

**Geochemical characterization of Jurassic source rock
from Cuba: 1. Cifuentes Formation in onshore Via
Blanca – Boca de Jaruco oils fields.**

by

**González B.M., Maria do Carmo Peralba, Simone Barrionuevo
and Wolfgang Kalkreuth**

reprinted from

**ENERGY
EXPLORATION
& EXPLOITATION**

Volume 31 2013

Number 6

©2013

MULTI-SCIENCE PUBLISHING CO. LTD.
5 Wates Way, Brentwood, Essex CM15 9TB, United Kingdom

Geochemical characterization of Jurassic source rock from Cuba: 1. Cifuentes Formation in onshore Via Blanca – Boca de Jaruco oils fields

B.M. González^{1*}, Maria do Carmo Peralba², Simone Barrionuevo¹ and Wolfgang Kalkreuth¹

¹*Instituto de Geociências, UFRGS, Rua: Bento Gonçalves 9500, Porto Alegre, Brasil*

²*Instituto de Química, UFRGS, Rua: Bento Gonçalves 9500, Porto Alegre, Brasil*

**Author for corresponding. E-mail: marlenybg@gmail.com*

(Received 11 March 2013; accepted 16 August 2013)

Abstract

The present study investigates the principal characteristics of organic matter contained in sedimentary rocks of the Jurassic Cifuentes Formation, Cuba and to assess its hydrocarbon generative potential. The Cifuentes Formation is part of the Placetas Tectono-Stratigraphic Unit (TSU) of the Northern Cuba Petroleum Province and is considered the principal hydrocarbon source rock of the area. A total of 37 core samples collected from 10 petroleum onshore exploration wells were analyzed ranging in depth from 1478 to 4037 m. Analytical methods included total organic carbon (TOC) determinations, Rock Eval, optical analyses and gas chromatography and mass spectrometry (GC-MS). Results indicate that these rocks have organic carbon contents ranging from 0.52 wt% to 9.91 wt%. The average hydrocarbon generation potential as determined by Rock-Eval pyrolysis (S2) is between 0.34- 83.37 mg HC/g of rock suggesting a fair to good hydrocarbon generation potential for many samples. Hydrogen Indices (HI) and Oxygen Indices (OI) suggest kerogen types ranging from I to II and II/III. Optical analyses based on palynofacies concepts indicate predominance of amorphous organic matter (AOM). Based on biomarker distribution depositional environments is range from anoxic/hypersaline to normal saline. Maturity parameter such as Tmax (°C), vitrinite reflectance (Rrandom %), spore coloration index (SCI) and biomarker ratios suggest the organic matter is immature to marginally mature.

Keywords: Cuba, Placetas Tectono-Stratigraphic Unit, Cifuentes Formation, Source rock

1. INTRODUCTION

About 25 onshore and offshore oil fields of medium and small size are known in Cuba. These fields are distributed in the western and central part of the island, situated in the Northern Cuba Fold and Thrust Belt Assessment Unit, respectively, as defined by their

position with respect to the over thrust belt (Fig. 1).

All of the known oil and gas fields of the Northern Geological Province (Fig. 2) lie within the Placetas Tectonostratigraphic Unit (TSU) as defined in Figure 3. The source for petroleum is interpreted to be primarily from Upper Jurassic to Lower Cretaceous organic-bearing carbonates, Upper Cretaceous carbonate mudstones, and Paleogene mudstones also might have contributed petroleum to this system.

In Cuba, the geology is complex and involves oil traps in highly thrustured zones, likely explaining some confusing geochemical information on the existing composition of hydrocarbons that may be found. Previous studies on geochemical characterization of the source rocks and oils concentrated on the origin and maturity levels of the oils, and their relationships to an impregnated Jurassic limestone succession in onshore wells sampled years ago (López *et al.*, 1994, 1995).

Most of the fields are located in the Northern Province which encompasses the northern part of the island and adjacent offshore area (Fig. 2). This region is about 1000 km long and 80-100 km wide. Sediments (up to 12 km thick) were deposited



Figure 1. Extension of the North Cuba Fold and Thrust Belt Assessment Unit All Known oil fields in northern Cuba are located within this assessment unit.

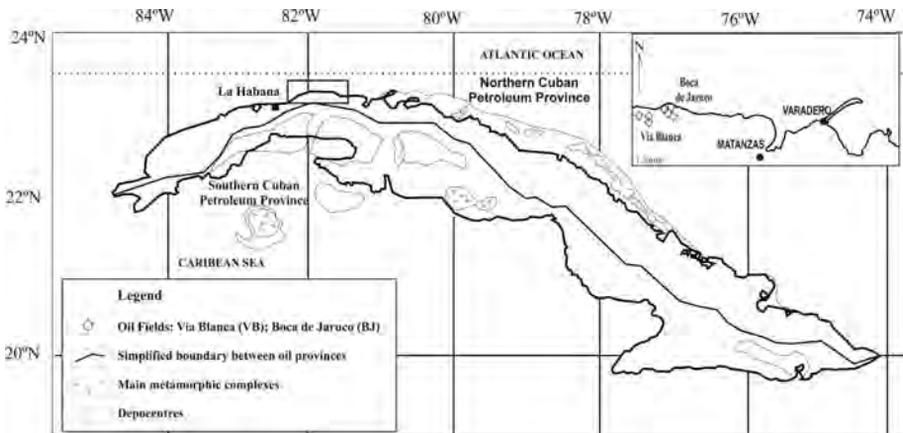


Figure 2. Locations of onshore oil fields Via Blanca and Boca de Jaruco in the Northern Cuban Petroleum Province.

beginning in Early Jurassic-Cretaceous time following the structural evolution of a stable continental margin (Echevarria-Rodriguez *et al.*, 1991). The fields are situated in folded and fractured limestones in over thrust sheets (Fig. 1), dominated by structural traps, mainly folds, fault-related folds, faulted anticlines, and duplex structures. The fragmented distribution of the fields has led to difficulty in modeling the basin and understanding the genetic relationships between the oilfields.

The rock samples considered in the present study were collected from the Cifuentes Formation of the Via Blanca and Boca de Jaruco productive onshore oils fields in the Northern Geological Province of Cuba (Fig. 2), stratigraphically identified as belonging to the Placetas Tectonostratigraphic Unit, Cifuentes Formation (Fig. 3).

The source rock properties of the samples were investigated in this paper by characterizing the organic richness, hydrocarbon potential of the organic matter and its thermal maturity level. Methods applied include determination of total organic carbon, Rock Eval Pyrolysis, incident and transmitted light microscopy and GC-MS analyses.

2. GEOLOGICAL SETTING

Basement rocks in the study area are composed of marbles and siliciclastic sediments of Late Proterozoic age. Overlying these basement rocks, Lower to Middle Jurassic (Callovian) age continental and lagoonal strata were deposited rich in humic organic matter. Carbonate deposition is represented by a number of separate tectonostratigraphic units (TSUs): Placetas, Camajauani, Rosario and Cayo Coco (Hatten *et al.*, 1988) dominated the Upper Oxfordian to the Turonian. These units are described in detail in Echeverria-Rodriguez *et al.*, 1991.

From previous studies (Pindell and Kennan, 2001, 2003), the geological structural domains of Cuba were recognized as a series of north-verging thrust-fault-bounded tectonostratigraphic units (TSUs), and the geologic definition of the TSUs has been

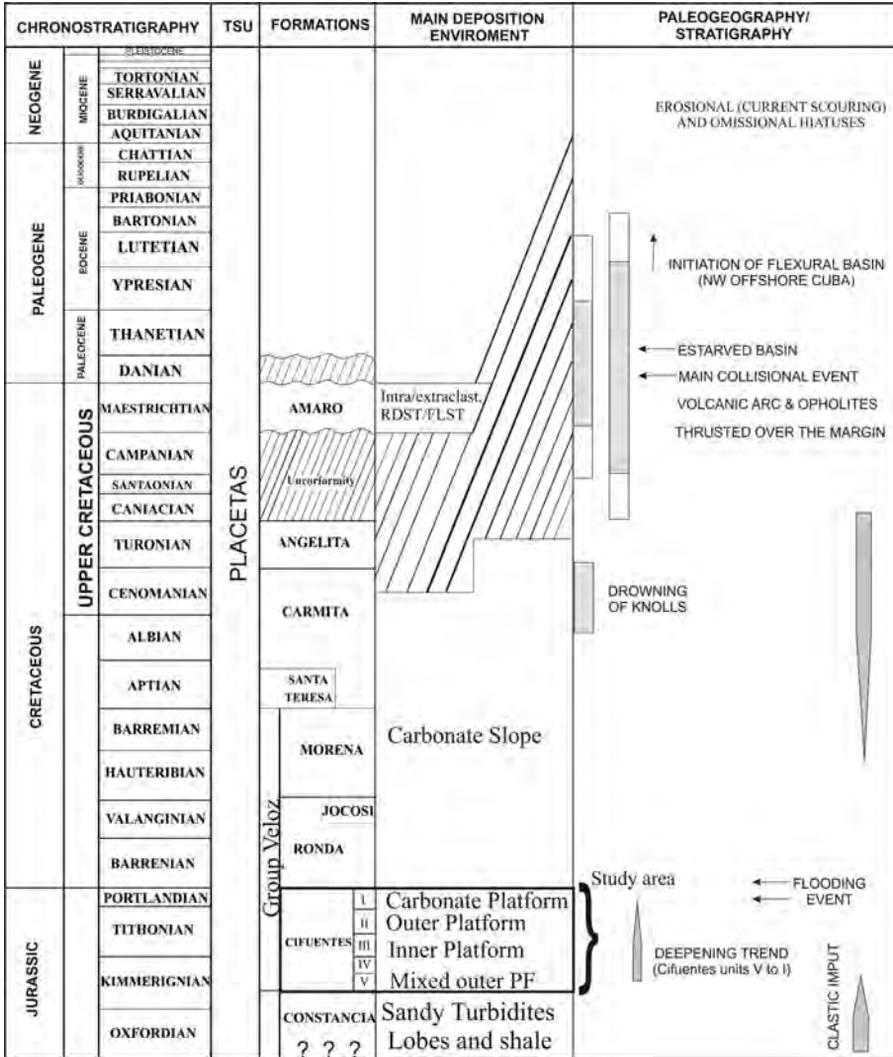


Figure 3. Lithostratigraphic column for northwestern Cuba showing reconstructed stratigraphy of the Placetas Tectonostratigraphic unit (modified from Sanchez Arango *et al.*, 2003).

the focus of many previous investigations. Tectonic studies in Cuba and in the northern Caribbean placed these TSUs in a framework of modern tectonic models (Pindell and Kennan, 2001, 2003; Pindell *et al.*, 2005), which demonstrated that the TSUs were products by the collision between shelf, slope, and basal sediments of a Mesozoic passive margin (Fig. 2).

The source rocks considered in the present study come from the Cifuentes Formation of the Placetas Tectono-Stratigraphic Unit (Fig. 3).

3. SOURCE ROCK EVALUATION

Geochemical analyses and interpretations of samples of potential petroleum source rocks, oils, and gases have quantitatively defined several source rocks and potential petroleum systems of the North Cuba area (Navarette-Reyes *et al.*, 1994; Lopez-Quintero *et al.*, 1997; Magnier *et al.*, 2004). These are (1) Lower to Middle Jurassic rift-related mudstones; (2) Upper Jurassic and Lower Cretaceous deep-water organic-rich carbonate mudstones; (3) Upper Cretaceous deep-water carbonate mudstones; and (4) possibly Paleogene mudstones. Of these, the Upper Jurassic and Lower Cretaceous deep-water carbonate mudstones are considered to be volumetrically the most significant petroleum source rocks in the basin. Paleogene source rocks and oil shows also have been reported, but these oil shows are not considered to be volumetrically significant because of the low level of thermal maturation of these sediments relative to the generative windows in the foreland basin (Magnier *et al.*, 2004).

Deep-marine, fine grained organic-bearing carbonate mudstones of the Upper Jurassic interval are considered to be the most significant petroleum source rock in the North Cuban Petroleum Province. Upper Jurassic rocks, specifically Tithonian deep-water carbonate were deposited basin ward of shallow-water carbonated platforms that rimmed the southeastern Gulf of Mexico in the Late Jurassic (Pindell and Kennan, 2001).

With respect to oil composition, prior studies suggested that different petroleum provinces existed with complex migration routes in the Northern and Southern Cuban Petroleum Provinces (Fig. 2). The fragmented distribution of the fields has led to difficulty in modeling the basin and to understand the genetic relationships between oilfields. The difficulty for correlation is augmented by the strong biodegradation of some of the oils.

The crude oils reported range from very light, mature low sulfur crudes, to high sulfur, NSO rich and biodegraded heavy oils (López *et al.*, 1997). It appears that two types of source rocks of Jurassic age are involved in the petroleum system of Cuba: A siliciclastic rock with sometimes traces of terrigenous input in west and central Cuba and anoxic marine source rocks in the northwest carbonate sediments.

4. SAMPLES AND METHODS

4.1. Sampling

The samples used in this study come from the Upper Jurassic Cifuentes Formation, TSU Placetas of the North Cuban Geological Province. 37 core samples were collected from 10 petroleum exploration wells in the Via Blanca (VB) and Boca de Jaruco (BJ) fields (Fig. 2), ranging in depth from 1468 to 4037 m (Table 1).

The samples were then prepared for the following analyses:

- 37 samples for microscopic whole rock analyses in reflected light
- 30 samples for determination of total organic carbon content (TOC) and Rock Eval Pyrolysis
- 25 samples for microscopic analyses of kerogen concentrates in incident and transmitted light mode
- 14 samples for gas chromatography-mass spectroscopy (GC-MS) analyses

Table 1. Rock-Eval/TOC data of selected Cifuentes Formation source rock samples.

Wells	No.	Depth (m)	TOC	S1	S2	Tmax	S3	HI	OI	PI	Ro	SCI
VB-1	1	2056	1.92	1.35	15.72	409	0.63	819	34	0.08	-	3.0
	2	2085	0.95	0.51	4.13	413	0.62	435	65	0.11	-	3.5
	3	2121	2.07	3.02	13.54	414	0.71	654	34	0.18	-	2.5
VB-2	1	2088	7.1	4.84	70.50	407	1.11	993	16	0.06	-	2.5
	2	2097	0.88	0.93	6.77	411	0.51	769	58	0.12	-	3.0
	3	2099	6.77	6.1	67.58	416	0.94	998	14	0.08	-	3.0
	4	2107	5.96	15.08	55.99	413	0.65	939	11	0.21	-	3.5
	5	2108	4.32	9.29	37.65	410	0.55	872	13	0.20	-	3.5
	6	2110	5.39	9.51	46.01	418	0.63	854	12	0.17	-	3.5
VB-3	1	2156	9.91	16.33	83.37	421	1	841	10	0.16	-	2.5
	2	2172	6.53	13.65	48.54	419	0.74	743	11	0.22	-	2.5
VB-4	1	2180	4.87	5.39	42.84	405	1.27	880	26	0.11	-	2.0
	2	2900	0.95	0.42	4.46	410	0.75	469	79	0.09	-	2.5
VB-5	1	2194	0.50	0.21	0.90	417	0.55	180	110	0.19	-	3.0
BJ-1	1	3640	1.76	0.27	9.06	417	0.79	515	45	0.03	-	2.0
	2	3861	0.52	0.01	2.93	425	0.39	563	75	0.00	-	4.0
BJ-2	1	2197	1.18	0.29	5.57	414	0.66	472	56	0.05	0.52	3.5
	2	3146	0.91	0.31	2.58	435	0.47	284	52	0.11	-	3.5
	3	3786	1.00	0.37	3.70	419	0.78	370	78	0.09	0.58	4.0
	4	4037	1.84	0.40	4.41	421	1.22	240	66	0.08	0.58	4.0
BJ-3	1	1522	3.21	6.61	24.58	408	1.01	766	31	0.21	-	3.5
	2	1612	2.51	8.02	23.10	418	0.71	920	28	0.26	0.59	4.0
	3	1642	0.82	0.27	1.21	390	0.67	148	82	0.18	-	4.0
BJ-4	1	1478	5.38	13.43	43.87	406	1.08	815	20	0.23	-	3.0
	2	1565	2.08	6.25	12.60	412	0.66	606	32	0.33	-	3.0
	3	1590	2.74	7.97	20.53	413	0.74	749	27	0.28	-	4.0
	4	1618	6.13	20.80	51.60	418	1.62	842	26	0.29	-	4.0
BJ-5	1	1823	0.80	2.39	3.93	414	0.67	491	84	0.38	-	4.0
	2	1860	4.66	13.98	34.27	411	0.93	735	20	0.29	0.53	4.5
	3	1900	3.27	7.46	28.41	407	0.73	869	22	0.21	-	4.5

4.2. TOC and Rock Eval Pyrolysis

The core samples were crushed and homogenized followed by total organic carbon determination (TOC wt. %) and Rock Eval pyrolysis. For organic carbon analysis about 0.5 g of pulverized rock sample was decalcified with HCl and washed repeatedly with distilled water to eliminate the products of the reaction. The decalcified samples were analyzed using a LECO WR – 12 analyzer. The resulting data on total organic carbonate are expressed as weight %. Rock-Eval pyrolysis was performed according to the method described by Espitalié *et al.*, (1977) providing information such as the level of maturity by Tmax (°C), and type of kerogen by determination of the Hydrogen Index (HI) and Oxygen Index (OI), Table 1.

4.3. Petrographic analyses

Petrographic examinations were carried out using standard petrographic preparation

techniques (Bustin *et al.*, 1989) and conducted on a) whole rock samples using a Leica microscope with reflected white and ultraviolet (UV) light sources, and oil immersion objectives. Mean vitrinite reflectance (% Rrandom) determination was carried out on dispersed vitrinite particles; b) Kerogen analyses using fluorescence and transmitted white light (Tyson, 1995), after concentration of kerogen by treating the samples with HCl and HF to remove carbonate and silicates, respectively (Durand, 1980).

4.4. Palynofacies analyses

Characterization of the organic matter applying concepts of palynofacies was based on quantitative analyses of the particulate organic matter following the classification as suggested by Tyson (1993). The following components were identified: amorphous organic matter (AOM), marine palynomorphs, algae, resins, phytoclasts, yellow-brown fragments, cuticles, plant tissue, wood and sporomorphs.

4.5. Extraction, liquid chromatography and GC-MS analyses.

The rocks were extracted with dichloromethane in a Soxhlet apparatus for 24 h. The organic extracts were fractionated by column chromatography in a 34 cm long and 0,9 cm in diameter column filled with 8 g of 5% water-deactivated alumina (top) and silica (bottom). The aliphatic hydrocarbons were separated by elution with 20 ml of n-hexane, followed by a gas chromatograph (Hewlett-Packard, Model HP-5890), equipped with a flame ionization detector and split less injector, and analyzed also for biomarker distribution by GC-MS using a Finnigan-MAT, model TSQ 70 interfaced to a Hewlett-Packard Model HP-5890.

5. RESULTS AND DISCUSSION

5.1. Source rock characteristics based on TOC and Rock-Eval Pyrolysis

Results of TOC determinations and Rock Eval Analyses are shown in Table 1.

5.1.1. TOC content

The Cifuentes samples range in TOC content from 0.50 to 9.91 wt% (Table 1), suggesting a fair to excellent content of organic carbon for these samples in respect to hydrocarbon potential (Peters and Cassa, 1994). Samples from well VB-2, VB-3, BJ-4 and BJ-5 were highly variable in TOC content in respect to the stratigraphic position, ranging from 2.08 to 9.91 wt. % (Fig. 4), indicating the highest TOC values in samples from a depth interval between 1400 and 2300 m.

The in general good preservation conditions of the organic matter in the Cifuentes Formation as shown in Figure 4 is related to the nature of the original source of lipid material, and to the amount and nature of admixed allochthonous terrestrial, marine macrophyte or degraded planktonic material (González, 2002, 2012).

5.1.2. Rock-Eval Pyrolysis

The amount of hydrocarbon yield (S_2) expelled during pyrolysis is a useful parameter to evaluate the generative potential of source rocks (Peters, 1986). Most of the analyzed samples have more than 2.0 mg HC/g rock (Table 1). Thus, pyrolysis S_2 yields indicate that the Cifuentes source rocks have a very good to excellent generative potential.

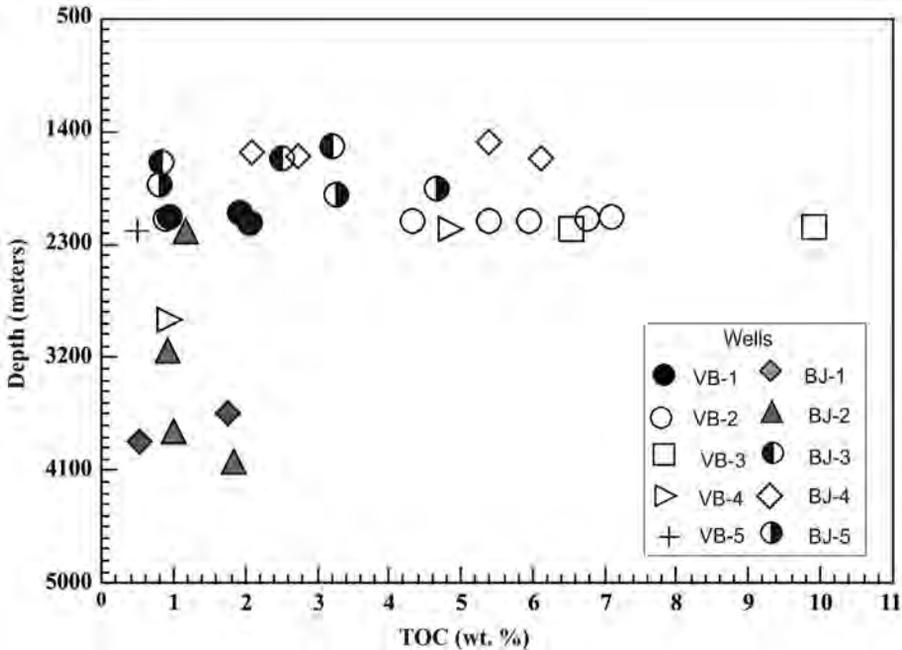


Figure 4. Diagram showing TOC versus depth for samples from Via Blanca (VB) and Boca de Jaruco (BJ) wells.

Cifuentes samples are characterized by hydrogen indices (HI) ranging from 148-998 mg HC/g TOC and oxygen indices (OI) ranging from 10-110 mg CO₂/g TOC (Table 1). Samples with HI values suggesting moderate to good oil source potential (> 300 mg HC/g TOC) all occur in the relatively high TOC samples of the VB-102, 103 and BJ- 3, 500, 321 exploration wells (Table 1).

Thus, low values of HI associated with low TOC, reflect potentially greater relative abundance of terrestrial material into hydrogen poor and poor preservation of organic matter phytoplankton (Hofmann *et al.* 1993). This relationship can generally be observed also in the present study (Fig. 5).

An understanding of organic matter type, and thus expected hydrocarbon products, can be obtained from the hydrogen (mg S₂ HC/g TOC) and Oxygen (mg CO₂/g TOC) indices (Table 1). These indices provide information similar to the atomic H/C and O/C ratios derived from elemental analyses (Espitalié *et al.*, 1977). The lowest hydrogen and highest oxygen indices are associated with the two samples from Boca de Jaruco (BJ2) and one sample from Boca de Jaruco (BJ5) (Fig. 6). These values are typical of samples containing marine organic matter that has been oxidized. These samples also show the lowest TOC contents, ranging from 0.50-1.84 wt%.

The other data show a wide distribution in HI and OI indices, with some samples plotting in an area between kerogen type II and III, and others characterized by high HI values typical for kerogen type I (Peters and Cassa, 1994).

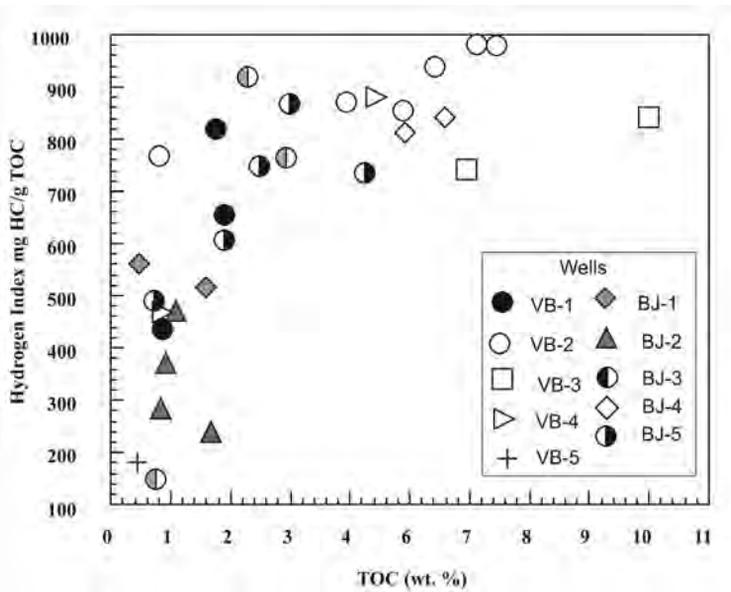


Figure 5. Diagram showing the relation of HI versus TOC for samples from the Cifuentes Formation, Via Blanca (VB) and Boca de Jaruco (BJ) oil fields.

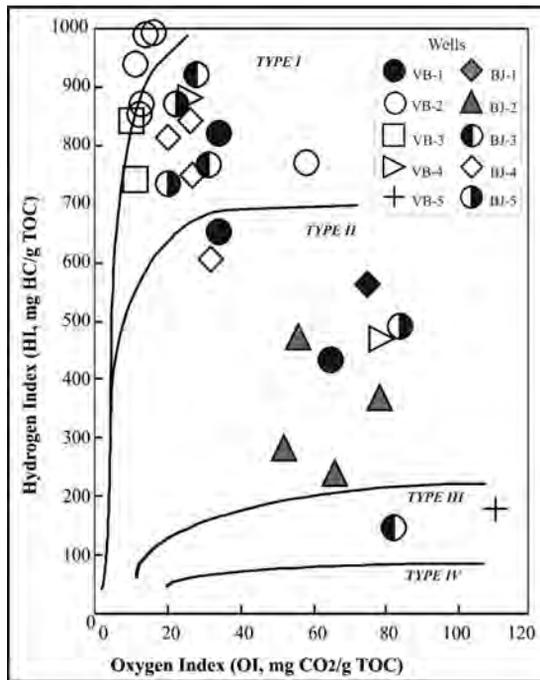


Figure 6. Diagram of hydrogen index versus oxygen index in samples from the Cifuentes Formation, Via Blanca (VB) and Boca de Jaruco (BJ) oil fields.

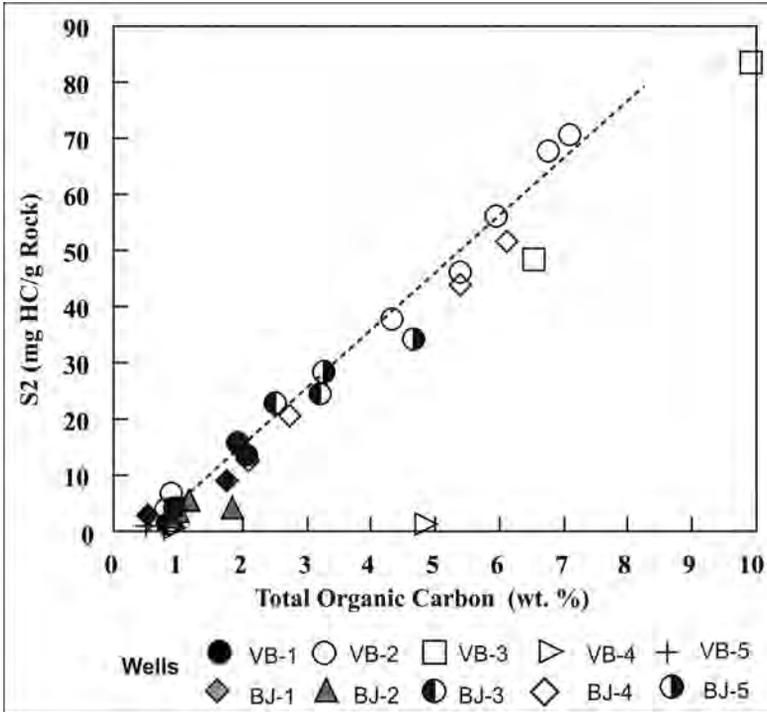


Figure 7. Plot of total organic carbon (TOC) versus S₂ from samples of the Cifuentes Formation, modified from (Langford and Blanc-Valleron, 1990).

Insight into the hydrocarbon potential of the organic matter is also provided by plotting TOC versus S₂ (Langford and Blanc-Valleron, 1990). Applying this concept to the samples from the Cifuentes Formation a highly linear regression line exists between TOC content and S₂ peak from Rock Eval Pyrolysis (Fig. 7).

According to the data the S₂ values range from 0.90 e 83.37 mg HC/g rock, suggesting a poor to excellent hydrocarbon generation potential for the samples based on this parameter (Peters and Cassa, 1994).

5.1.3. T_{max} values

The organic matter in the samples from the Cifuentes Formation is characterized by T_{max} values in the range of 390 to 435 °C (Table 1), which suggest a maturity level at the transition, from immature to marginal mature. Since the T_{max} value has been found to be influenced by organic matter type (Hunt, 1996) and mineral matrix (Katz, 1983), maturity levels determined by Rock Eval Pyrolysis should be confirmed by other maturity parameters such as vitrinite reflected measurement and/or spore coloration index.

A plot of hydrogen index (HI) and pyrolysis T_{max} from Rock-Eval pyrolysis can be used to classify the type of organic matter and maturity (Espitalié *et al.*, 1977), and

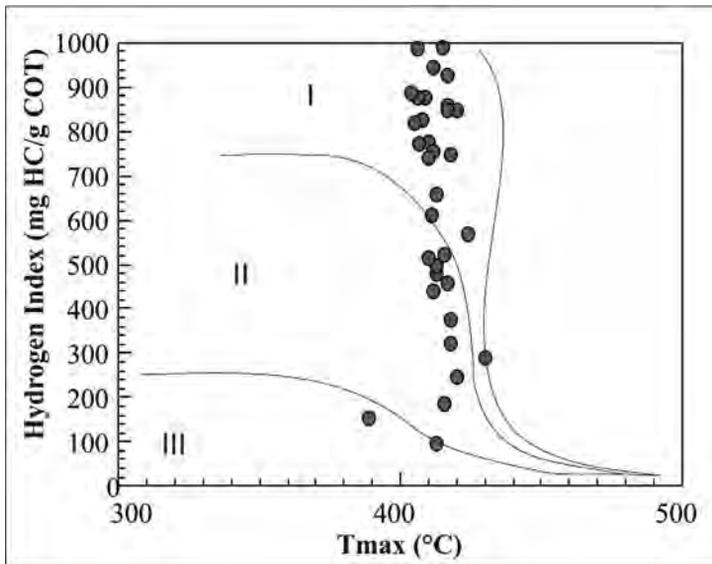


Figure 8. Plot of hydrogen index (HI) versus pyrolysis T_{max} for Cifuentes samples, showing kerogen and thermal maturity stages.

a show that the Cifuentes shale samples generally plot in immature to early mature zone of Type I–II and mixed type II-III kerogen (Fig. 8).

5.2. Palynofacies

Predominant organic component as determined by palynofacies analyses is the amorphous organic matter (AOM) ranging from 57.4 to 100%, followed by spores and pollen (nil to 29.0). Phytoclasts are rare, generally between nil and 5.0%, except for one sample in well BJ2, where they make up 23.2%. Marine microfossils were observed in many samples (Table 2) and consist mainly of dinoflagellate cysts and acritarchs.

The woody organic matter is represented by small irregular angular fragments (opaque particles) and tracheids without pits (Fig. 9). The AOM has variably “clotted” (grumose) appearance, yellow to dark brown coloration and its matrix exhibits moderate-strong orange and heterogeneous fluorescence color. AOM shows intense yellow to orange fluorescence, a fluorescence characteristic of early thermal maturity (Fig. 9) and has been mainly considered to be of marine origin (Tissot and Welte, 1984; González, 2012).

The pollen assemblage is characterized by the predominance of specimens representing the genera *Classopollis*. These sporomorphs are thin-walled and small and were thus easily transported off-shore. The spores and pollen have orange-yellow fluorescence under UV excitation, whereas the dinoflagellate cysts, microforaminiferal linings and acritarchs show intense yellow fluorescence color (Fig. 9).

Palynofacies interpretations, showing the predominance of amorphous material with

Table 2. Evaluation of petrographic composition of organic matter in samples of the Upper Jurassic Cifuentes Formation based on transmitted light microscopy.

Wells	Depth(m)	Amorphous (AOM)	Fhytoclcasts	Spores and Pollen	Marine Microfossils
VB 1	2956	93.6	1.6	2.8	-
	2085	96.0	2.4	1.6	-
	2121	24.0	5.0	16.0	3.0
VB 2	2088	98.0	0.6	1.4	-
	2099	99.0	-	-	1.0
	2107	97.0	-	2.0	-
	2108	99.0	-	-	1.0
VB 3	2172	98.0	-	0,6	1,4
VB 4	2180	98.0	-	2.0	-
	3534	100	-	-	-
	3563	91.2	-	8,2	0,8
BJ 1	3640	86.0	-	-	14.0
	3861	70,4	1.8	27,4	-
	3740	99.4	-	0.6	-
	3861	100	-	-	-
	3936	100	-	-	-
BJ 2	2197	92.0	3.4	2.8	-
	3146	57.4	23.2	19.2	-
	3786	84.8	-	15.0	-
	4037	86.0	-	3.0	14,4
BJ 3	1612	93.0	0.2	-	0.6
BJ 4	1478	97.2	-	-	0.6
	1565	95.0	-	4.0	1.0
	1590	64.0	0.6	29.0	6.0
BJ 5	1618	100	-	-	-

contributions of sporomorphs and phytoclcasts (Fig. 9), are consistent with the results from Rock Eval, which indicate kerogen type I and II/III for most of the samples.

5.3. MATURITY

In addition to maturity determination by Rock Eval pyrolysis (Tmax °C), vitrinite reflectance and spore coloration index (SCI) were used in this study to assess the maturity of the organic matter. Vitrinite was only found in 5 samples, with the particles of low quality, characterized by small sizes, impurities and granulated surfaces. The mean values of vitrinite reflectance range between 0.52 and 0.59 % Rrandom (Table 1), suggesting a marginally mature stage for the 5 samples.

The maturity assessment by the spore coloration index (SCI) show that the SCI values range from 3.5-4.5 (Table 1), suggesting a maturity level of the organic matter ranging from immature to marginally mature.

The results of vitrinite reflectance and SCI are generally in agreement with Tmax °C values from Rock Eval pyrolysis, placing the organic matter of the Cifuentes Formation for Via Blanca and Boca de Jaruco wells in the immature to marginally mature stage.

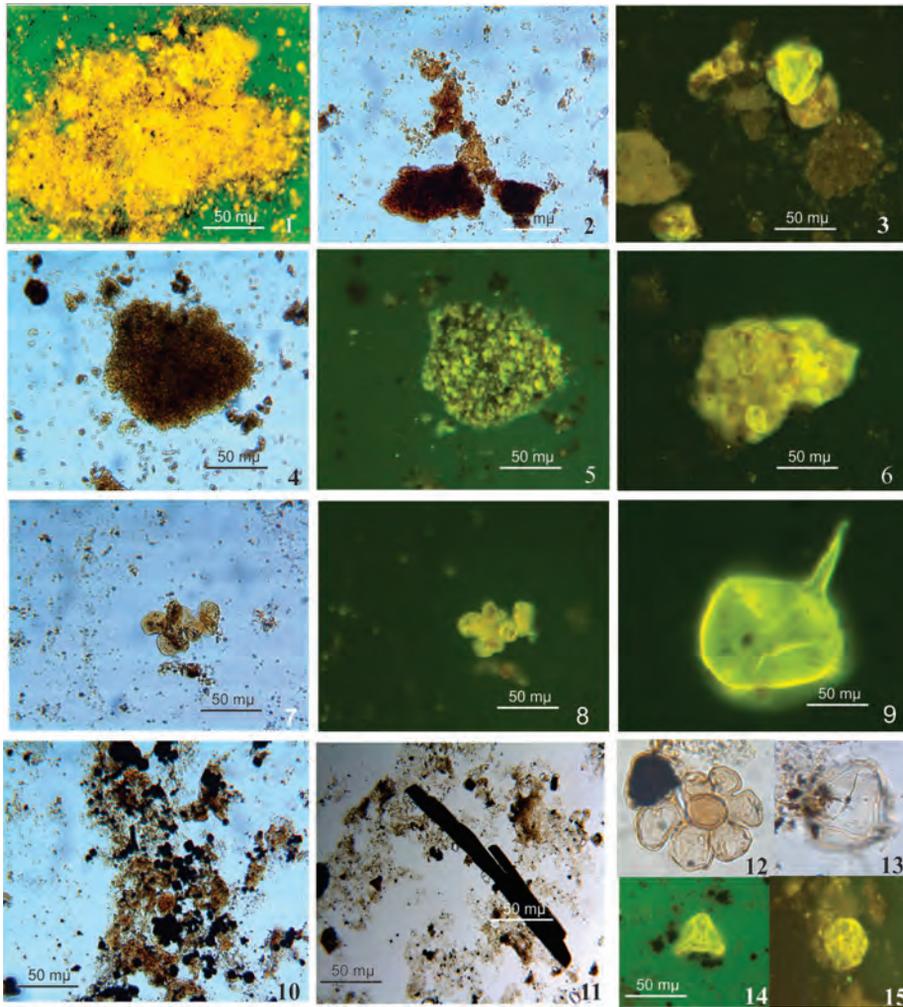


Figure 9. Representative photomicrographs of kerogen in the Upper Jurassic Cifuentes rock under visible white transmitted and ultraviolet light excitation.

1. Strongly fluorescing, granular amorphous organic matter (AOM) with homogeneous matrix in UV light; 2. Massive-granular AOM in transmitted light; 3. Yellow-brown AOM with homogeneous matrix and dinoflagellate cysts; 4 and 5. AOM in transmitted light and UV light (massive appearance) with heterogeneous matrix; 6. Yellow dinoflagellate cysts in UV light; 7 and 8. Pollen in transmitted light and yellow fluorescence under UV excitation; 9. Dinoflagellate cyst in yellow UV light; 10. Granular AOM with small irregular angular fragments (opaque phytoclast) in transmitted light; 11. AOM with elongate opaque phytoclast; 12. Microforaminifers linings; 13. Dinoflagellate cyst; 14. Spore have yellow UV light; 15. Pollen (Classopollis).

Table 3. N-alkane and isoprenoids rations and biomarker parameters of selected Cifuentes samples.

Well	No.	Depth (m)	Pr/ n-C17	Fh/ n-C18	Pr/Ph	G/C30	H29/H30	C35/ C34	Ts/ (Ts + Tm)	C ₃₂ 22S/ 22R
VB-2	1	2088	12.72	7.63	0.83	0.44	0.68	0.70	0.23	0.56
	2	2097	2.0	3.53	0.80	0.41	0.70	3.76	0.27	0.57
	3	2099	2.08	3.64	0.81	0.42	0.70	1.27	0.26	0.57
	4	2107	2.9	1.02	0.83	0.43	0.66	4.00	0.26	0.57
	5	2108	4.15	7.09	0.57	0.44	0.77	0.98	0.25	0.57
	6	2110	2.88	9.96	0.66	0.15	0.66	0.99	0.22	0.57
VB-3	2	2172	1.03	1.13	0.83	0.49	0.67	6.14	0.25	0.57
VB-4	1	2180	3.38	1.80	0.51	0.47	0.60	2.68	0.33	0.49
BJ-2	1	2197	1.13	1.38	0.5	0.93	0.40	1.04	0.09	0.49
	3	3786	0.86	1.17	0.43	0.41	0.49	0.76	0.38	0.57
	4	4037	1.37	2.11	0.53	0.16	0.55	1.28	0.32	0.57
BJ-3	2	1612	5.51	12.3	0.43	0.38	0.82	1.17	0.25	0.56
BJ-4	4	1618	5.85	22.28	0.53	0.36	1.00	5.32	0.29	0.52
BJ-5	2	1860	3.11	1.01	0.28	0.38	0.80	0.98	0.29	0.52

5.4. Liquid chromatography

Liquid chromatography (MPLC) analyses of the rock extract show on average a dominance of NSO compounds (61 %) over saturated (23 %) and aromatic (16 %) fractions.

5.5. GC and GC-MS analyses

The n-alkane distribution typically reach peak abundance in the n-C₁₅ to n-C₂₃ range (Figs. 10A and B), consistent with predominantly algal input, and have carbon-preference indices (CPI) ranging from 0.67 – 1.73. Characteristic of these samples are the very high values of Pr/n-C17 and Ph/n-C₁₈ (often >1) (Table 3) indicative that the organic extracts are biodegraded. The low pristine/phytane ratios (<1) (Table 3, Fig. 10) suggest a marine-derived source rock material deposited under highly reducing condition (Peters *et al*, 1996).

Gas chromatography of the samples extracted from the Jurassic Cifuentes Formation, Via Blanca and Boca de Jaruco areas showed differences in the degree of biodegradation. One group of samples showed a chromatographic pattern dominated by n-alkanes in the range of n-C14 to n-C25 carbon atoms, whose main sources are precursors of marine origin (Fig. 10A). A second group of samples indicate a chromatographic bi-modal population, with the first population in the range of n-alkanes C₁₄ - C₂₃ n-alkanes and the second population between C₂₇ – C₃₆ (Fig. 10B). Alkanes with carbon number of atoms near C₂₇, C₂₉, C₃₁, are related to higher plants (Peters and Moldowan, 1993; Peters *et al*, 2005). A third group of samples has a general characteristic of showing changes in a base line gas chromatography and abundant presence of unresolved compound (UCM) and absence of lighter n-alkanes (Fig 10C) indicative of biodegradation of the sample.

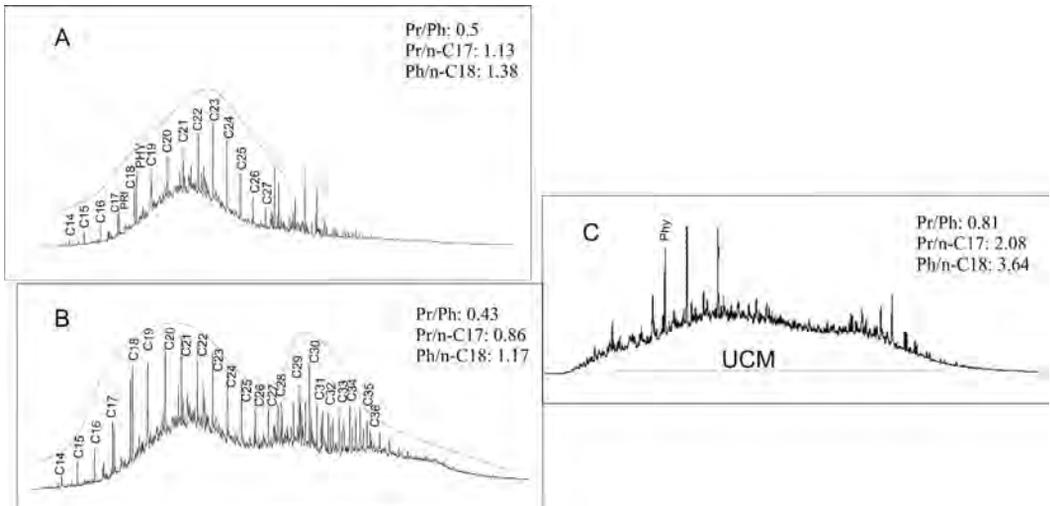


Figure 10. Saturated fraction gas chromatogram (GC) for a representative rock extract from: A- Boca de Jaruco 2-1, 2797 m; B-Boca de Jaruco (BJ) 2-3, 3786 m and C-Via Blanca (VB)-2-3, 2099 m. Cifuentes Formation.

5.5.1. Hopanoid hydrocarbons

Hopane distribution (m/z 191) of samples from Boca de Jaruco (BJ) -2-1, 2797 m and Boca de Jaruco 2-3, 3786 m is shown by the relative concentration of pentacyclic > tricyclics biomarkers (Fig. 11).

The tricyclic distribution in all Cifuentes samples is characterized by a pattern with a maximum C_{23} tricyclic terpane peak (Figs. 11A and 11B), suggesting that these samples with the maximum C_{23} tricyclic pattern all have a high source rock potential.

The ratio of Gammacerane/ C_{30} is relatively high (Table 3) ranging from 0.16 to 0.93. The ratio is generally considered to be high in organic matter originating in a restricted hypersaline environment (Ruble *et al.*, 1994), with tetrahymanol being considered the precursor of gammacerane (ten Haven *et al.*, 1989).

The series of 17 α (H), 21 β (H)-hopanes is dominant, with molecules ranging from C_{27} to C_{35} , which are resolved at the C-22 position into S and R epimers. Hopane (C_{30}) is the most abundant component, followed usually by norhopane (C_{29}). The component 17 α (H)-trishnorhopane Tm commonly exceeds its counterpart 18 α (H) - trishnaneohopane (Ts). However, this ratio is strongly influenced by presence of minerals that catalyze structural rearrangement from Tm and Ts. Field studies and pyrolysis experiments (Rullkötter *et al.*, 1984) have shown that this parameter is more indicative of source rock mineralogy (e.g. catalytic vs. inert minerals) than thermal maturity. Most of the Via Blanca extracts have Ts/(Ts + Tm) ratios ranging from 0.22 and 0.33, whereas Boca de Jaruco extracts exhibit ratios ranging from 0.22 to 0.38, with the exception of one sample in well Boca de Jaruco 2-1, characterized by a low ratio of 0.09 (Table 3).

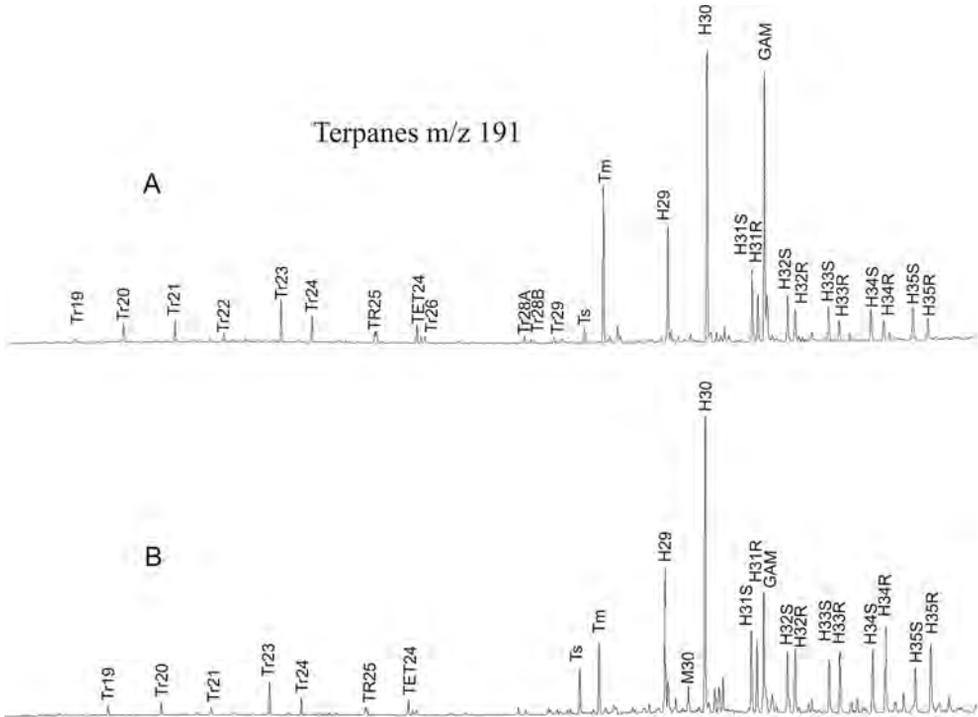


Figure 11. Mass fragmentograms of hopane (m/z 191) for a representative sample from Boca de Jaruco (BJ) -2-1, 2197 and Boca de Jaruco 2-4, 4037 m. Cifuentes Formation.

Relatively high $T_s/(T_s + T_m)$ ratios observed in some samples from wells Via Blanca 4-1 and Boca de Jaruco 2 (Table 3), ranging from 0.29 to 0.38 may indicate a somewhat higher maturation or a different source of organic matter, in which catalytic effects were more important than those involved in the others extracts.

The stereoisomeric ratios, $22S/22R$, of the extended hopanes (C_{31} - C_{35}), also have been used as maturity indicators (Seifert and Moldowan, 1980; Mackenzie *et al.*, 1980). In general, $22S/22R$ ratios less than about 1.2 are considered immature, whereas ratios of about 1.3 or greater indicate that the rocks are near or within the oil generation window. Using these values as guidelines, the Cifuentes samples, characterized by average $22S/22R$ ratios of 0.49 – 0.57 for the C_{32} hopanes, are considered immature (Table 3).

The extended hopanes C_{31} - C_{35} for Cifuentes samples, which occur as doublets or stereoisomeric pairs, commonly show a staircase distribution pattern (Fig. 11A). Another distribution is characterized by an irregular extended hopane pattern with C_{32} and/or C_{34} hopanes exceeding the C_{31} and C_{33} hopanes, respectively (Fig. 11B).

Gas chromatography of the extracted showed differences in the degree of biodegradation, which is complicating the interpretation on the origin of the oils and their classification. However, the presence and relative concentration of certain

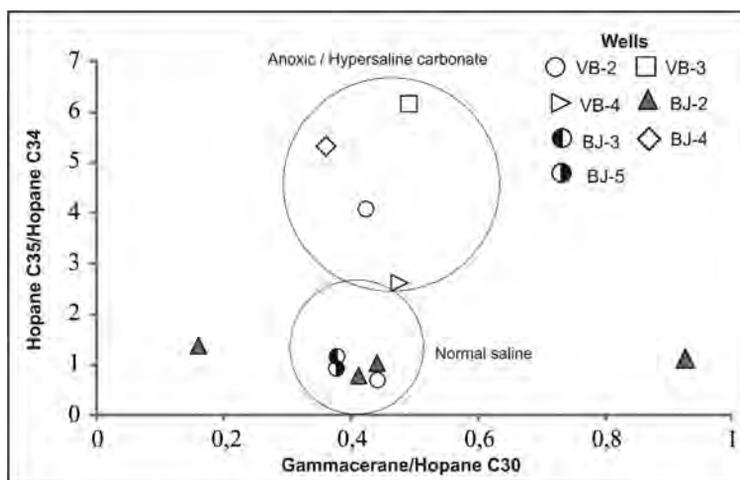


Figure 12. Plot of source indicators suggesting the hypersaline and normal saline depositional environments of the organic extracted from Cifuentes Formation.

biomarker such as the pentacyclic pentanes resistant to post-genetic alteration processes was used to characterize the extracts in respect to source material and depositional environments.

A high ratio of C_{35}/C_{34} pentacyclic hopanes (>1) often infers to a hypersaline carbonate/anoxic depositional environment. When plotting two carbonate indicators for this data set, the gammacerane/hopane C_{30} ratio vs. the hopane C_{35} /hopane C_{34} ratio, two families may be observable in extracts (Table 3, Fig. 12). It is suggested that one family is derived from a normal saline environment, including samples from the Boca de Jaruco 2, 3, 5 wells and 1 sample from well Via Blanca 2 (lower content of C_{35}/C_{34} pentacyclic hopane ratio <1). A second family suggests that the samples from Via Blanca 2, 3, 4 wells and well Boca de Jaruco 4 have a more anoxic source (content of C_{35}/C_{34} pentacyclic hopane >1). This compound occurs in variable amount in many oils of different origin (Moldowan *et al.* 1985), and so its presence is not, in principle, indicative of specific origins. However, the oils originating from anoxic hypersaline source rock tend to have large amounts of this triterpenoid relative to the content in $17\alpha(H)$, $21\beta(H)$ -hopanes (Mello *et al.*, 1988).

5.5.2 Steroid hydrocarbons

The m/z 217 mass fragmentogram patterns of sterane distributions in two typical Boca de Jaruco and Via Blanca samples is shown in Figure 13. Huang and Meinschein (1979) have shown that the C_{27} , C_{28} and C_{29} sterols and presumably their reduced equivalents (the steranes), can be used as indicators of depositional environments. An abundance of C_{29} over C_{27} steranes is considered to suggest a terrestrial source, whereas C_{27} steranes predominating over C_{29} steranes would indicate mainly a marine source (Hunt, 1996).

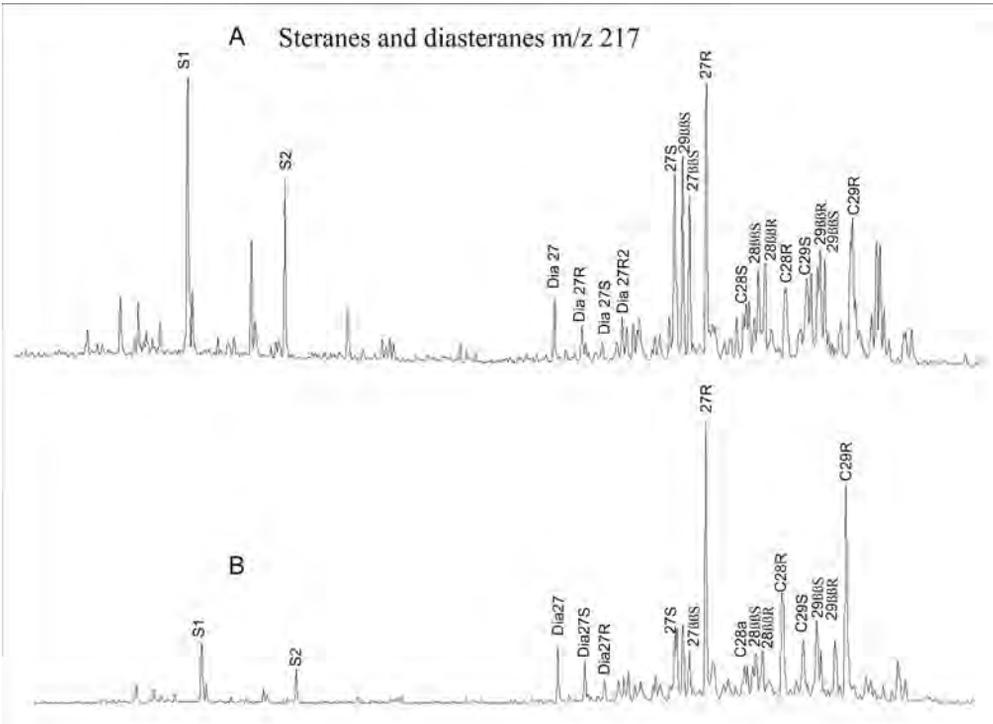


Figure 13. Traces of m/z 217 fragmentograms, illustrating sterane distributions in representative samples from Boca de Jaruco (BJ) -2-1, 2197 and Boca de Jaruco 2-4, 4037 m. Cifuentes Formation.

The application of this relationship for the samples from the Cifuentes Formation indicates that most of the organic matter in the carbonate rocks is of marine origin. Yet the biomarker analyses indicate that the C_{29} sterane concentrations exceed or at best are equivalent to the C_{27} sterane concentrations in Boca de Jaruco extracts (Table 4). Possibly, in a carbonate-evaporitic environment, conditions such as intense microbiologic activity and highly preservative saline conditions could lead to a greater production of the C_{29} steranes.

The relative distribution of C_{27} , C_{28} , and C_{29} steranes was plotted on a ternary diagram showing the relative sterane distributions, which indicates that the steranes of most extracts are shifted towards C_{27} , indicating the close similarity in sterane distribution and suggesting a marine origin of the organic matter (Table 4, Fig. 14). In addition, the presence of C_{30} steranes in most extracts is a strong indicator of a contribution from marine-derived organic matter (Moldowan *et al.*, 1985).

The applicability of biomarker ratios for maturity assessment was also tested by cross plotting of two C_{29} steranes ratios, the 20S/20R ratio and the C_{29} $\alpha\beta\beta(\alpha\beta\beta+\alpha\alpha\alpha)$ ratio according to Seifert and Moldowan (1981). According to this model ratios of 0.50 - 0.55 and 0.67- 0.71, respectively indicate full equilibrium and

Table 4. Sterane biomarker for rock extracted from Cifuentes Formation.

Wells	No.	Depth (m)	C ₂₉ /C ₂₇	%C ₂₇	%C ₂₈	%C ₂₉	C ₂₉ αββ/ (αββ+ααα)	C ₂₉ 20S/ (20S+20R)
VB -2	1	2088	0.66	40.95	26.18	32.88	0.51	0.37
	2	2097	0.67	40.69	26.73	32.58	0.50	0.36
	3	2099	0.66	40.95	26.18	32.88	0.51	0.37
	4	2107	0.66	40.61	26.67	32.72	0.51	0.37
	5	2108	0.67	40.57	26.68	32.75	0.51	0.37
	6	2110	0.69	40.16	26.26	33.57	0.50	0.37
VB-4	1	2180	0.67	41.84	24.95	33.21	0.47	0.37
VB-3	2	2172	0.66	40.73	25.32	33.95	0.50	0.46
BJ-2	1	2197	1.75	50.27	24.64	25.09	0.50	0.39
	3	3786	0.91	34.53	28.76	36.71	0.31	0.21
	4	4037	0.94	34.49	28.70	36.80	0.23	0.12
BJ-3	2	1612	0.87	36.68	25.12	38.20	0.46	0.35
BJ-4	4	1618	1.12	36.07	25.89	38.05	0.40	0.51
BJ-5	2	1860	0.72	39.57	27.36	33.08	0.49	0.39

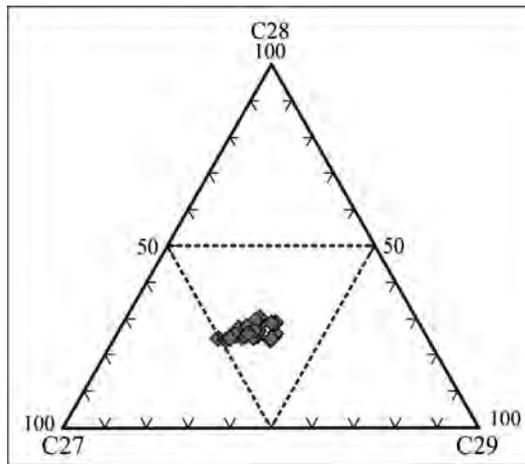


Figure 14. Distribution of regular steranes from Via Blanca and Boca de Jaruco rock extract. Cifuentes Formation.

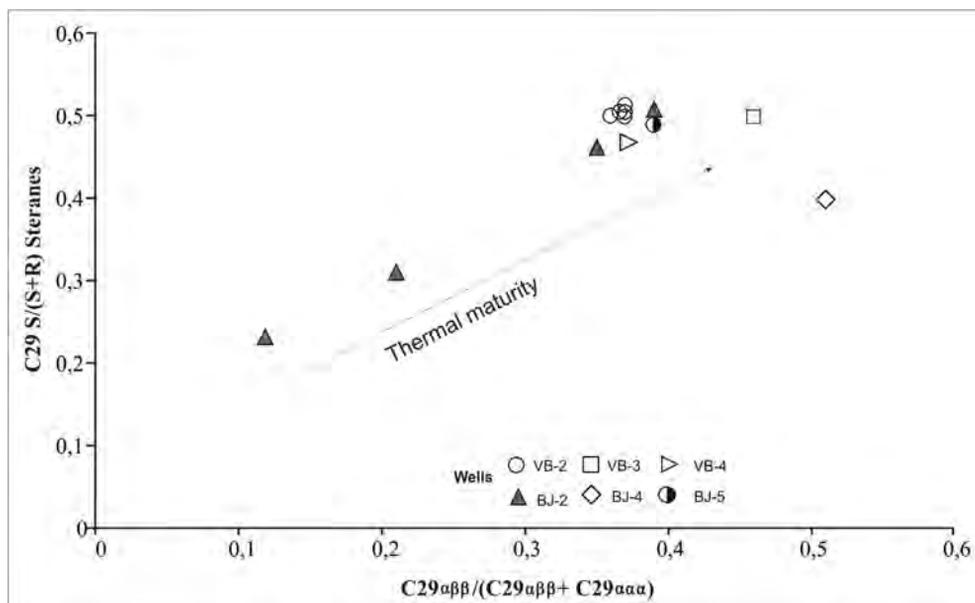


Figure 15. Thermal maturity ratios from biomarker analyses in the Via Blanca and Boca de Jaruco rock extract.

maturity of the organic matter. In the extracts from the Cifuentes Formation the indices vary from, 0.12 to 0.51 and from 0.23 to 0.51, respectively, suggesting a range from immature to early mature (Table 4, Fig. 15).

6. CONCLUSIONS

Based on geochemical parameter, the Cifuentes samples collected from the Via Blanca and Boca de Jaruco wells have more than the minimum TOC required to generate hydrocarbon, with values between 0.52 and 9.91 wt %.

The parameter S2 derived from Rock Eval Pyrolysis, indicates a fair to good hydrocarbon generation potential. Based on HI and OI indices the organic matter is predominantly type I, II and II/III kerogen.

Optical analyses show that the kerogen is autochthonous and is characterized by predominantly marine amorphous organic matter. The high amounts of organic matter are interpreted to relate to a good preservation of amorphous organic matter from degradation of marine plankton in suboxic-anoxic environments.

Results from Gas-chromatographic analyses of the saturated fractions, including pristane/phytane values less than 1, abundant C_{14} to C_{23} n-alkane and a predominance of cycloalkanes, indicate that Cifuentes organic matter is derived mainly from marine plankton and microorganism, confirming the results from optical kerogen analyses. Geochemical fossil (biomarker) distributions also indicate a marine depositional environment, evidenced by abundant C_{27} sterane relative to C_{29} sterane, and the

relatively low quantities of C19 and C20 diterpanes. Biomarker ratios such as C₃₄/C₃₅ hopanes versus gammacerane/C₃₀ hopane suggest a marine environment with organic matter deposited in hypersaline/anoxic cycles and normal marine cycles.

Maturity of the organic matter as determined by Tmax (°C), vitrinite reflectance (%), spore color index (SCI) and biomarker ratios is immature to marginally mature.

ACKNOWLEDGMENTS

The author wishes to express her gratitude to Oil Geology Program, UFRGS, and CAPES for financial support. The Laboratory for Coal and Source Rocks, UFRGS provided the infra-structure to carry out the study as well as financial support for sample analyses.

REFERENCES

- Bustin R.M., Cameron A., Grieve D. and Kalkreuth W., 1989. Coal Petrology – Its Principles, Methods and Applications. Short Course Notes, 33th Edition. Geological Association of Canadá, pp. 273.
- Durand B., 1980. Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen. in: Kerogen: Insoluble Organic Matter from Sedimentary Rock. Editions Technip, Paris, pp. 14-34.
- Echevarria-Rodriguez G., Hernandez-Perez G., López-Quintero J.O., López-Rivera J.G., Rodriguez-Hernandez R., Sanchez-Arango J.R., Socorro-Trujillo R., Tenreyro-Perez R. and Yparraguirre-Pena J.L., 1991. Oil and gas exploration in Cuba. *Journal of Petroleum Geology*. **14**(2), 259-274.
- Espitalié J., Laporte J.L., Madec M., Marquis F., Leplat P., Paulet J. and Boutefeu A., 1977. Méthode rapide de caractérisation des roches mères de leur potential pétrolier et de leur degré dévoluton. *Oil & Gas Science and Technology – Rev* **32**(1), 23-42.
- González M.B., 2002. Petrografia e Geoquímica das rochas geradoras de hidrocarbonetos nas formações Constancia e Cifuentes, Jurássico Superior da Bacia da Margem Continental Cubana, Master, Universidade Federal do Rio Grande do Sul, UFRGS, Porto Alegre, Brasil, pp. 113 .
- González M.B., 2012. Análise dos Parâmetros Petrográficos e de Geoquímica Orgânica das Rochas Geradoras das Formações Constancia e Cifuentes (Jurássico Superior). Bacia da Margem Continental Cubana. D.Thesis, Universidade Federal do Rio Grande do Sul, UFRGS, Porto Alegre, Brasil, pp 190.
- Hatten C.W., Somin M.L., Millan G., Renne P.R., Kistler R.W. and Mattinson J.M., 1988. Tectonostratigraphic units of Central Cuba. In *Trans. 11 th Caribbean Geology Conf., Barbados* **35**, pp. 1-14.
- Huang W.Y. and Meinschein W.G., 1979. Sterols as ecological indicators. *Geochemica et Cosmochimica Acta* **43**(5), 739-745.
- Hunt J.M., 1996. Petroleum Geochemistry and Geology. Second Ed. W. H. Freeman, New York, pp. 743.

- Katz B.J., 1983. Limitations of Rock-Eval pyrolysis for typing organic matter. *Organic Geochemistry* **4(3)**, 195-199.
- Lopez-Quintero J.O., Campos-Jorge P.G., Navarrete-Reyes L.E. and Principe Valdes M.L., 1994. Cuban source rocks. In Mello, M.R., Trinidad L.A.F. and Hessel M.H.R. (eds.), Fourth Latin American Congress on Organic Geochemistry, Extended abstracts volume, Bucaramanga, Colombia, pp. 102-108.
- Langford F.F. and Blanc-Valleron M.M., 1990. Interpreting Rock-Eval pyrolysis data using graphs of pyrolyzable hydrocarbons vs. total organic carbon. *American Association of Petroleum Geologist Bulletin*, **74(6)**, 799-804.
- López J.G., López J.O. and Pascual O., 1997. Setting and petroleum systems for exploration in Cuba. Internal Report of CEINPET, Cuba.
- Mackenzie A.S., Maxwell V.M. and Durand B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. In: Changes in the configurations of cyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta.* **44 (11)**, 1709-1712.
- Magnier C., Moretti I., Lopez J.O., Gaumet F., Lopez J.G. and Letouzey J., 2004. Geochemical characterization of source rock, crude oils and gases of Northwest Cuba. *Marine and Petroleum Geology* **21(2)**, 195-214.
- Mello M.R., Gaglianone P.C., Brassell S.C. and Maxwell J.R., 1988. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. *Marine and Petroleum Geology* **5(3)**, 205-223.
- Moldowan J.M., Seifert W.K. and Gallegos E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *American Association of Petroleum Geologist Bulletin*. **69(8)**, 1255-1268.
- Navarrete L.E. Lafarge, E., 1994. "Geochemistry of Cuban oils and source rock", Memorias del IV Congreso Latinoamericano de Geoquímica Orgánica de ALAGO, Bucaramanga, Colombia. Pp.122-128.
- Peters K.E., Walters C.C. and Moldowan, J.M., 2005. The Biomarker Guide Biomarkers and Isotopes in Petroleum Exploration and Earth History. University of Cambridge Press, Cambridge, pp. 475-1155.
- Peters K.E., Moldowan J.M., Mccaffrey M.A. and Fago, F.J., 1996. Selective biodegradation of extended hopanes to 25-norhopanes in petroleum reservoirs. Insights from molecular mechanics. *Organic Geochemistry* **24(8/9)**, 765-783.
- Peters K. E. and Cassa M.R., 1994. Applied Source Rock Geochemistry. In: Magoon, L.B. and Dow, W.G., The Petroleum System- from source to trap: AAPG Memoir 60: 93-120.
- Peters K.E. and Moldowan J.M., 1993. Interpreting molecular fossils in petroleum and ancient sediments. Prentice Hall, Englewood Cliffs, pp. 110-265.
- Pindell J.L. and Kennan L., 2001. Kinematic evolution of the Gulf of Mexico and the Caribbean. In. Petroleum systems of deep-water basins: global and Gulf of Mexico experience., Proceedings, 21st Annual Research Conference, Society of Sedimentary Geology, December 2-5, 2001. Houston, Tex, pp. 159-192.

- Pindell J.L., and Kennan L., 2003. Timing, kinetics, and paleogeography of the evolution of the southeast Gulf of Mexico and northern proto-Caribbean sea—Template for the Paleogene Cuban orogeny [abs.]: Havana, Cuba, Fifth Cuban Congress on Geology and Mineralogy, p. 14.
- Pindell J.L., Kennan L., Maresch W.V., Stanek K-P., Draper G., and Higgs R., 2005. Plate-kinematic and crustal dynamics of circum-Caribbean arc-continent interactions—Tectonic controls on basin development in proto-Caribbean margins, *in* Lallemant, H.G.A., and Sisson, V.B., eds., Caribbean-South America plate interactions, Venezuela: Geological Society of America Special Publication 394, p. 7–51.
- Ruble T.E., Bakel A.J. and Philp R.P., 1994. Compound specific isotopic variability in Uinta Basin native bitumens: paleoenvironmental implications. *Organic Geochemistry*, **21(6/7)**, 661-671.
- Rullkötter J., Aizenshtat Z. and Spiro B., 1984. Biological markers in bitumen and pyrolyzates of Upper Cretaceous bituminous chalks from the Ghareb Formation (Israel). *Geochimica et Cosmochimica Acta* **48(1)**, 151-157.
- Sanchez-Arango J.R., Socorro R., Lopez S., Sora A., Dominguez R. and Toucet S., 2003. Estratigrafía integrativa aplicada en la Zona Económica Exclusiva (ZEE) de Cuba en el sureste del Golfo de México (Aguas profundas): *Memorias Geomin*, La Habana, Marzo 24-28, 8 p.
- Seifert W.K. and Moldowan J.M. 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *Physics and Chemistry of the Earth* **12**, 229-237.
- Seifert W.K. and Moldowan J.M., 1981. Paleo-reconstruction by biological markers. *Geochemistry Cosmochim Acta* **45**, 783-794.
- Ten Haven H.L., Rohmer M., Rullkotter J. and Bisseret P., 1989. Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. *Geochimica et Cosmochimica Acta* **53(11)**, 3073– 3079.
- Tissot B. and Welte D.H. 1984. Petroleum Formation and Occurrence, 2nd. Springer Verlag, New York, pp 554.
- Tyson R.V., 1993. Palynofacies Analysis. In: Jenkins D.G. (ed.), Applied Micropaleontology. Springer Netherlands, pp. 153-191.
- Tyson R.V., 1995. Sedimentary Organic Matter: Organic Facies and Palynofacies Analysis. Springer, London, pp 615.

