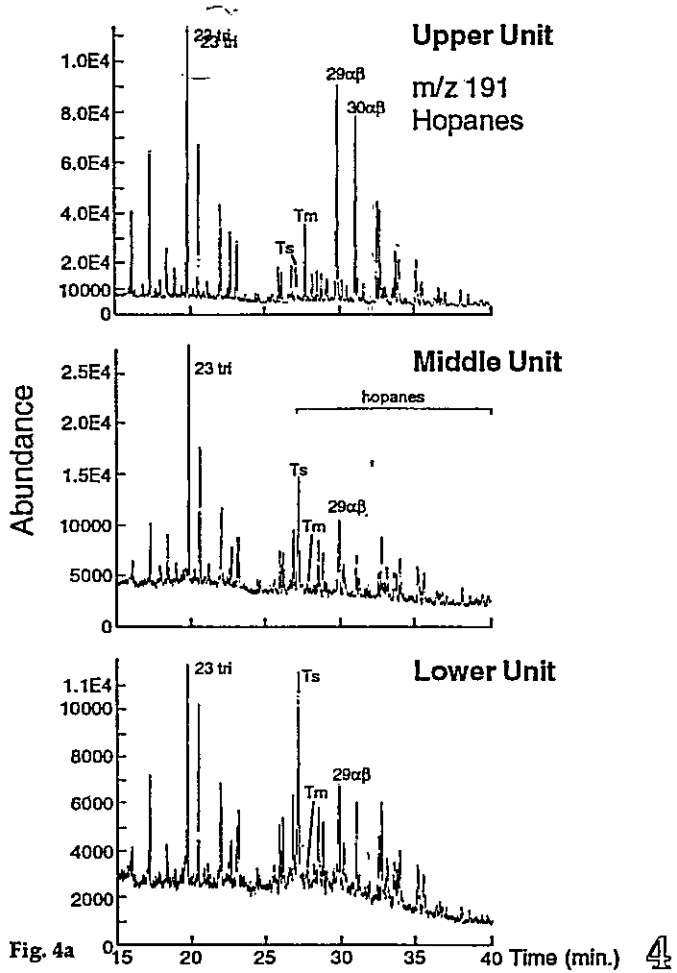


Fig. 4 Typical mass chromatograms of the units of Machiques Fm.

Fig. 4a

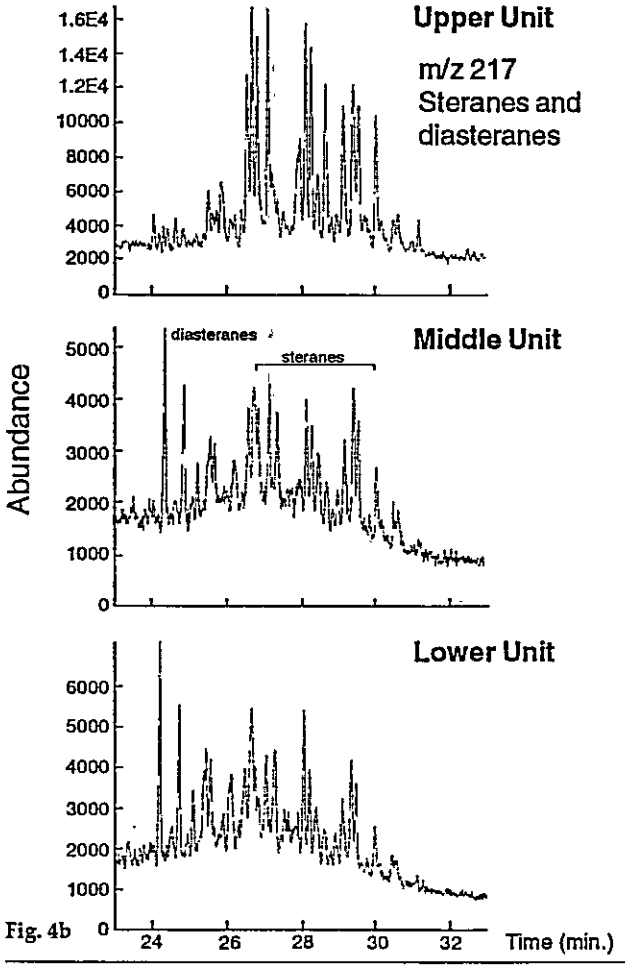

Upper Unit
m/z 217
Steranes and
diasteranes
1.6E4
1.4E4
1.2E4
10000
8000
6000
4000
2000
0
diasteranes
steranes
Middle Unit
Abundance
5000
4000
3000
2000
1000
0
Lower Unit
6000
5000
4000
3000
2000
1000
0
24
26
28
30
32
Time (min.)

Fig. 4b

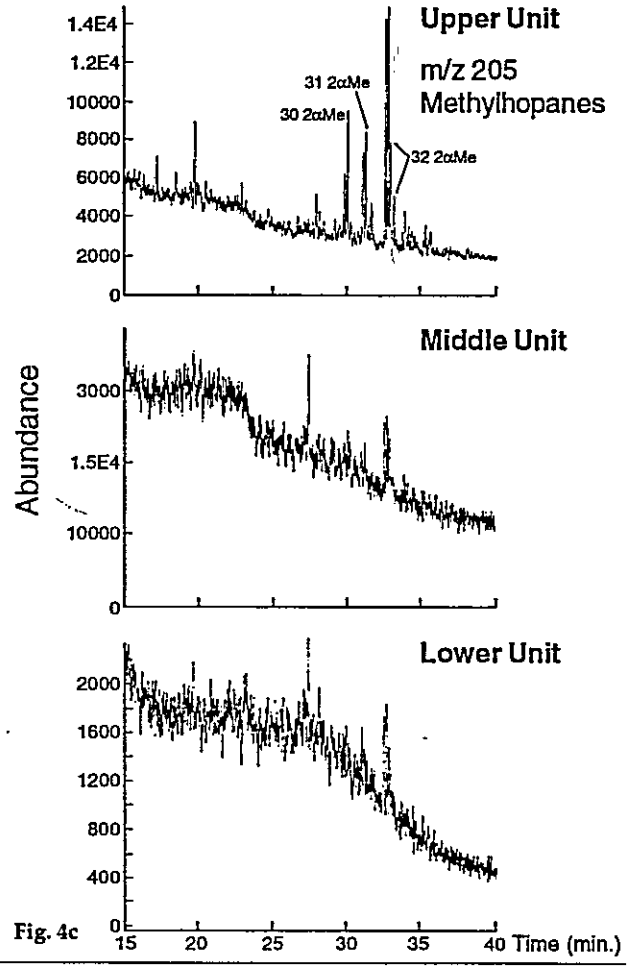
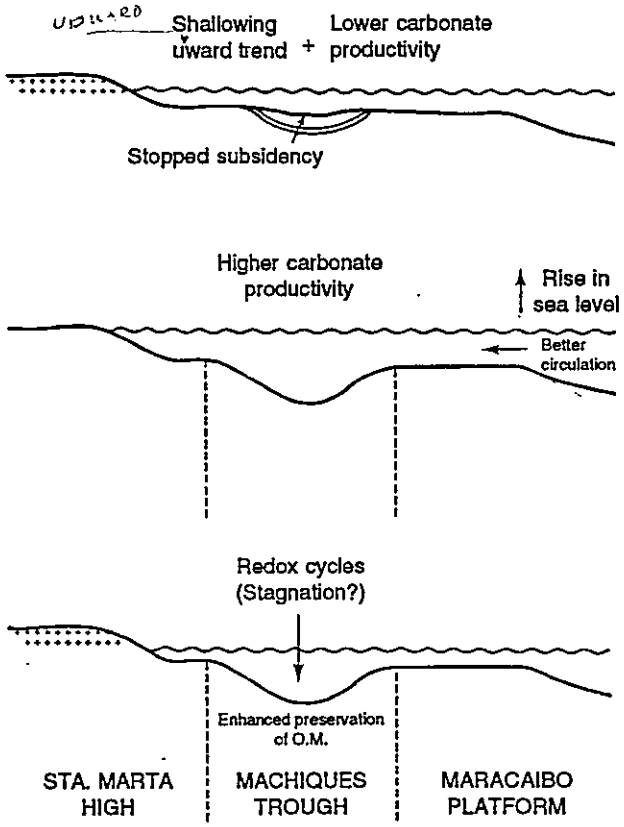

Upper Unit
m/z 205
Methylhopanes
1.4E4
1.2E4
10000
8000
6000
4000
2000
0
31 2αMe
30 2αMe
32 2αMe
Middle Unit
Abundance
3000
1.5E4
10000
0
Lower Unit
2000
1600
1200
800
400
0
15
20
25
30
35
40
Time (min.)

Fig. 4c

A depositional Model of Machiques Fm.



Upper Unit:
The bottom part of this unit records short intervals of more strongly dysoxic to anoxic conditions associated with the latest periods of stagnation. Subsidence in the Machiques Trough became similar to the rate on the surrounding platform, with progression to well oxygenated conditions. The uppermost shale has normal shallow marine fauna.

Middle Unit:
The $\delta^{13}C$ values are enriched $\delta^{13}C$ by 2-3‰ (-20.5 to -23.5‰). This could be related to an increase in carbonate productivity, associated with improved water circulation and nutrient supply. These conditions may be produced by the coincidence of subsidence and sea level rise. Micropalaeontological data support this hypothesis with the appearance of pelagic foraminiferal fauna (Hedbergella) and radiolaria, suggesting deep to moderate palaeo-depth. During this time span the Machiques Trough received only small amounts of terrigenous sediment.

Lower Unit:
Initial high subsidence along the Machiques Trough may have produced stagnation or poor circulation, leading redox cycles and development of organic-rich shale-marl rhythms of the lower unit. $\delta^{13}C$ values range from -22.3 to -25.7‰ PDB.

Fig.5 A depositional model for Machiques Fm.

Conclusions

❑ The proposed depositional model is consistent with the geochemical variations observed in the Machiques Fm. responding to two main processes :

- *Variations in the productivity of carbonates*
- *Redox cycles*

❑ The organic matter input into the Machiques Trough is mainly marine. However, some biomarker differences are observed. Continuing research on both biomarker and kerogen composition and their relationships with lithology and palyno-facies should clarify the palaeoenvironmental significance of these differences. However, the micropalaeontological and isotopic data presented here suggest that these variations can be interpreted as a response to palaeoecological changes associated with a shallowing upward trend within the Machiques-Perija Trough around the Aptian-Albian boundary.

Acknowledgments:

We would like to extend our thanks to Prof. Judy McKenzie and Daniel Ariztegui for their assistance in obtaining the stable isotope data at E.T.H., Zürich, Switzerland. We are also grateful to Dr. Richard Tyson (Newcastle University) for helpful comments and Dr Max Furrer (Corpoven, Venezuela) for the micropalaeontological analyses.

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RESULTS AND DISCUSSION

Variations in lithology, organic carbon content (TOC) and hydrogen index (HI; Figure 1) allow the division of the Machiques Formation into three different units. The lower unit is characterised by rhythmically interbedded marls and shales, individual layers commonly being less than 20 cm. thick. It contains the highest TOC values seen within the Machiques Formation (up to 10%), but the organic content varies strongly with carbonate content, decreasing abruptly in the lighter-coloured marls (less than 1% TOC). The layers with high TOC values are finely laminated and pyrite-rich, whilst the low TOC layers show abundant macrobenthos, suggesting fluctuations in palaeo-oxygenation. The middle unit represents a change to more uniform environmental conditions with thicker carbonate layers and lower TOC values (<3%), but the upper unit again records short intervals of more strongly dysoxic to anoxic conditions with deposition of organic-rich laminated shales with up to 7 % TOC.

Micropalaeontological observations on thin sections indicate changes in the ecology of the environment that could be related to variations in the palaeowater-depth during deposition of the Machiques Formation. The middle unit of the Formation shows the appearance of pelagic foraminiferal fauna (*Hedbergella*) and a decrease in the number of radiolarian specimens compared with the basal unit, perhaps suggesting a change from deep to moderate palaeo-depth. The uppermost shale beds of the upper unit present an abundance of normal shallow marine macrofauna including gastropods and pelecypods, indicating a progression to the more oxygenated conditions that had been maintained on the surrounding Venezuelan carbonate platform during latest Aptian-earliest Albian times.

The maturity of the organic matter in the Machiques Formation in Quebrada Maraca is quite homogeneous through the whole interval, being mature with respect to hydrocarbon generation (vitrinite reflectance 0.8 to 1.0% Ro; Tmax. 442 to 446 °C; complete side-chain isomerisation of hopanes and steranes).

The kerogen of the differentiated units falls into three distinct isotopic regimes. The $\delta^{13}C$ values range from -22.3 to -25.7‰ PDB in the lower unit, are enriched in $\delta^{13}C$ by 2-3‰ in the middle unit (-20.5 to -23.5‰) and become lighter again in the upper unit (-25.5 to -27.7‰). These isotopic signatures are likely to reflect the changing organic matter input to the sediments. However, a major change in the CO_2 isotopic equilibrium across the Aptian-Albian boundary cannot be discounted and requires further research and comparison with both carbonate and organic carbon stable isotopic ratios of similar palaeoenvironments at different localities.

The organic matter in the Machiques Formation presents notable geochemical differences compared with that of the black shales of the younger La Luna Formation (Cenomanian-Campanian) which was deposited in an open carbonate platform environment (e.g Martinez and Hernandez, 1992; Mendez, 1989). These differences include an absence of methylhopanes, a higher ratio of diasteranes to steranes, and larger amounts of 18α(H)-trisnorneohopane (Ts). However, these biomarker differences compared with La Luna Formation become less obvious in the upper section of the Machiques Formation. Continuing research on both biomarker and kerogen composition and their relationships with lithology and palynofacies should clarify the palaeoenvironmental significance of these differences. However, the micropaleontological and isotopic data presented here suggest that these variations can be interpreted as a response to palaeoecological changes associated with a shallowing upward trend within the Machiques-Perija Trough around the Aptian-Albian boundary.

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We would like to extend our thanks to Prof. Judy McKenzie and Daniel Aristegui for their assistance in obtaining the stable isotope data at E.T.H., Zurich, Switzerland. We are also grateful to Dr. Richard Tyson for helpful comments and careful review of the manuscript.

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5.15 Hopanes and methylhopanes in Cretaceous marls from Tunisia

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The hopanoids comprise a ubiquitous suite of biological marker compounds in the geosphere, largely ascribed to bacterial origins. However, certain hopanoid skeletons are far more restricted in their occurrence, and therefore hold great potential as indicators of depositional environment and/or early diagenetic conditions within the sediment. This paper discusses possible source relationships between hopanes, 28,30-bisnorhopane and a series of methylhopanes in a suite of Cretaceous marls from Tunisia.

The five marl samples are variably rich in organic carbon (2.8-6.5%), but all have high hydrogen indices (518 to 701 mg HC/g TOC; Table 1) and low sulphur contents (0.13-0.32%). The organic matter is predominantly algal/bacterial in origin (Farrimond *et al.*, 1990). The samples are marginally mature, the steranes displaying partial side-chain isomerization (*ca.* 35% 20S).

Palaeoenvironmental Changes in an Aptian restricted marine basin: the Machiques Formation of Western Venezuela

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Introduction

Although the upper Cretaceous (Cenomanian-Turonian-Conacian) La Luna Fm. is the best known and most important petroleum source rock of the Maracaibo Basin in Western Venezuela, several other organic-rich units have been described in the area, including the Machiques Fm. (Aptian).

The Machiques Fm. (alternating carbonate-rich beds and organic carbon-rich shales), has been recognized in outcrops and wells at the western part of the Maracaibo Basin (Fig. 1), with a maximum thickness of 200m. at the central Perija area but thinning quickly to the North, South and East, suggesting that its deposition was restricted by the Aptian palaeogeography (see Fig 2).

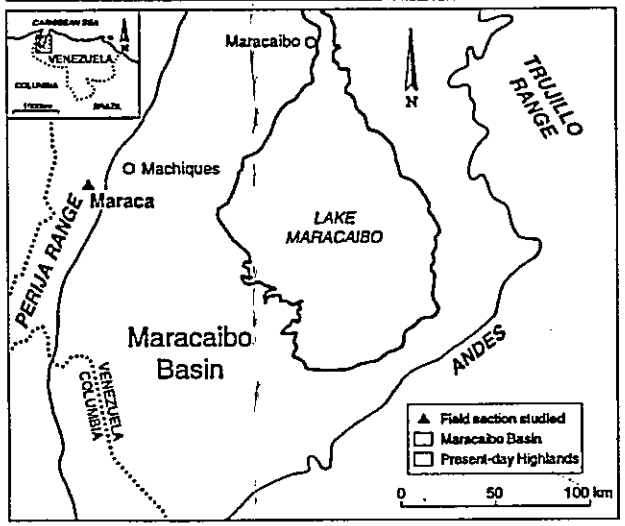

Fig. 1 Location map of the section studied.
Maraca Ravine, in the Central Perija Foothills, is located 20km to the Southwest of Machiques City. This location is among the better exposures of Cretaceous rocks in the Maracaibo Basin, therefore it has been a site for many palaeomagnetic, palaeonteological and sedimentological studies.

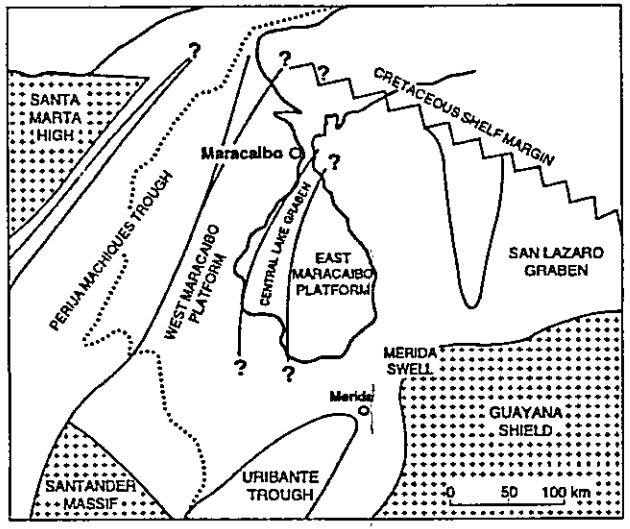

Fig. 2 Palaeogeography of the lower Cretaceous in the Maracaibo Basin, according to Bartok et al., (1981).
The distribution of the Machiques Formation coincides with an area of increased subsidence called the Machiques-Perija Trough which formed part of a graben system on the Proto-Caribbean plate (Mendez, 1989). The boundaries of this trough are difficult to define because they have been masked by further orogenic episodes and movement of the Caribbean Plate, but its original extent was probably between 10,000 and 70,000km^2

This work presents a geochemical evaluation of the Machiques Fm. in outcrops from Maraca Ravine at the Central area of the Perija Foothills where the unit is approximately 160m. thick. Over 80 samples collected from this section were evaluated using bulk geochemical and stable isotopic analysis, molecular geochemistry and optical methods.