ORGANIC GEOCHEMICAL DATA FROM THE CABALLOS FORMATION, UPPER MAGDALENA VALLEY, COLOMBIA

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ABSTRACT—A section of the Caballos Formation in the Upper Magdalena Valley exhibits two lithological segments that represent probable hydrocarbon source rocks. In order to explore its generation potential, basic organic geochemical data are presented and discussed. The results indicate the presence of marine and terrestrial organic matter in the two segments sampled. In the youngest segment a few samples contain only marine derived kerogen. The geochemical parameters indicate in general rather poor oil source rock characteristics. The hydrocarbon generation in this segment was not achieved in the section studied as indicated by the slightly low thermal maturity values.

RESUMEN—La Formación Caballos presenta en la sección estratigráfica estudiada dos segmentos litológicos que pueden representar rocas fuente de hidrocarburos. Se presentan resultados de geoquímica orgánica que revelan datos sobre su composición orgánica y potencial generador. Los resultados muestran la presencia de materia orgánica de origen marino y terrestre en ambos segmentos. Algunas muestras del segmento más jóven contienen únicamente kerógeno marino. Los parámetros de roca fuente indican en general un bajo potencial generador debido a que la madurez termal necesaria para liberar hidrocarburos no fue alcanzada en la sección muestreada.

1. INTRODUCTION

Within the Upper Magdalena Valley (UMV) the Caballos Formation has proved to be an excellent reservoir, yielding a significant amount of the production of the basin, currently around 60,000 BOPD. The few organic geochemical studies that have become of public domain have focused on the superseding "Villeta" Formation in the UMV or Putumayo basin, which has been identified as source rock for these basins (e.g. Maldonado and Mantilla, 1989). Apart from the fact that the Caballos Formation is one of the most important oil reservoirs in the basin, the organic matter bearing rocks within this unit may also represent a hydrocarbon source, worth being tested. This paper presents basic organic geochemical data from this unit and discusses its probable source rock potential.

The geological setting of the basin is related to the opening of a supracontinental rift system or back arc basin that acted as a sediment trap along the present day Eastern Cordillera and Magdalena Valley (Macía et al., 1985, among others). In the UMV the name Caballos Formation was used in the basin since 1967 but it was formally introduced in the literature by Corrigan (1979), through an edition of serial guidebooks of geological field trips. More recent works have described in detail the unit in diverse localities (e.g. Mendivelso, 1982; Moreno and Robles, 1987; Peñas and Vargas, 1989; Flórez and Carrillo, 1994; Renzoni, 1994; Vergara, 1994). Vergara et al. (1995) furnished comments about the nomenclature and stratigrahic relationships as handled in some of the above mentioned works.

Within the predominantly sandstone beds of this unit, a dark shale intercalation is known from earlier works (Corrigan, 1979; Beltrán and Gallo, 1979). In this paper not a single but two shale-carbonate segments are described and their potential as source rocks is explored.

2. STRATIGRAPHY

The following lithological succession was measured in detail at the section that starts in the Quebrada Palmarosa and ends at the Quebrada Bambucá, near Aipe (Huila). For localization of the section see Fig. 1. The lower limit is placed at the top of the highest traceable mudstone of the underlying Yaví Formation. The upper limit of the Caballos Formation is picked here at the top of a segment of thick bedded sandstones overlain by a thick succession of dark shales of the Hondita Formation (Vergara, 1994).

Five segments are easily separated at the section of the Quebradas Palmarosa and Bambucá (fig. 2), from oldest to youngest. 1) Consists of 49 m of medium bedded sandstones with inner undulose and inclined laminae. The sandstones may be

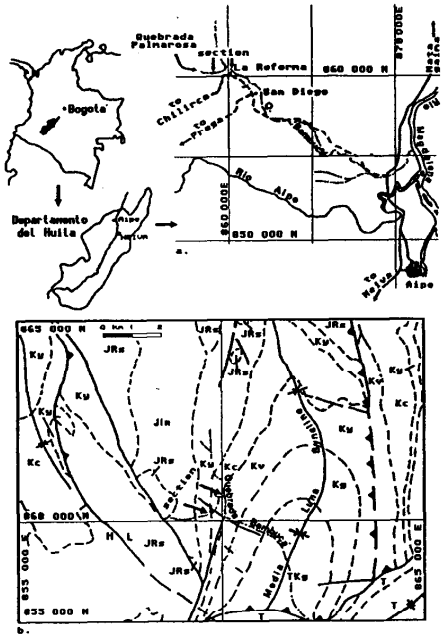

Figure 1. *a) Access to the section studied; b) geology of the section (after Fúquen et al., 1989) Jin=Los Naranjos Stock; JRs=Saldaña Formation; Ky= Yaví Formation; Kc= Caballos Formation; Kv= "Villeta" Formation; Kg= "Guadalupe" Formation; TKg= "Guaduas" Formation; T= Tertiary*

sandstones may be arkosic or lithic. Some thin sideritic lenses are present. 2) Overlying this basal segment a 20 m thick segment of black laminated shales intercalated with carbonates occurs. The lower contact is marked by the oldest limestone bed of the succession. The shales contain abundant fish scales, some planktic foraminifera and dinoflagellates. A biosparudite bank of rudstone texture occurs at this level. 3) Segment 3 is a 122 m thick interval of predominantly quartz arenites with little feldspar, some rock fragments and clay matrix. At the Quebrada Palmarosa, 23 m of the lower portion of this segment are slightly overturned, evidenced by the relation of stratification to squistosity in mudstones (S_0 steeper than S_1). 4) This segment is formed by 70 m of dark shales and carbonates. The latter are represented by biomicrites, a biosparudite similar to that of segment 2 (rudstone), stratified and concretionary siderite, and dolomite. Fossils include planktic as well as benthic foraminifera, ostracodes and mollusks. Towards the top, the carbonate beds decrease, ichnofossils become abundant and thin mudstone intercalations with flaser structures occur. 5) This is a 40 m thick interval of mainly fine grained sandstones sometimes with poikilotopic texture of calcite cement filling the pores.

Biostratigraphy of this succession is presented by Vergara (1994). However, a re-evaluation of the age of the segments of the Caballos Formation is discussed in Vergara et al. (1995), who established a Late Aptian age for Segment 2 and placed the Aptian/Albian limit in the lower part of Segment 4.

The depositional environment can be summarized as diverse littoral subenvironments that occur in segments 1, 3 and 5, whereas in segments 2 and 4 deposition over the shelf is registered. For the paleobathymetrical appraisal of these two segments not only the lithological relationships but also the information provided by foraminifera and palynomorphs were utilized. Sea level changes account for the cyclic pattern observed, and three depositional sequences that comprise the lower Cretaceous units are recognizable (Vergara, 1992, 1994).

In segments 2 and 4 of the Caballos Formation, the presence of gray to black parallel laminated shales devoid of bioturbation are indicative of poorly oxygenated or anoxic conditions at the sediment-water interface (e.g. Demaison and Moore, 1980). These segments may represent anoxic sub-events associated with the Aptian-Albian oceanic anoxic event documented widely in the geological record (Arthur et al., 1988 and references therein).

3. ORGANIC GEOCHEMISTRY

3.1 Methods

Elemental analyses and Rock-Eval Pyrolysis were performed systematically on all samples from segments 2 and 4 of the Caballos Formation. A CHN-O-RAPID Analyser of the brand Heraeus and a Rock-Eval device of Delsi Instruments were used. The measurements were run on some 30 mg of whole and decarbonated samples, all previously pulverized in a ball mill. Decarbonation included treatment with 10 % concentrated HCl, neutralization and drying at 50°C. The total organic carbon (TOC; in weight%) was obtained from the equation:

$$TOC\ (\%) = [100 - (8.333 * TC)] / [100/TOC) - 8.33]$$

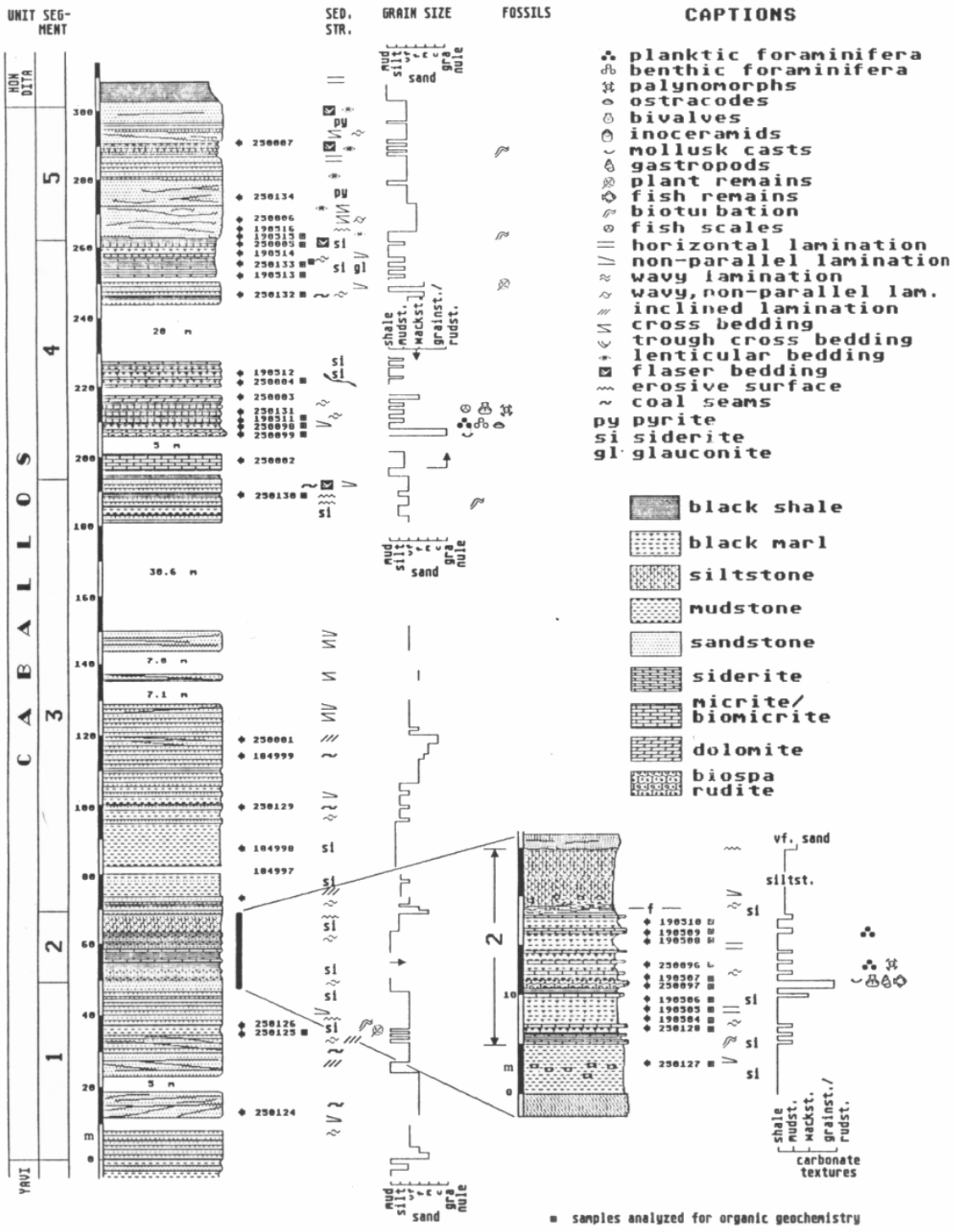

Figure 2. *Stratigraphic column of the Caballos Formation in the Quebradas Palmarosa and Bambucá.*

where TC is the total carbon content and TOC is the carbon content in the carbonate-free sample. The amount of $CaCO_3$ was calculated from the formula: $CaCO_3$ (%) = (TC - TOC) * 8.333

The organic carbon/nitrogen (C/N) ratio was derived from dividing TOC by the nitrogen content (N tot) measured in the elemental analysis (whole sample). This parameter, commonly used in Quaternary marine research, gives some information about the composition of the organic matter: marine plankton has a mean C/N ratio of 6, while a ratio of >>15 indicates a higher land plant provenance (Bordowskiy, 1965 cited in Stein et al., 1989). In ancient or organic lean rocks, however, C/N ratios should be used with discretion (cf. Stein et al.) because the values indicative of marine or terrestrial organic matter appear to be considerably higher.

The Rock-Eval pyrolysis method (Espitalié et al., 1985) was used in this work. The analyses were run on 100 mg of bulk sample and the following parameters were calculated:

-Production Index (PI)= S1/S1 + S2

-Hydrogen Index (HI)= S2 * 100/TOC (in mg of hydrocarbons/ g C)

-Oxygen Index (OI)= S3 * 100/TOC (in mg CO2/ g C)

-T max= oven temperature at the maximum hydrocarbon generation (S2 peak apex).

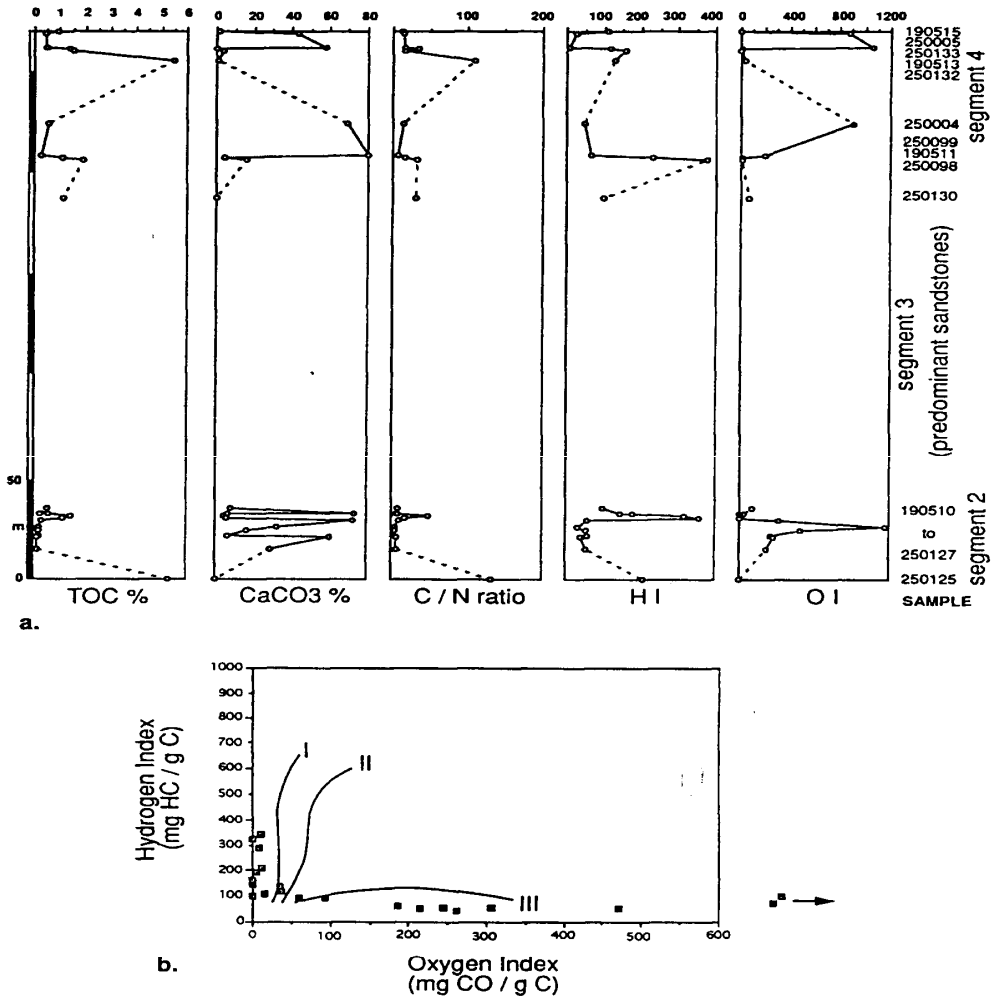

Figure 3. *a) Basic organic geochemical data from segments 2 and 4 of the Caballos Formation at the Aipe section; b) corresponding van Krevelen-type diagram.*

For the characterization of organic matter the ranks of TOC, S1, S2, PI, Tmax, C/N, HI and OI as qualified by Peters (1986) were followed. The thermal maturity evaluation given by T max depends on kerogen type and HI, OI is related to vitrinite reflectance, assumed here to be 0.6% (cf. Peters, 1986).

3.2 Results and interpretation

The geochemical analyses performed on the organic matter bearing segments (2 and 4) of the Caballos Formation are presented in Table 1 and plotted in Fig. 3. Apart from these segments, in segment 1 and in the underlying Yaví Formation, stumps or small coaly lenses with plant remains are common, as in sample 250125, which contains 5.7% of TOC (see table 1).

In segment 2, TOC values seem to be poor for hydrocarbon generation, with an average of 0.47%. Very low TOC values constitute a limitation for addressing the type of organic matter with Rock-Eval data as demonstrated by Katz (1983). Hence, single high HI or OI values should be interpreted with discretion. The TOC spikes represented by samples 190507 and 250096 are matched by high HI values, suggesting a marine provenance of the organic matter. This is supported by the presence of dinoflagellates and marine derived organic matter as observed in palynological slides of sample 250096 (LV-14 of Prössl and Vergara Streinesberger, 1993). However, the predominantly low HI values suggest a significant terrestrial input, particularly in the lower part of this segment.

Segment 4 of the Caballos (early-middle Albian) shows variations in the geochemical signal, particularly in HI and TOC values, some of them indicating fair to good source rock properties. An exceptionally high TOC value (5.47%) for sample 250132 is due to the presence of plant remains in the sample. Excluding this value the TOC averages 0.97%, which can be regarded as fair to good source rock generative potential according to the rank scheme of Peters (1986).

Figure 4 shows a gas chromatograph of an organic extract from sample 250098, which comes from the lower part of this segment. The C+10 saturated hydrocarbon fraction of the chromatogram shows a Pristane/Phytane (Pr/Ph) ratio greater than 1, which supports oxic conditions according to Didyk et al. (1978). Although Pr/Ph has been questioned as an environmental indicator of oxicity (Ten Haven et al., 1987), in this case the interpretation of a rather oxic environment seems reasonable because a fair

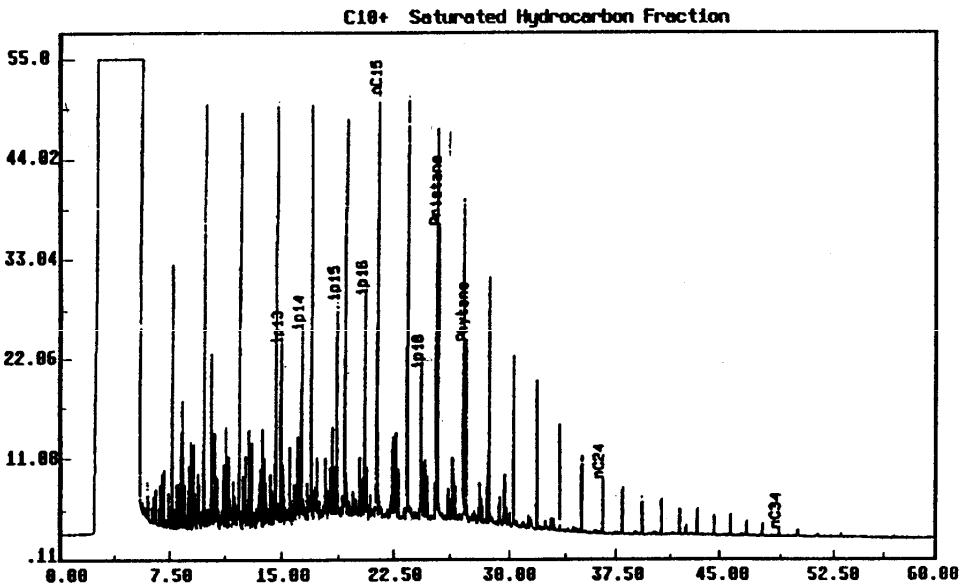

Figure 4. *Gas chromatography of an organic extract from sample 250098 of segment 4 of the Caballos Formation (courtesy of Occidental de Colombia).*

sample	age	lithology	TC	TOC^	N tot	TOC%	C/N	CaCO3%	T max	HI	OI	PI
250125	Late Aptian	mudstone, plant remains	5.31	5.52	0.04	5.70	143.00	0.00	429	193	5	0.09
250127	Late Aptian	mudstone	3.63	0.2	0.02	0.14	6.86	29.10	434	56	222	0.43
250128	Late Aptian	micrite	7.35	0.36	0.02	0.14	7.00	58.30	423	41	271	0.37
190504	Late Aptian	dark shale	0.99	0.25	0.06	0.23	3.70	6.20	431	60	253	0.12
190505	Late Aptian	dark shale	2.24	0.25	0.04	0.21	4.83	16.60	439	53	486	0.25
190506	Late Aptian	dark shale	4.1	0.33	0.04	0.22	5.01	31.50	446	32	1165	0.12
250097	Late Aptian	biosparudite	9.05	1.26	0.03	0.35	11.50	64.90	420	58	316	0.44
190507	Late Aptian	dark shale	1.85	1.19	0.06	1.12	18.90	5.50	429	357	0	0.08
250096	Late Aptian	dark shale	1.95	1.52	0.03	1.45	48.50	3.60	433	317	10	0.09
190508	Late Aptian	dark shale	1.35	0.62	0.06	0.58	10.20	6.00	434	177	0	0.11
190509	Late Aptian	micrite	9.06	0.93	0.04	0.25	6.05	67.70	431	145	36	0.14
190510	Late Aptian	dark shale	1.5	0.6	0.06	0.55	8.87	7.50	436	98	96	0.1
250130	Early Albian	dark shale, carbonaceous	1.13	1.13	0.04	1.13	28.00	0.00	438	97	62	0.08
250099	Early Albian	biomicrite	1.6	1.16	0.07	0.26	6.35	71.20	421	65	192	0.08
250098	Early Albian	dark shale	3.81	2.28	0.06	1.11	16.60	3.70	433	228	13	0.08
190511	Early Albian	dark shale	9.83	1.29	0.04	1.92	32.00	12.70	427	375	11	0.6
250004	E/M Albian	siderite	8.87	1.78	0.04	0.55	15.60	59.00	437	48	902	0.07
250132	E/M Albian	dark shale, coaly	5.57	5.51	0.05	5.47	101.00	0.50	432	128	38	0.06
190513	E/M Albian	dark shale	1.95	1.58	0.09	1.52	17.00	3.10	434	156	0	0.07
250133	E/M Albian	dark shale	1.4	1.38	0.04	1.38	39.40	0.20	437	115	16	0
250133A	E/M Albian	shale, glauc., phosph.	7.42	1.18	0.03	0.50	19.30	52.00	406	8	1061	0
250005	E/M Albian	sparite, glauc., qtz	5.61	0.78	0.03	0.45	15.90	40.20	434	27	878	0.21
190515	E/M Albian	dark shale	1.11	0.94	0.07	0.92	13.00	1.40	432	109	0	0.06

Table 1. *Organic carbon and Rock-Eval pyrolysis data from the Caballos Formation.*

fauna of benthic foraminifera and ostracodes was recovered from this sample. The predominance of short carbon chains (C_{10}-C_{15}) indicate marine, algal/bacterial kerogens, while the terrestrial fraction is absent in the chromatogram.

In general, the HI/OI ratios support the presence of marine derived organic matter in the lower part of the segment and terrestrial organic matter towards the top. This is in agreement with the sedimentological observations that indicate a shallowing of the basin up-section (Vergara, 1992). The geochemical signature suggests that segment 4 of the Caballos Formation has experienced intermittent oxic-anoxic conditions and received both marine and terrestrial organic input during its deposition.

Regarding the thermal maturity, low averages of Tmax (431°) and production index, together with a mean vitrinite reflectance value of 0,5% for sample 250098, indicate that the sampled shales of segment 4 of the Caballos Formation were immature for oil generation, but close to the birth line of the oil window.

4. CONCLUSIONS

The lithological succession of the Caballos Formation exhibits two shale-carbonate segments that may represent source rocks. They correspond to periods of relative sea level rise during which organic carbon accumulation was due to poorly oxygenated or anoxic conditions. However, periods of better oxygenation hindered its preservation in larger amounts.

In the absence of organic petrographical information, other data are used here to support the pyrogram interpretation (palynology, gas chromatography). It is shown according to basic parameters of geochemical exploration that organic matter of marine and terrestrial type is present in both of the segments. In the youngest of these segments (4) oil-prone kerogen has been identified at its lowest part. In spite of this, in the section studied of the Quebradas Palmarosa and Bambucá, the generation of hydrocarbons was hampered by the unsufficient maturity achieved by the potential source rocks.

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