Biomarker distribution of the Apón and La Luna Formations in core samples from Lake Maracaibo, Venezuela

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ABSTRACT

New geochemical data of biomarkers has been obtained from two cores recovered from La Luna Formation and the Machiques Member of the Apon Formation in the Lake Maracaibo area. This data includes: maturity, type and quality of organic matter and mineralogical assemblage in the matrix. Organic matter in La Luna Formation at this location is mature (Tmax 437-444°C) and biomarker distribution is consistent with carbonate mineralogy, a general anoxic environment and bacterial plus algal contribution (kerogen II). TOC and Dibenzothiophene ratios corroborate excellent preservation of organic matter. Organic matter in the Apón Formation, Machiques Member is also mature (436-440°C). Biomarker distribution is consistent with predominantly clay mineralogy, a general disoxic environment and a combination of marine and terrestrial organic matter (kerogen II+III) that are also very well preserved. Biological markers reveal unique characteristics for each sedimentary sequence that can be applied to oil-source rock correlations thereby contributing to a better understanding of the conditions of sedimentation in these two important organically rich sedimentary sequences.

Keywords: Biomarkers, La Luna Formation, Apón Formation, Machiques Member, Maracaibo Basin.

INTRODUCTION

Previous geochemical studies of La Luna (Cenomanian-Campanian) and Apón (Aptian-Albian) formations have been the focus of organic and inorganic geochemistry in the Perija area (Alberdi and Tocco, 1999; Davis, 2002; Perez et al., 1996; Lo Mónaco et al., 2002). Moreover, in this report, new geochemical data of biological markers as well as type and quality of organic matter have been recorded in core samples from a Lake Maracaibo oilfield.

La Luna is the most prolific source rock in South America. It has been the focus of many studies because of its contribution to petroleum systems and the fact that it contains the sedimentary record of the most important Oceanic Anoxic Event (Cenomanian-Turonian).

Machiques Member, as part of the Apón Formation also shows abundant organic matter and high potential for oil generation. Nevertheless, a geochemical oil-source rock correlation has not yet been established. Trace metals enrichment and isotopic signatures at the base of the sequence have been correlated with the Aptian-Albian Oceanic Anoxic Event (Perez et al., 1996)

Taking into account the economic and scientific significance of these two sequences, this study incorporates new geochemical data by paying special attention to the saturate and aromatic biological markers.
EXPERIMENTAL

Twenty core samples of Cretaceous source rock from two wells in the Maracaibo area were analyzed by mineralogy, TOC, Rock Eval pyrolysis. Selected samples were analyzed by GC/MS (gas chromatography/mass spectrometry) to biological markers. Samples were pulverized and mineralogical composition was determined by X-ray diffraction (Siemens XD-8 advance); concentrations of total organic carbon by LECO C-144, inorganic carbon or carbonatic carbon were determined using the Bernard’s calciminer (Hesse, 1971) and total sulfur by LECO SC-432. Bitumen was extracted with CH$_2$Cl$_2$ in a soxhlet extractor. GC/MS for biomarker evaluation was performed on a HP-5890 Gas Chromatography/HP-5971 Mass Spectrometer with multi-ion recorded. Terpanes, steranes, dibenzothiophenes and phenanthrene are reported in this study.

RESULTS AND DISCUSSION

I. La Luna Formation core samples:

Mineralogical analysis meant the presence of calcite, quartz, pyrite, illite and kaolinite in La Luna Formation, and calcite, quartz, kaolinite, pyrite, montmorillonite and illite in the Apón Formation. The organic matter is mature with Tmax values ranging from 437°C in core A to 444°C in core B.

La Luna Formation saturated biomarkers maintain notorious signs of tricyclic terpanes and a C$_{27}$>C$_{28}$>C$_{29}$ ββ regular sterane distribution as a classic signature of algal contribution. The C$_{30}$Hop/C$_{29}$Sterane ratio ranged between 1.5 and 3.7 highlighting the bacterial input during sedimentation.

Besides the maturity changes between Core A and Core B, the C$_{30}$nor-Hop/C$_{30}$-Hop ratio close to the unit as well as a Ts<<Tm and a low content of diasteranes reveal a concordant response of the organic matter in the sediment to a carbonatic lithology in the rock matrix.

Good preservation of organic matter is shown with a TOC concentration of over 3%. HI (pirolysis rock Eval) higher than 300 mgHc/g TOC represent a good potential indicator for oil generation in mature samples. La Luna Formation, as in previous geochemical studies, maintains a high content of TOC and Kerogen II. A very low Pr/Ph ratio (0.62) and the Pr/n-C$_{17}$ vs. Ph/n-C$_{18}$ indicate an anoxic environment of sedimentation. Sulphur concentration in whole rock and kerogen reveals a general anoxic environment with free H$_2$S as a response to a general sulfate reductor process, supported by a DBT/P ranging between 1.8-3.2 and a C$_{35}$Hop> C$_{34}$Hop.

It is interesting to note the presence of pyrite, cobaltpentlandite, and roserbengite in the kerogen extracts as a demonstration of the role of the organic matter as speciation agent to metals fixation.
II. Apón Formation (Machiques Member) core samples:

Mineralogical analysis meant the calcite, quartz, kaolinite, pyrite, montmorillonite and illite in the Apón Formation. The Apón Formation saturate biomarkers maintain a good record of tricyclic terpanes as a classic signature of algal contribution but the regular sterane distribution is slightly different from La Luna Formation. \( \text{C}_{27} \beta \beta \) regular sterane and similar concentrations of \( \text{C}_{28} \) and \( \text{C}_{29} \beta \beta \) regular sterane predominate thereby suggesting a change in the faunal assemblage from the Lower Cretaceous to the Mid Cretaceous. This is supported by a decrease in the \( \text{C}_{30} \text{Hop}/\text{C}_{29} \text{Sterane} \) ratio (0.8 –1).

A high content of diasteranes, in agreement with a Ts/Tm close to the unit, a relationship of \( \text{C}_{34} \text{Hopane} > \text{C}_{35} \text{Hopane} \), the presence of \( 17\alpha \) (H) diahopane (\( \text{C}_{30}^* \)) and a clear signal of \( 18\alpha \) (H)-30-norneohopane (\( \text{C}_{29} \text{Ts} \)) as well as lower DBT/P ratio (0.3) reveal a response of the organic matter to an input of clays in the rock matrix deposited under a general oxic-suboxic environment with concentrations of dissolved free oxygen along the water-sediment interphase (Peters and Moldowan, 1993). These results are concordant with a Pr/Ph ratio of around 1.00 and indicate that the Apón Formation is a slightly more oxidizing environment than La Luna Formation.

In addition, the pyrolysis Rock Eval indicates that type II kerogen predominates with the contribution of some terrestrial input. The quantity of organic matter (TOC) is quite elevated with values ranging from 3.5 to 7.8%. HI values of 600 mgHc/g TOC indicate an excellent oil-prone source rock. An average Tmax value of 436 °C in cores samples for A indicates thermal maturity at the beginning of the oil window and a value of 440 °C in core samples for B show a late stage of oil generation.

Apart from the fact that a detailed study should be carried out on the biological markers related to brackish and stratified waters, gammacerane seem to be much more concentrated in Apón than in La Luna formation. This reveals an environment of restricted circulation while the Apón formation deposition took place along the Machiques Trench.

CONCLUSIONS

New geochemical data has been generated from the two core samples in sedimentary sequences that received special attention as source rocks and their relationship with two OEA: La Luna Formation (Cenomanian-Campanian) and the Apón Formation, Machiques Member (Aptian-Albian).

Several biological markers and their ratios have been identified to discriminate the organic matter independent of their maturity trend: Ts/Tm, \( \text{C}_{29} \text{Norh}/\text{C}_{30} \text{Hop} \), \( \text{C}_{29} \text{Ts} \), \( \text{C}_{34} \text{Hop}/\text{C}_{35} \text{Hop} \), \( \text{C}_{30} \) diahopane, \( \text{C}_{30} \text{Hop}/\text{C}_{29} \) steranes, regular sterane distribution and DBT/P. All these ratios reveal differences in lithology, faunal assemblage and redox conditions.

Gammacerane should be corroborated in future research to corroborate a stratified or restricted basin during the Apón Formation (Machiques-Member) deposition.
REFERENCES


Davis C., 2002, Organic and Inorganic Geochemistry of Early and Late Cretaceous Black Shales from Western Venezuela: Implications for the Paleoceanographic Evolution of Northern South America, AAPG Annual Meeting.


