EARTH SCIENCES
RESEARCH JOURNAL

Earth Sci. Res. J. Vol. 25, No. 2 (June, 2021): 179-192

UNIVERSIDAD NACIONAL DE COLOMBIA

GEOLOGY

Thermal evolution of Los Cuervos formation in the southern area of the Cesar sub-basin (Colombia), based on geochemical and petrophysical data

Gladys Marcela Avendaño-Sánchez[1,2], Mario García-González[1,3], Luis Enrique Cruz-Guevara[1,3], Luis Felipe Cruz-Ceballos[1,2].
1. Universidad Industrial de Santander
2. Grupo de Investigación en Geología Básica y Aplicada (GIGBA)
3. Energy and Other Non-Renewable Resources Research Group (EONr3g)

ABSTRACT

The tectonic complexity that occurred during the Cenozoic at the Cesar-Ranchería Basin (Colombia) has generated changes in the evolution of its petroleum system. Proof of this is the lack of stratigraphic records in the Cesar sub-basin during both the early Eocene and in the late Eocene-early Miocene interval. In this study, authors analyzed information already published regarding the sub-basin and new geochemical data obtained from Rock-Eval pyrolysis analyses and vitrinite reflectance (Ro%). The core samples used are from the ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. Based on this information, Los Cuervos Formation was classified as a source rock for its geochemical characteristics. Additionally, the geochemical and petrophysical results indicate continuous deposition of sediments from the Paleocene to the late Eocene. These results were obtained using samples from two wells (Calenturitas and La Jagua) at Los Cuervos Formation and the paleo-geothermometer data of Paleocene formations. Based on density and compaction conditions, it is clear that it corresponds to a sequence of quartz sandstones. Therefore, it is expected the Eocene Sedimentites unit has reached a thickness between 2.5 to 3.5 km. According to recent thermo-chronological studies, this unit began to be eroded from the late Eocene to the early Miocene. The evidence obtained helped improve the knowledge in the thermal evolution model of the petroleum system, establish the time when the organic transformation ratios (TR) occurred, and estimate the current state of the Cretaceous source rocks of the Cesar sub-basin.

Keywords: Cesar-Rancheria Basin; Cesar sub-basin; Los Cuervos Formation; Source Rock; Geochemical Modelling; Porosity-Depth Relation.

Evolución termal de la formación Los Cuervos, en el área sur de la subcuenca Cesar, con base en datos geoquímicos y petrofísicos

RESUMEN

La complejidad tectónica a la cual fue sometida la cuenca Cesar-Ranchería durante el Cenozoico generó cambios en la evolución de su sistema petrolífero. Prueba de ello es la falta de registro estratigráfico en la subcuenca Cesar durante el Eoceno temprano y el intervalo Eoceno-Mioceno temprano. En este estudio los autores analizan la información publicada y nuevos datos de pirolisis Rock-Eval y de reflectancia de vitrinita (Ro%) con muestras de núcleos de perforación de dos nuevos pozos (ANH-La Loma-2 y ANH-CR-Los Cerezos-1X). Basados en esta información fue posible clarificar las características geoquímicas de la Formación Los Cuervos como roca fuente de hidrocarburos. Adicionalmente, los resultados geoquímicos y petrofisicos, obtenidos con muestras de dos pozos (Calenturitas y La Jagua) de la Formación Los Cuervos y datos de paleogeotermómetros de formaciones del Paleoceno, indicaron la existencia de una depositación continua de sedimentos desde el Paleoceno hasta el Eoceno tardío. Con base en las condiciones de densidad y compactación observadas es claro que esto corresponde a una secuencia de areniscas de cuarzo. Por lo tanto, se espera que la unidad de sedimentitas del Eoceno haya alcanzado un espesor de 2.5 – 3.5 km. Esta unidad de roca, de acuerdo con estudios recientes de termocronología, comenzó a ser erosionada en el Eoceno tardío y hasta el Mioceno temprano. La evidencia obtenida permitió mejorar el modelo de evolución termal del sistema petrolífero, establecer el tiempo en el cual ocurrieron las transformaciones orgánicas y estimar cómo están actualmente las rocas generadoras del Cretáceo de la subcuenca Cesar.

Palabras clave: Algoritmo de localización 3D; interferencia masiva y no masiva; geoestratigrafía; roca circundante; REE; rastro.

Record
Manuscript received: 03/04/2020
Accepted for publication: 16/10/2020

How to cite item
Avendaño-Sanchez, G. M., Garcia-Gonzalez, M., Cruz-Guevara, L. E., & Cruz-Ceballos, L. F. (2021). Thermal evolution of Los Cuervos formation in the southern area of the Cesar sub-basin (Colombia), based on geochemical and petrophysical data. *Earth Sciences Research Journal*, 25(2), 179-192. DOI: https://doi.org/10.15446/esrj.v25n2.86025

Introduction

Numerous studies have been carried out in the Cesar sub-basin. This sub-basin is part of the Cesar-Ranchería Basin, northern side of Colombia (Figure 1). These studies have determined the source rock formations and their hydrocarbon potential, and have also indicated the generation potential, the organic matter contents, and the potential of accumulation as shown in the study from García *et al*. (2008). Other authors such as Mesa and Rengifo (2011) pointed out that about 50 wells were drilled in the Cesar sub-basin and it was determined a petroleum system in the sub-basin consisting of source rocks: Lagunitas, Aguas Blancas, La Luna, Molino, and Los Cuervos formations; reservoir rocks: with fractured reservoirs of Lagunitas and Aguas Blancas formations; and seal rocks: represented by a thick mudstone sequence of the Molino Formation. The hydrocarbon traps are pop-up structures, and fault propagation folds. The overburden sequence is integrated by Lagunillas to Cuesta-San Antonio formations, and the regional seal on top is the Miocene Cuesta-San Antonio Formation.

In the Cesar Basin, the Barco Formation consist of quartz sandstone and claystone, and Los Cuervos Formations consists of claystone, siltstone, and several coal seams, according to Guo *et al*. (2018). Barco and Los Cuervos formations were deposited during the Paleocene in a continental environment as a product of a slow regression (Hernández, 2003). Los Cuervos Formation corresponds to a sequence of carbonaceous shales, siltstones, sandstones, and coal beds (Mesa and Rengifo, 2011).

Studies carried out by Barrero *et al*. (2007) and Mesa and Rengifo (2011) show the importance of the exhumation of the Perijá Range (PR) for the Cesar Sub-Basin petroleum system. This is because this exhumation generates the formation of traps and marks the change in the existing conditions in terms of accommodation space. Consequently, it also controls the increase of the lithostatic charge, thus increasing the maturation of the source rocks. Evidence of the time of occurrence of this event was provided by Bayona *et al*. (2007), who stated that the northern sector of the PR was at the Early Paleocene-Eocene period; contributions were already being made to both the Ranchería sub-basin and the Maracaibo Basin (Bermúdez *et al*., 2017). Other authors, like Shagam *et al*. (1984), established that this uplift started from the Cretaceous-Paleogene limit and had successive pulses of uplift throughout the Cenozoic.

This study uses published information of the Cesar sub-basin, 31 data from the maximum pyrolysis temperature (Tmax) and 13 data from vitrinite reflectance (Ro%) from Los Cuervos Formation in the Calenturitas and La Jagua wells; and new geochemical data, 24 samples from Tmax and 14 samples from Ro% from the ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. This study aims to establish the current maturity state and the potential for hydrocarbon generation (quality and quantity) of the rocks in the Los Cuervos Formation. Furthermore, the goal is to recreate the burial history scenario through numerical modelling with the PetroMod software (version 2012). The modelling is based on geochemical data, the stratigraphic/structural architecture as interpreted by 2D seismic reflection data, and the several uplift events of the Perijá Range that affected the burial history. It also provides insights that

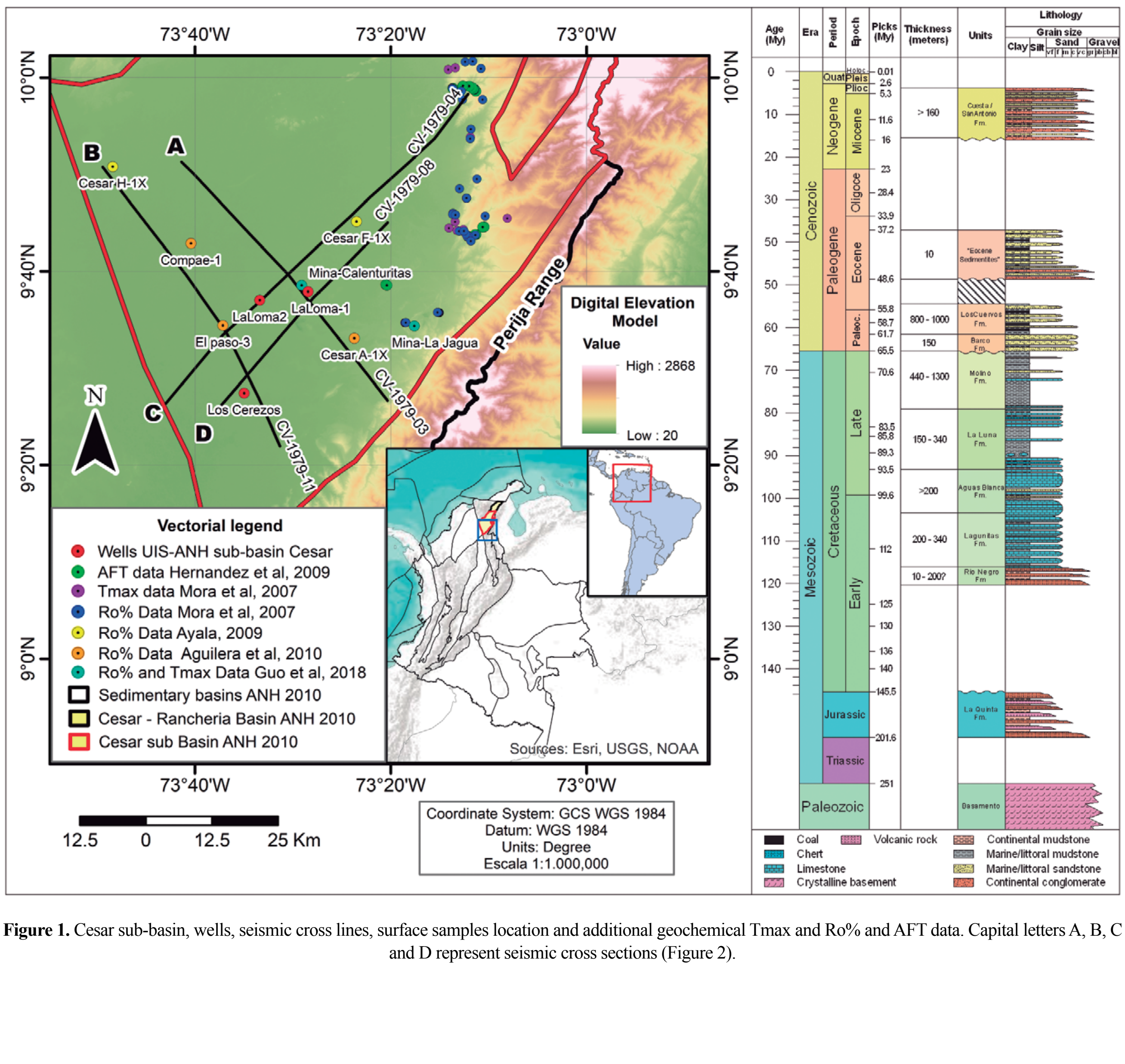

Figure 1. Cesar sub-basin, wells, seismic cross lines, surface samples location and additional geochemical Tmax and Ro% and AFT data. Capital letters A, B, C and D represent seismic cross sections (Figure 2).

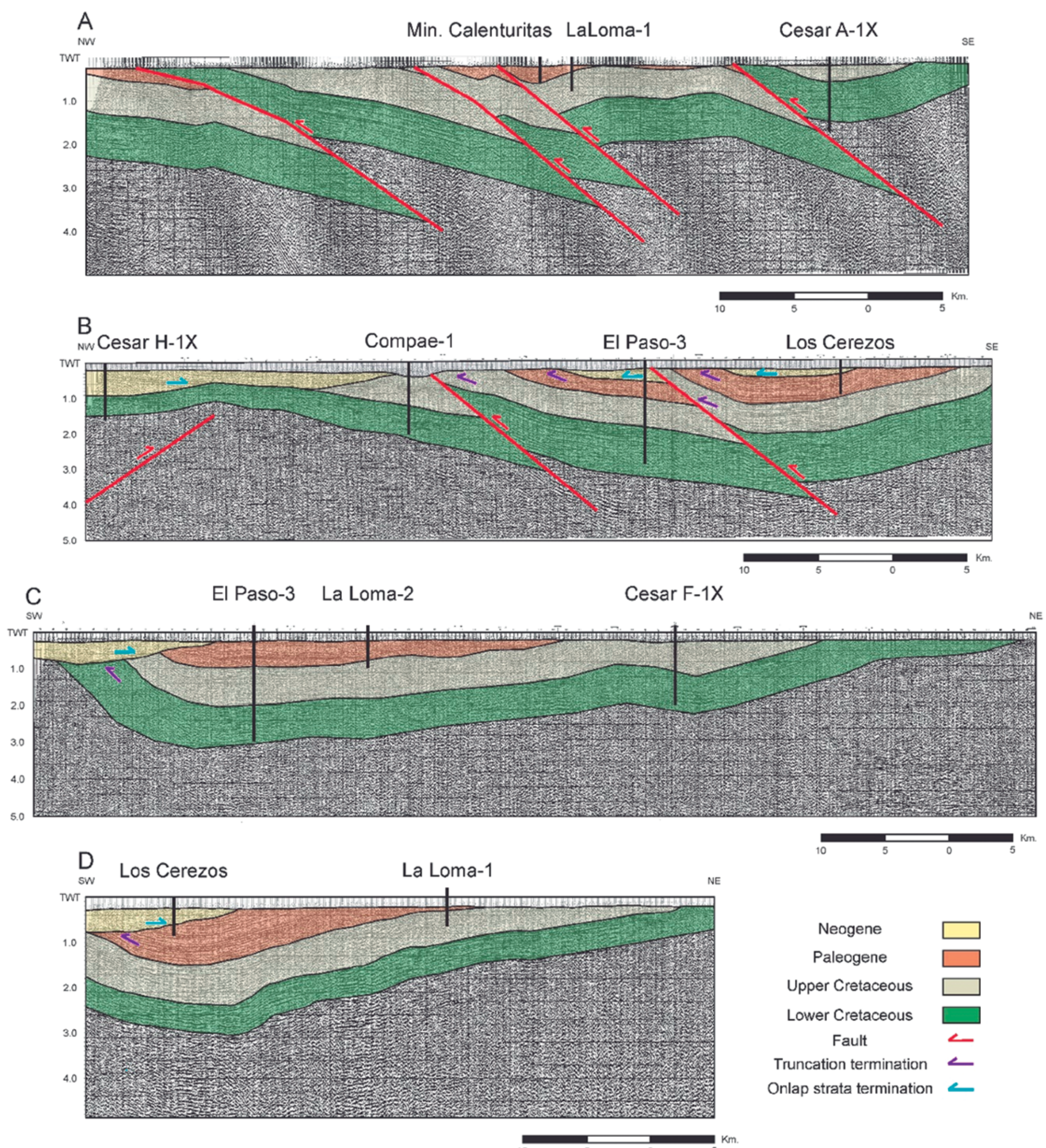

Figure 2. Interpreted 2-D seismic lines in two-way time (TWT) with location of the wells; A. CV-1979-03 seismic line; B. CV-1979-11 seismic line; C. CV-1979-04 seismic line; D. CV-1979-08 seismic line.

would help understand the current state of maturity, as well as the organic transformation ratios (TR) of the Cretaceous formations underneath Los Cuervos and Barco formations. This is fundamental for any understanding of the organic geochemical characteristics of Los Cuervos Formation, as well as how the basin was filled with sediments. This process has direct implications regarding the maturation of organic matter of the units as well as the generation of hydrocarbons.

The interpreted 2-D seismic lines with structural reconstruction, main faults, truncated seismic refractor and on lap-strata terminations of the Cretaceous, Paleogene, and Neogene formations are presented in Figure 2.

Data and methods

Geochemical analysis was used to establish the type and quality of organic carbon and other geochemical properties of rocks, which contributed to the evaluation of the potential production of conventional or unconventional hydrocarbons in a prospective play. Geochemical data were obtained using core samples from Los Cuervos Formation of two wells, ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. Vertical sampling was not performed at equal intervals (Figure 3). The selection criterion was based on the visible presence of organic matter using an ultraviolet lamp.

The geochemical analysis was carried out at UIS Petroleum geochemistry laboratory (PGL). Geochemical analysis of Rock-Eval pyrolysis (HI, OI, PI, S1, S2, S3, Tmax, PY), total organic carbon (TOC), and total sulphur content (TS) (Table 1), Ro% (Table 2). Additional existing geochemical data (Tmax and Ro%) used were obtained from Hernández and Jaramillo (2008); Mora *et al*. (2007); Ayala (2009) and Guo *et al*. (2018). Thermal maturation data of the Cesar A-1X, Compae-1, and El Paso-3 wells was obtained from Aguilera *et al*. (2010), Ayala (2009), Mora *et al*. (2007) and Guo *et al*. (2018) including Ro% and Tmax data of surface samples. Petrophysical analysis including permeability and porosity of sandstones and mudstones (514 samples) were performed at the UIS Petrophysical analysis laboratory (Supplementary Materials Table S1). The Colombian Agencia Nacional de Hidrocarburos (ANH) and the Universidad Industrial de Santander (UIS) have granted access and approved the use of all data for this study.

Table 1. Geochemical analysis results of Los Cuervos Formation from core samples in ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. TOC and TS (%); HI (mg HC/g TOC); OI (mg CO_2/g TOC); PI (TOC%); S1, S2 and PY (mg HC/g rock); S3 (mg CO_2/g rock) and Tmax (ºC).

Well name	Coordinates WGS 84	Depth (m)	TOC %	TS %	HI	OI	PI	S1	S2	S3	Tmax ºC	S2/S3	PY=S1+S2
ANH- La Loma -2	Longitude -73.5527 Latitude 9.6142	292.7	0.50	0.22	59.42	79.23	0.26	0.14	0.40	0.30	416.00	1.33	0.54
ANH- La Loma -2		309.3	0.81	0.09	62.84	85.02	0.15	0.12	0.69	0.51	422.00	1.35	0.81
ANH- La Loma -2		310.8	2.75	0.19	82.67	60.46	0.08	0.14	1.66	2.27	424.00	0.73	1.80
ANH- La Loma -2		364.1	4.17	1.06	21.56	296.81	0.03	0.44	12.39	0.90	423.00	13.77	12.83
ANH- La Loma -2		364.3	4.28	0.66	49.75	104.63	0.09	0.46	4.48	2.13	419.00	2.10	4.94
ANH- La Loma -2		392.7	0.65	0.09	76.51	68.86	0.39	0.29	0.45	0.50	428.00	0.90	0.74
ANH- La Loma -2		394.1	0.44	0.11	72.02	56.27	0.39	0.16	0.25	0.32	426.00	0.78	0.41
ANH- La Loma -2		546.0	0.31	0.02	94.69	71.83	0.58	0.31	0.22	0.29	424.00	0.76	0.53
ANH- La Loma -2		590.1	2.99	2.17	66.97	44.54	0.13	0.20	1.33	2.00	419.00	0.67	1.53
ANH- La Loma -2		619.6	1.06	0.18	33.90	115.84	0.07	0.09	1.23	0.36	431.00	3.42	1.32
ANH- La Loma -2		650.7	1.97	0.19	23.37	259.57	0.02	0.10	5.11	0.46	429.00	11.11	5.21
ANH- La Loma -2		657.4	2.13	1.77	49.34	95.39	0.03	0.06	2.03	1.05	426.00	1.93	2.09
ANH-CR- Los Cerezos -1X	Longitude -73.5826 Latitude 9.4569	513.74	2.04	0.406	72.00	50.94	0.08	0.13	1.47	1.04	417.00	1.41	1.60
ANH-CR- Los Cerezos -1X		521.76	0.63	0.166	65.00	85.61	0.23	0.12	0.41	0.54	420.00	0.76	0.53
ANH-CR- Los Cerezos -1X		566.53	0.82	0.065	60.74	100.83	0.19	0.12	0.50	0.83	422.00	0.60	0.62
ANH-CR- Los Cerezos -1X		640.23	2.04	1.552	48.16	67.81	0.06	0.06	0.98	1.38	427.00	0.71	1.04
ANH-CR- Los Cerezos -1X		678.18	15.68	1.416	271.81	48.58	0.06	2.74	42.63	7.62	426.00	5.59	45.37
ANH-CR- Los Cerezos -1X		751.91	7.09	2.913	66.00	103.52	0.03	0.15	4.68	7.34	419.00	0.64	4.83

The TOC analysis was carried out in 38 samples to quantify the amount of organic matter present in the sample. In the first instance, following the usual methodology reported in (Schmacher, 2002), the content of carbonates present in the sample was eliminated by using HCl to dissolve inorganic $CaCO_3$. After that, the total carbon was determined using the Leco SC-144DR automated analyzer. It also allowed us to calculate the TS. Likewise, to evaluate the quality of this organic matter, a Rock–Eval pyrolysis analysis was performed in each of the 24 samples with Rock–Eval 6 technology equipment. This technique presented by Barker (1974) and Behar *et al*. (2001) uses programmed heating to a small amount of rock (70 mg) or coal (30–50 mg) in an inert atmosphere (helium or nitrogen) in order to determine the quantity of free hydrocarbons present in the sample (S1 peak), as well as those that potentially can be released after maturation (S2 peak). This procedure permitted us to know the maximum pyrolysis temperature (Tmax) and the current state of thermal maturation. The TOC had to be determined along with the mineral carbon content (MinC), the volume of free hydrocarbon generated before pyrolysis (S1), the amount of hydrocarbon generated during pyrolysis (S2), and the amount of emitted carbon dioxide (S3). Derivations of these parameters such as hydrogen index (HI = S2/TOC × 100), the oxygen index (OI = S3/TOC × 100), the production yield (PY = S1 + S2), and the production index (PI = S1/(S1 + S2)) are calculated.

The vitrinite reflectance (Ro%) that indicated organic matter content, was measured in 14 samples using Zeiss imager microscopy. Vitrinite reflectance was measured according to the method proposed by the ASTM D7708-14 (2014). Sample chips or sidewall core samples were cleaned to remove drilling mud or mud cake and then crushed using a mortar and pestle to a grain-size of less than 3 mm. These samples were mounted in cold-setting resin and polished “as received”, so that whole-rock samples were examined, excluding concentrates of organic matter. The core samples were mounted and sectioned perpendicularly to the bedding. Vitrinite reflectance measurements were made using immersion oil of refractive index 1.518 at 546 nm at 23ºC and at spinel and garnet standards of 0.42, 0.917, as well as 1.726% reflectance for calibration. After calibrating the equipment an average of 28.4 Ro% readings were taken for each polished

Table 2. Measurements of maceral materials of Los Cuervos Formation from ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. Ro% (minimum, maximum and mean), TOC and TS.

Well name	Coordinates WGS 84	Depth (m)	Ro% Min.	Ro% Max.	Measurements (Number)	Standard deviation	Ro% mean	TOC %	TS %
ANH-La Loma-2	Longitude -73.5527 Latitude 9.6142	322	0.51	0.54	14	0.01	0.53	3.62	5.23
ANH- La Loma -2		344	0.51	0.54	15	0.01	0.53	5.26	3.44
ANH- La Loma -2		364	0.53	0.61	40	0.02	0.57	4.17	1.06
ANH- La Loma -2		509	0.53	0.55	10	0.01	0.54	0.20	3.56
ANH- La Loma -2		549	0.49	0.58	35	0.02	0.55	4.71	5.27
ANH- La Loma -2		590	0.52	0.57	22	0.01	0.55	0.04	1.29
ANH- La Loma -2		657	0.51	0.55	23	0.01	0.53	2.13	1.77
ANH- La Loma -2		661	0.52	0.56	26	0.01	0.54	4.76	3.78
ANH- La Loma -2		669	0.51	0.57	43	0.02	0.54	52.68	8.64
ANH-CR-Los Cerezos-1X	Longitude -73.5826 Latitude 9.4569	604	0.44	0.47	30	0.01	0.45	7.17	1.41
ANH-CR-Los Cerezos-1X		640	0.49	0.56	35	0.02	0.51	2.04	1.55
ANH-CR-Los Cerezos-1X		678	0.47	0.52	50	0.01	0.49	15.68	1.42
ANH-CR-Los Cerezos-1X		751	0.45	0.47	15	0.01	0.46	1.65	12.12
ANH-CR-Los Cerezos-1X		752	0.44	0.49	40	0.01	0.46	7.09	2.91

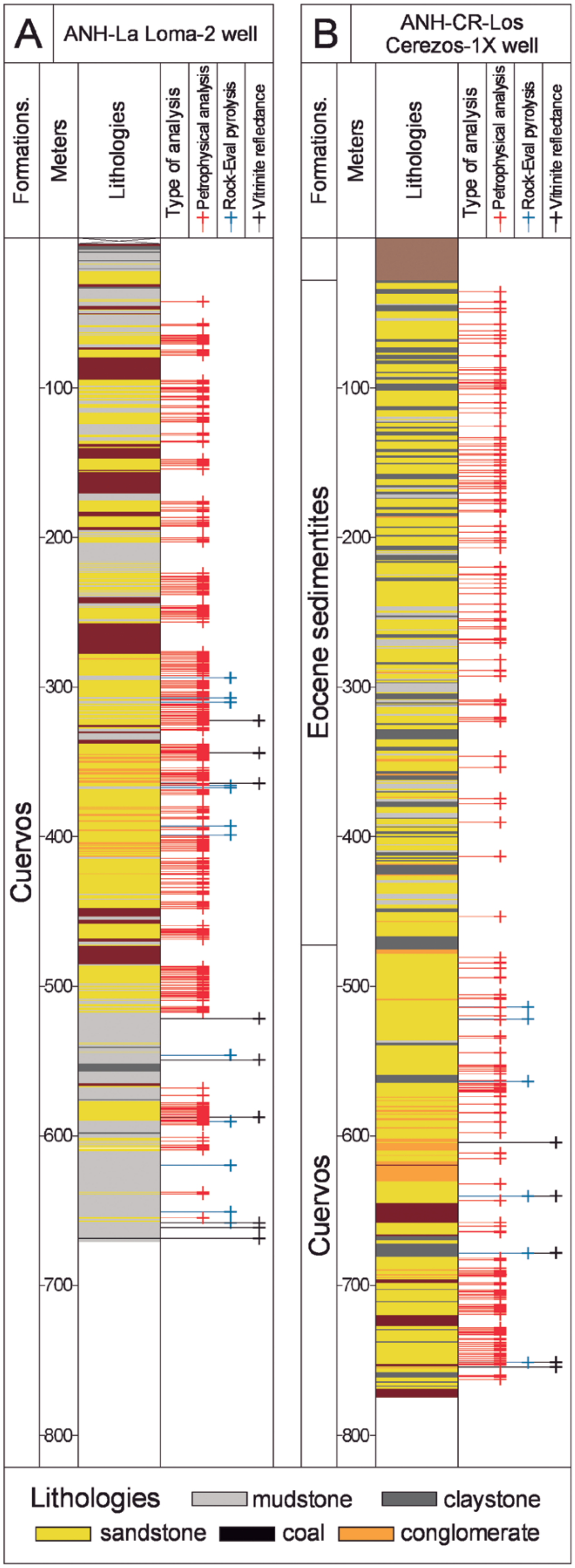

Figure 3. Lithologies, samples site (+) with Ro%, Pyrolysis Rock-Eval and petrophysical analysis for ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells.

section. During optical analysis the vitrinite macerals were identified on the polished surface, taking into account that the standard deviation of the 28.4 readings of Ro% per polished section must be less than 0.003. A correlation of TS concentration vs Ro% was performed to determine the reflectance of suppressed vitrinite according to Mukhopadhyay (1994), who indicated that the suppression occurs between values of 0.2 to 1.4, this suppression takes place in vitrinite due to excess sulphur of more than 1% [w/w] according to Carr (2000). This last author established that in some situations, vitrinite reflectance values may be either 'suppressed' or 'enhanced' and said that low vitrinite reflectance or vitrinite suppression may be caused by perhydrous-vitrinite, impregnation of vitrinite with hydrogen rich amorphous material, and in coals with high sulphur content. Fluorescence-mode observations were made on all samples, providing supplementary evidence concerning organic matter type, exinite abundance, and maturity. For fluorescence-mode, a 3-mm BG-3 excitation filter was used with a TK400 dichroic mirror and a K490 barrier filter. The data correlation of the average Ro% versus Tmax is presented in Figure 4 to show the change in thermal maturity of Los Cuervos Formation in the La Loma-2 and ANH-CR-Los Cerezos-1X wells.

Petrophysical analyses were performed in addition to the organic geochemistry analysis to give greater certainty of the thermal evolution of the Rancheria Sub-Basin. Petrophysical analysis, porosity and permeability in ANH-La Loma-2 Well were determined for 262 and 55 samples of sandstone and mudstone, respectively; and in ANH-CR-Los Cerezos-1X Well were determined for 141 and 56 samples of sandstone and mudstone, respectively. Porosity and permeability were measured at UIS Petrophysical analysis laboratory, using conventional core analysis practices from American Petroleum Institute (1998). Petrophysical sample analysis consists of two stages. First: sample preparation that comprises cutting, profiling, cleansing and drying plugs; and second: determination of petrophysical properties (porosity and permeability). Petrophysical information was plotted to visualize its distribution on profiles using free software PanPlot2 as described by Sieger and Grobe (2013).Petrophysical data allowed establishing and characterizing the thickness of the sequence deposited, during the early Eocene, in the interval from the late Eocene to the early Miocene. This sedimentary sequence was lost in the geological record due to regional tectonic events (see Figure 2). This lost sequence managed to exert a lithostatic charge that increased the maturation of the source rocks and decreased the porosity of reservoir rocks. The 2D seismic lines in two-way time (TWT) used in this research were CV-1979-03, CV-1979-11, CV-1979-04 and CV-1979-08; the interpretation of the lines was used for the purpose of defining the cutting relationships between lithological units present in the basin. Additionally, the seismic lines had the geographic and stratigraphic positions of the wells used for this study. One-dimensional modelling was generated using the PetroMod software in order to reconstruct the burial history and thermal maturation of the geological units present in the wells. This modelling used the vitrinite thermal maturation model (EASY Ro%) proposed by Sweeney and Burnham (1990), based on the Arrhenius first-order parallel-reaction approach with a distribution of activation energies. EASY Ro% were calibrated to a more rigorous model of vitrinite maturation based on the chemical properties of coal vitrinite. The ages and minimum and maximum thicknesses of the Rio Negro, Lagunitas, Aguas Blancas and lower part of the Molino formations reported for the sub-basin by Mesa and Rengifo (2011) were used. For Barco, Los Cuervos and upper Molino formations, we used the data obtained in ANH-La Loma-2, ANH-CR-Los Cerezos-1X, La Jagua and Calenturitas wells. The eroded thickness in the sequence was estimated considering the maximum thickness reported and the thickness present in the wells. The heat flow was established according to Mesa and Rengifo (2011): the syn-rift stage goes from 200 to 116 million years ago (mya) and the post-rift stage from 116 to 20 mya (Figure 5A). The paleo water depth (PWD) for La Luna and Molino formations was established considering Patarroyo *et al*. (2017) see Table 3 and Figure 5B. Sediment water interface temperature (SWIT) was calculated based on Wygrala (1989), assuming a current position in the northern hemisphere on the continent of South America at a latitude of 10° (Figure 5C) as obtained by Montes *et al*., (2019). Multiple kinetics based on lithology were used: Lagunitas, Aguas Blancas, La Luna and Lower Molino Formations, the kinetics IES-TII_Brown_Limestone, for the Middle Molino Formation the kinetics IES-TII_Toarcian_Shale, for Los Cuervos Formation the kinetics Handil_MahakamDelta-TIII and IES-TIII_Tertiary_Coal_2C according to DiPrimio and Horsfield (2006).

Table 3. Paleo-batimetry conditions (PWD) vs time used to generate the geochemical modelling. PWD for La Luna and Molino formations (Patarroyo *et al*., 2017). 0 m deep during the early rift stage (120 mya) according to Mesa and Rengifo (2011).

Age(Ma)	PWD(m)
0	0
50	0
70	15
79	100
92	200
103	100
116	100
120	0

The burial history and exhumation event of the Cesar Sub-Basin was obtained from Hernández and Jaramillo (2008). The burial depth of Los Cuervos Formation and the thickness of Eocene age formation, were obtained using the relationship between porosity and depth, known as 'compaction trend' (Lee *et al*., 2019), and the one-dimensional geochemical model obtained.

Results and discussion

In this section we summarize the results obtained, corresponding to geochemical and petrophysical analysis for ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. The Figure 3 shows a stratigraphic column with samples collected for vitrinite reflectance (Ro%), pyrolysis Rock-Eval and petrophysical analysis. The Figure 4 shows a correlation between Tmax versus Ro% for the samples analyzed from ANH-La Loma-2 well (depths of 95.2 to 668.6 m) and ANH-CR-Los Cerezos-1X well (depths of 513.7 to 751.9 m), respectively. Figure 4 shows a good correlation between data to illustrate the change in thermal maturity of Los Cuervos Formation in the ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells. Figure 5 shows the basin modelling boundary conditions (heat flow, paleo water depth, SWIT). Multiple scenarios cases for erosions events allow us to discriminate the best calibration for each well (Figure 6 and 7). The burial history diagrams for ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells, and for Calenturitas Mine and La Jagua Mine wells, respectively (Figure 8 and 9). The transformation ratios (TR) are shown at the Figure 10. The transformation ratio (TR), as defined by Tissot and Welte (1984), is the ratio of the petroleum (oil and gas) actually formed by the kerogen to the total amount of petroleum that the kerogen is capable of generating. It depends on the origin of the organic material (kerogen type) and the maturation history associated to the geological history of a basin. Figure 11 and 12 shows the variations in depth of permeability and porosity for ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells, respectively. Figure 13 shows permeability vs porosity correlation in ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells, respectively. These results of porosity and permeability were used to determine the depth to which the lithologies were buried (Figure 14 and 15).

In the ANH-La Loma-2 well (Figure 3) the following results were obtained for 18 mudstone samples with TOC values with a min. of 0.306%, max. of 5.257%, a mean of 2.595% and a standard deviation (sd) of 1.709%. The sulphur content with a min. of 0.016% [w/w] (were [w/w] means percentage concentration by weight), max. of 5.274% [w/w], mean of 1.516% [w/w] and sd of 1.778% [w/w]. A sample of coal with 52.68 TOC and sulphur content of 8.64% [w/w]. The 2 samples of sandstone with TOC values with a min. of 0.04%, max. of 0.20%, a mean of 0.120%. The sulphur content with a min. of 1.286% [w/w], max. of 3.564% [w/w], mean of 2.425% [w/w].

In the ANH-CR-Los Cerezos-1X well (Figure 3) the following results were obtained for 10 mudstone samples with TOC values with a min. of 0.631%, max. of 15.684%, a mean of 6.112% and a sd of 5.638%. The TS with a min. of 0.166% [w/w], max. of 12.125% [w/w], mean of 2.587% [w/w] and sd of 3.465% [w/w]. A sample of sandstone with 0.82 TOC and sulphur content of 0.065% [w/w].

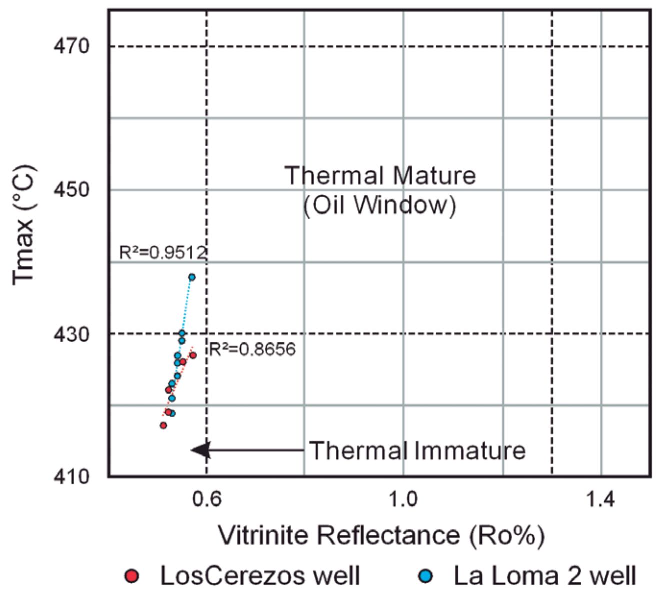

Figure 4. Data correlation of maximum pyrolysis temperature (Tmax) versus vitrinite reflectance (Ro%), to indicate source rock thermal maturity in Los Cuervos Formation of the ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells.

Multiple modellings were made using Tmax and Ro% data and with different thicknesses of the Eocene sequence (e.g. from 2000 to 4700 in 300 m intervals) were made (Figure 6B and 6D). The modelling that best fit for ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells was 3200m and 3500m respectively (Figure 6A and 6C). Figure 7 shows a calibration with Ro% and Tmax for La Jagua and Calenturitas mines using data of Guo *et al*. (2018).

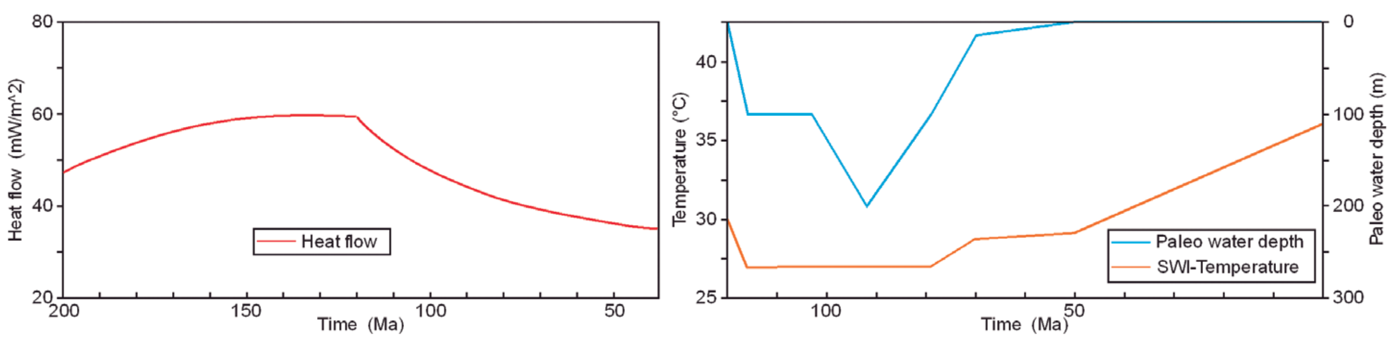

Figure 5. Boundary conditions used for 1D modelling of burial history of lithological units in the ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells: (A) heat flow, (B) paleo water depth, and SWIT.

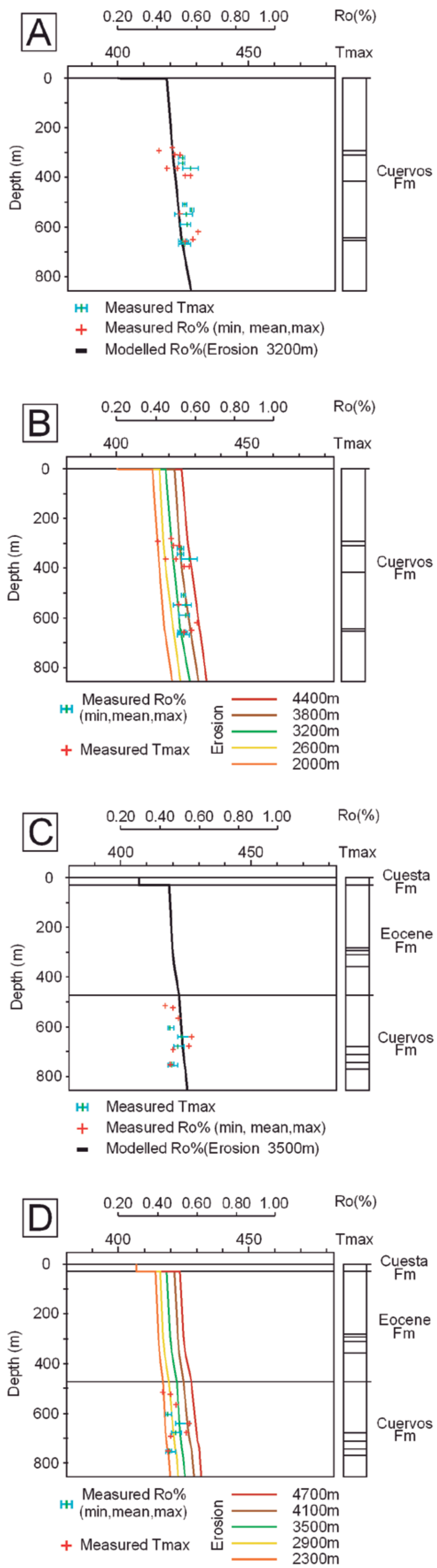

Figure 6. Best calibration and multiple models for calibration of vitrinite reflectance (Ro%) and Tmax with depth: (A) and (B) for the ANH-La Loma-2 Well, and (C) and (D) for ANH-CR-Los Cerezos-1X Well.

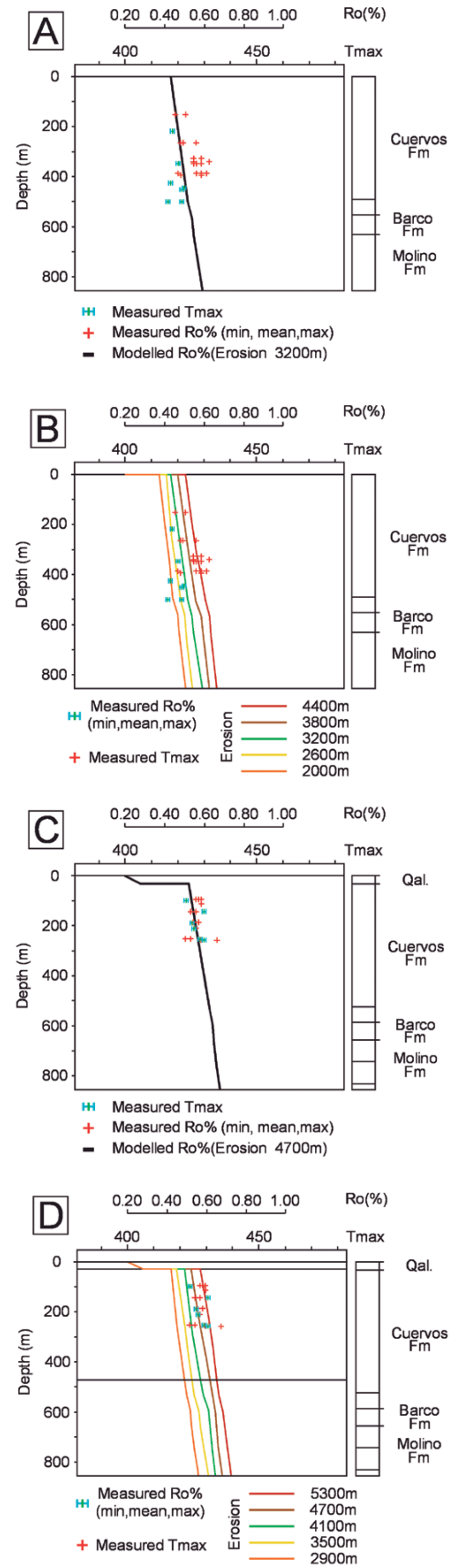

Figure 7. Best calibration and multiple models for calibration of vitrinite reflectance (Ro%) and Tmax with depth: (A) and (B) for the Calenturitas Well, and (C) and (D) for La Jagua Well.

The burial diagrams obtained for the ANH-La Loma-2, ANH-CR-Los Cerezos-1X, Calenturitas and La Jagua wells (Figures 8 and 9) are consistent with the two major deformational phases affecting the Cesar-Ranchería Basin, first to a Middle Eocene convergent phase related to the accretion of the Great Arc of the Caribbean (Sánchez and Mann, 2015; Cardona *et al*., 2011; Villagomez *et al*., 2011); and a second phase in the Miocene age characterized by large-displacement thrusting in the eastern Cesar Ranchería Basin driven by Late Miocene collision of the Panama Arc with South America Plate (Sánchez and Mann, 2015; Taboada *et al*., 2000; Vargas and Mann, 2013).

The geochemical modelling (Figures 8 and 9), assumes a continuous deposition during the Middle Eocene. Since Middle Eocene the accumulated thickness Cretaceous-Middle Eocene begins their erosion, without significant loss of sedimentary record. This erosion event is prior to the deposition of the Cuesta Formation and is more pronounced closer to the Perijá Range (PR). The minimum thickness values of each formation in the Cesar Sub-Basin used to generate model (Figure 8) was obtained from the seismic interpretation (Figure 2B) and Mesa and Rengifo (2011). The model of burial history (Figure 8 and 9), with overlapping values and the different hydrocarbon generation windows were coloured as proposed by Sweeney and Burnham (1990).

These models projected to the economic basement (Río Negro Formation), the Lagunitas, Aguas Blancas and Luna formations are expected to enter the main oil generation window, while the Molino Formation is expected to enter the early oil window in the Middle Eocene just before the loss of sedimentary record.

The geochemical modelling of the Calenturitas and La Jagua wells (Figures 9A and 9B) was achieved using data of Guo et al. (2018). The modelling permit simulate the evolution in thermal maturation and transformation ratios over time. It was only possible to determine how the sedimentary sequence behaved for the Calenturitas Well using seismic (Figure 2A). But a fault was found just below the synchronization line where Los Cuervos formation is completed. The fault repeats the Cretaceous sequence and cause errors in the determining the thickness units to be modelled. Los Cuervos Formation in the Calenturitas Well, is expected to be immature and the Molino Formation enters the early oil window during the Middle Eocene (Figure 9A). The Molino Formation in La Jagua Well, is expected that reached the early oil window during the same period (Figure 9B).

The diagrams of TR variation in time from source rocks in ANH-La Loma-2 and ANH-CR-Los Cerezos-1X wells, are presented in Figure 10A and 10B). These subsidence model implies that the TR of source rocks do not increase after the Eocene. The units of the Lower Cretaceous (Lagunillas and Aguas Blancas formations) reached the highest TR of the modeled source rocks, obtaining its maximum advance during the Paleocene. The formations of the Upper Cretaceous (La Luna and Los Cuervos formations) reached its maximum advance during the Eocene. Los Cuervos Formation is not expected to have such high TR but around 66%, while La Luna Formation is expected to be hovering around 95% of TR in this area. Likewise, it is evident that Los Cuervos Formation did not advance in the transformation of its organic matter in hydrocarbons. Based on the models, the TR are larger in ANH-CR-Los Cerezos-1X Well followed by ANH-La Loma-2 Well.

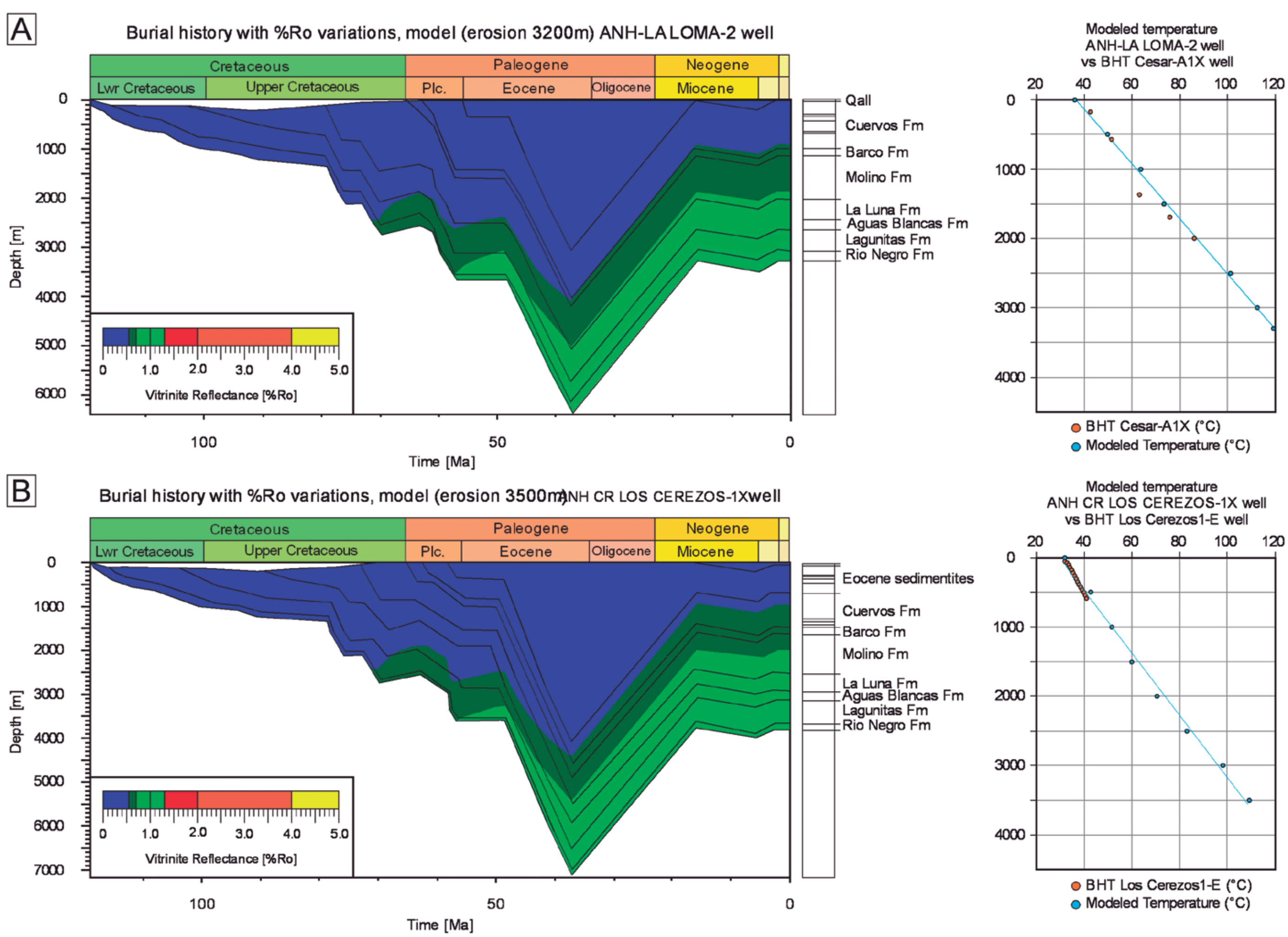

Figure 8. Burial history using modelled temperature variation: (A) for ANH-La Loma-2 Well and (B) for ANH-CR-Los Cerezos-1X Well.

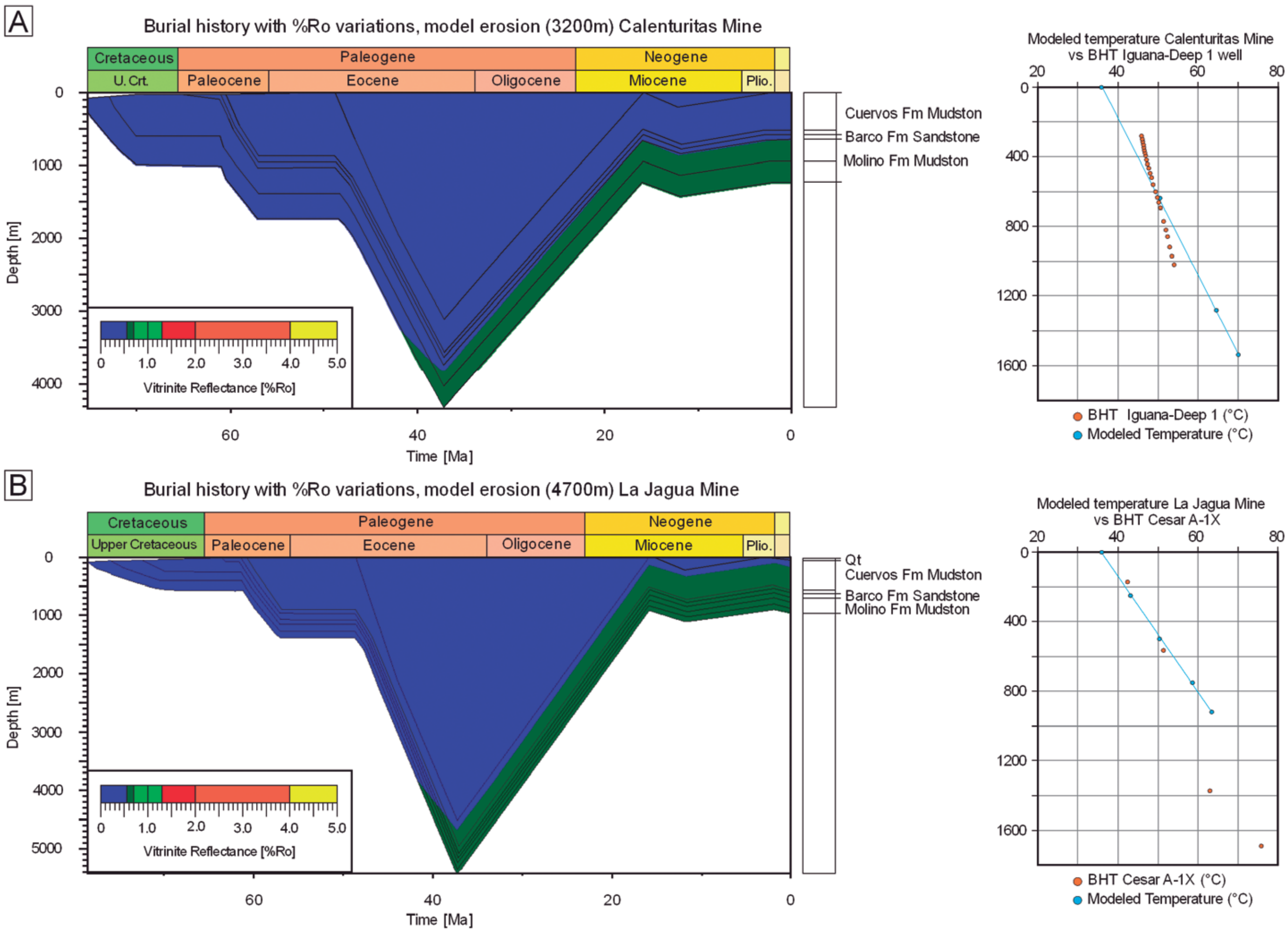

Figure 9. Burial history using modelled temperature variation: (A) for Calenturitas Well and (B) for La Jagua Mine Well.

The petrophysical analysis results of the porosity and permeability of the sandstone and mudstone lithologies of the ANH-La Loma-2 Well, show a decrease in their values with increasing depth (Figure 11). Sandstones beds with high permeability values are also highlighted. However, these are local and are distributed especially towards the top of the well, while the permeability values in the mudstone remain very low. For ANH-CR-Los Cerezos-1X Well, the porosity and permeability values (Figure 12) also decrease with increasing depth. However, higher values in mudstone permeability are evident, which can be up to 3 times higher in some cases, while sandstones are maintained with permeabilities that do not exceed 2500 mD, unlike those observed for ANH-La Loma-2 that can reach 6000 mD.

The porosity and permeability values show a positive correlation (Figure 13), in ANH-La Loma-2 Well (Figure 13A), a significant number of samples of sandstones are dominated by porosity from 13.16% to 29.62%, with mean of 21.37% and a standard deviation (sd) of 5.52%. For mudstones, a porosity values predominates between 4.86% and 14.60%, with mean of 10.75% and sd of 4.61%. Permeability values range from 0.1 to 560 mD for sandstones, with mean of 461.27mD and sd of 930.54mD. For mudstones permeability values are between 0.01 and 1.27mD, with mean 0.95mD and sd of 1.62mD.

In ANH-CR-Los Cerezos-1X Well (Figure 13B), a significant number of samples of sandstones are dominated by a porosity between 15.25% and 31.02%, with mean of 24.78% and sd of 4.72%. For mudstones, a porosity predominate value is between 8.98% and 23.96%, with mean of 17.64% and sd of 6.68%. Permeability values range from 0.39 to 250 mD for sandstones, with mean of 322.54 mD and sd of 565.12 mD. For mudstones are between 0.37 and 6.47mD, with mean 3.89 mD and sd of 6.55 mD.

Bjørlykke (2014) describes two different types of compaction processes (mechanical and chemical). Compaction generates a loss of porosity in siliceous sediments during burial in sedimentary basins. Being the mechanical compaction caused by the effective stress more relevant before exceeding temperatures greater than 100 °C. Chemical compaction begins after 100 ºC to dominate the process of loss of porosity, it is based on the chemical reactions that occur according to the lithology (mineralogy). In Cesar Sub-Basin, through modelling with PetroMod (Avendaño-Sánchez *et al*., 2019), shows that the analyzed lithologies did not exceed this temperature limit, therefore it is considered that the loss of porosity was due to the effect of mechanical compaction. Accordingly, and using the models of Kim *et al*. (2018) who performed numerical modelling of the decrease in porosity with respect to depth in sandstone, mudstone, and limestone, the following low-end, mean and high-end curves were obtained. The porosities obtained by petrophysical analysis for the ANH-La Loma-2 Well (Figure 14) in both sandstones and mudstones show that these lithologies were at depths between 2.5 and 3 km. While for the ANH-CR-Los Cerezos-1X Well (Figure 15) is expected these lithologies were at depths less than 2.5 km.

The stratigraphic record deposited between the Eocene and the Neogene in the Cesar Sub-Basin is very thin, Hernández (2003) reported 10 meters of slightly conglomerate quartz sandstone in La Jagua de Ibirico syncline, these would be the 10 meters that Mesa and Rengifo (2011) describe in its generalized column of the basin as the Eocene Sedimentitas unit. In Ayala (2009), a paraconformity is proposed between the Eocene Sedimentitas unit and Los Cuervos Formation. Both are considered the product of continuous succession without the presence of erosive contact. In the Ranchería Sub-Basin,

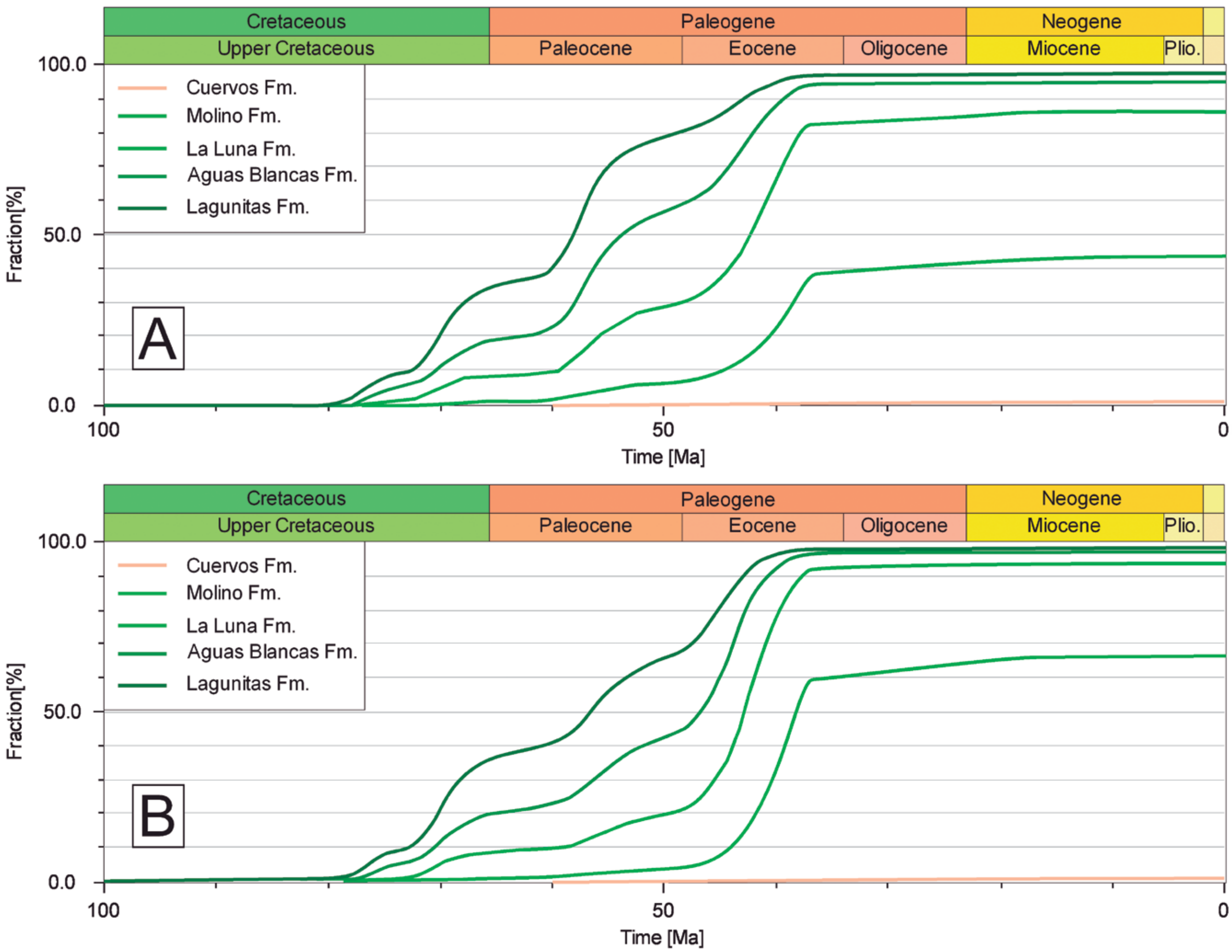

Figure 10. Hydrocarbon transformation ratios (TR) for the Cretaceous and Paleocene formations: (A) in the ANH-La Loma-2 Well, and (B) in ANH-CR-Los Cerezos-1X Well.

Ronderos (1957) reported that Eocene Aguas Nuevas Formation is made up of reddish conglomeratic sandstones, glauconite-containing sandstones, reddish sandstones, and shales. The lack of Eocene age sedimentary record in the Cesar-Rancheria Basin that Kellogg (1984) describes as the result of compressional and transpressional tectonics associated with tectonic convergence along the southern margin of the Caribbean and the northern sector of the Andes during the Cenozoic.

Authors such as Mesa and Rengifo (2011) propose subsidence models for the Cesar Sub-Basin, in which a significant Cenozoic sedimentation occurred during the Paleocene (about 2.1 km) corresponding to the Barco Formation. The formations deposited during the Eocene have been little investigated, with a reported thickness of 300 meters, which is presumed to have been completely eroded. The model also presents a large amount of sedimentation in less than 5 million years (my) time, while sedimentation was scarce for the 20 my of the Eocene. However, authors such as García *et al*. (2008), and Sánchez and Mann (2015) give more relevance in their models to the formation deposited in the Eocene, assigning a thickness of 1 km and 2 km, respectively. García *et al*. (2008), and Sánchez and Mann (2015) establishes that its sequence was eroded during the Oligocene-Miocene and Oligocene-Pliocene, respectively. But it is important to highlight that the three models mentioned do not show the calibration with paleo-geo-thermometer data and do not show the boundary conditions used. García *et al*. (2008) used a variation of the heat flow that reached 100 mW m^{-2} between 110 and 90 mya. These values differ with those used in our modelling, which do not exceed 60 mW m^{-2}. These values are in the phase with crustal thinning and increased accommodation space that occurred in the Cretaceous.

Patiño *et al*. (2019) with new and by compiling thermochrometry data of apatite fission track AFT (Villagómez et al., 2011) and new apatite (AHe) and zircon (ZHe) (U-Th)/He, established that the highest peak of exhumation rates of 0.9 km/my. This event affected the Sierra Nevada de Santa Marta (SNSM) during the late Eocene to early Miocene and resulted in their vertical exhumation of 15-19 km, based on geobarometry of granitoids (Cardona et al, 2011). Bermúdez (2009) from AFT analysis on synorogenic sediments supports the Eocene-Oligocene origin of the Andes Range in Venezuela. This exhumation rates coincides with the deformation front of the Caribbean began a more eastern migration with respect to South America in the late Eocene - Oligocene as proposed by Montes *et al*. (2019).

It can be concluded that late Eocene to early Miocene tilting event that occurred in the Maracaibo block may have been the cause of the total or partial loss of the deposited sedimentary units between Paleocene to the Middle Eocene in some areas of the Cesar Sub-Basin. The correlation between Tmax and Ro% data which are conditioned by the increase in temperatures, and the porosity data that are conditioned by the compaction of the sedimentary units, excluding the possible effect of cementation, allow to corroborate that it is not necessary to assign higher values in the heat flow within the sub-basin in order to reach the same point of thermal maturation.

The results obtained in the burial modelling carried out in this study contrast with the work proposed by Martínez *et al*. (2012), where the methodology used to replicate the effect of the Perijá Range (PR) thrusting on the Cesar Sub-Basin. Here, the maturation of the Cesar Sub- Basin rocks is a consequence of the effects of continuous sedimentation until the Middle Eocene, at which time the regional uplift event of the Maracaibo Block

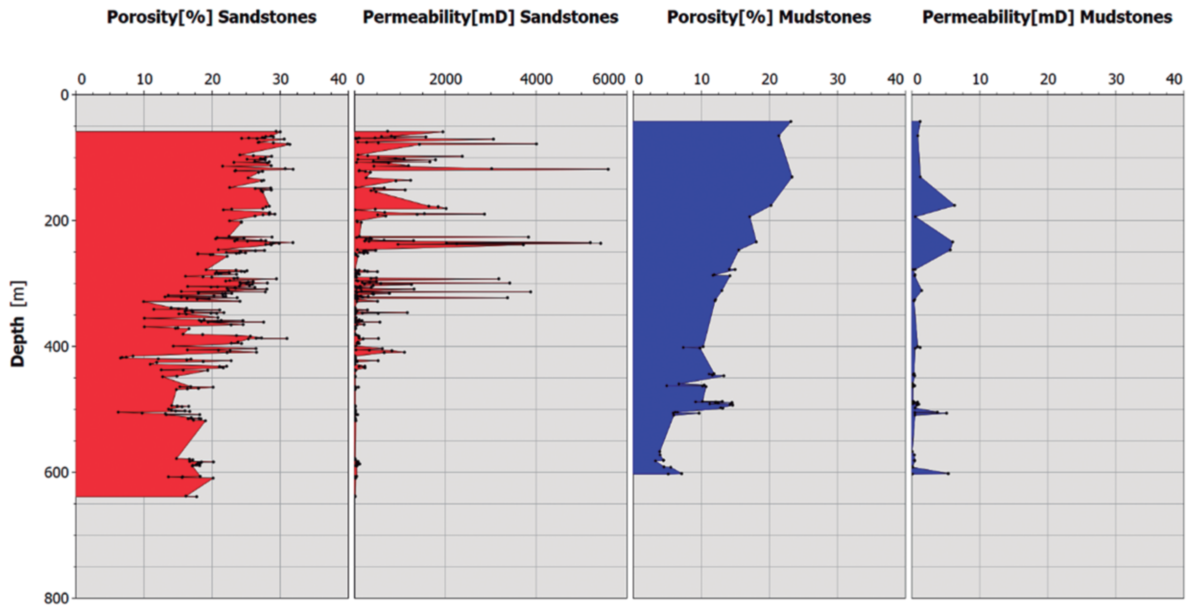

Figure 11. Variations in depth of permeability and porosity from different lithologies for ANH-La Loma-2 Well.

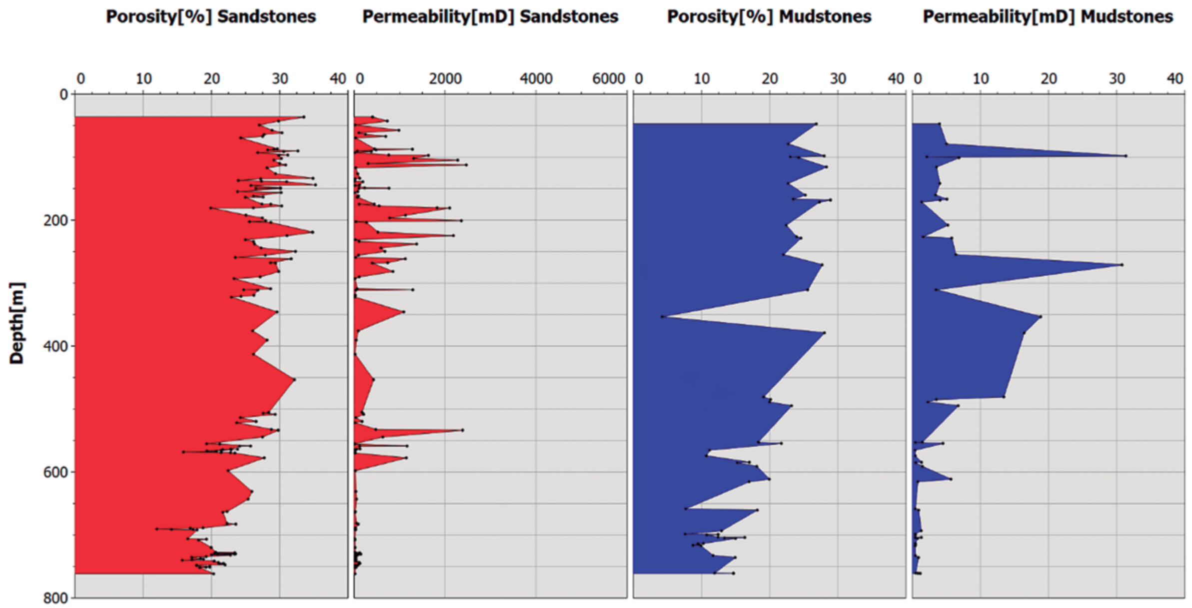

Figure 12. Variations in depth of permeability and porosity from different lithologies for ANH-CR-Los Cerezos-1X Well.

interrupted de sedimentation. This model coincides with that proposed by Sánchez and Mann (2015), which also proposes that the thickness of the units deposited in the Eocene is greater in the direction of the Maracaibo Basin.

Conclusions

It can be concluded that late Eocene to early Miocene tilting event that occurred in the Maracaibo block may have been the cause of the total or partial loss of the deposited sedimentary units between Paleocene to the Middle Eocene in some areas of the Cesar Sub-Basin.

The maturation of the Cesar Sub- Basin rocks is a consequence of the effects of continuous sedimentation until the Middle Eocene, at which time the regional uplift event of the Maracaibo Block interrupted de sedimentation.

The correlation between Tmax and Ro% data which are conditioned by the increase in temperatures, and the porosity data that are conditioned by the compaction of the sedimentary units, excluding the possible effect of cementation, allow to corroborate that it is not necessary to assign higher values in the heat flow within the sub-basin in order to reach the same point of thermal maturation.

Using the data geochemical obtained for Los Cuervos Formation (416 - 431 ºC of Tmax, and 0.46-0.57 of Ro%), it can be established that this formation in the southern area of the Cesar Sub-Basin is thermally immature, near the oil generation window, but this formation presents higher values reported in the La Jagua Well towards the Perijá Range.

Based on the porosity values, it is expected that the sandstones and mudstones of Los Cuervos Formation, have reached depths from 2 to 3 km in the study area. Furthermore, according to the values of Tmax and Ro%, it is expected that Los Cuervos Formation has been at a depth from 2600 to 3800m for ANH-La Loma-2, from 2900 to 4100m for ANH-CR-Los Cerezos-1X, from 2600 to 4400m for Calenturitas Well, and from 3500 to 5300 for La Jagua Well, taking into account that this thickness was considered with the properties of quartz sandstones.

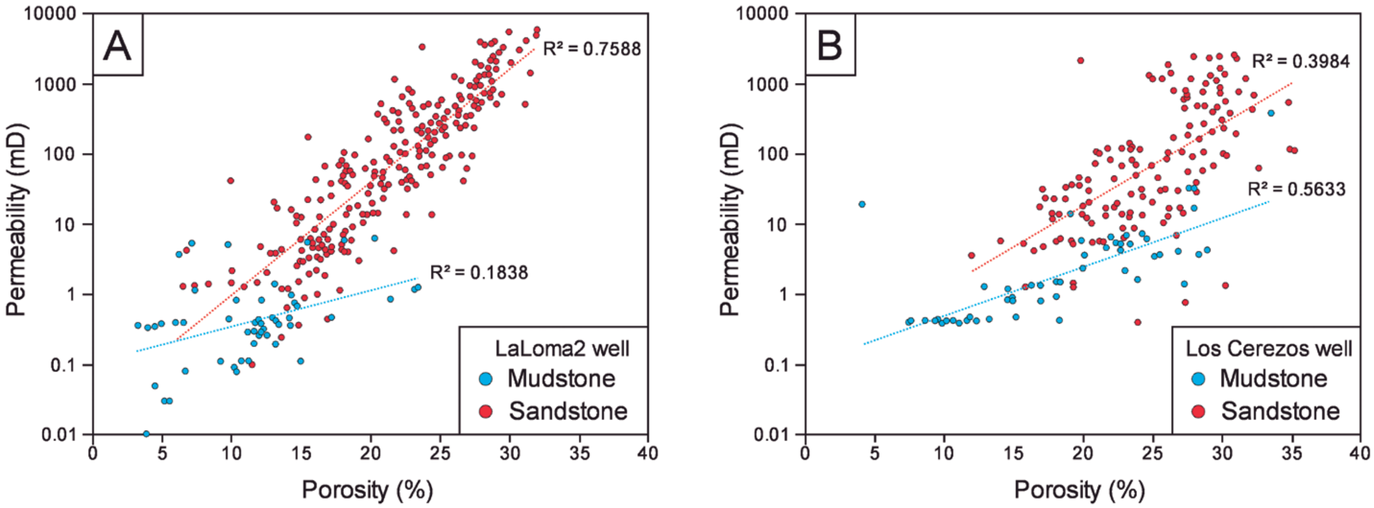

Figure 13. Permeability vs porosity for (A) ANH-La Loma-2 and (B) ANH-CR-Los Cerezos-1X wells.

According to the modelling carried out for this study area, the Late Cretaceous formations (Aguas Blancas and Lagunitas) have had their greatest advance in hydrocarbon transformation ratios during the Paleocene, while the Early Cretaceous formations (La Luna and Molino) peaked in hydrocarbon transformation ratios from the early Eocene to the middle Eocene. Similarly, through the modelling of the Lagunitas, Aguas Blancas and La Luna formations, it is concluded that they had transformation ratios greater than 80% while the Molino Formation has transformation ratios around 50%.

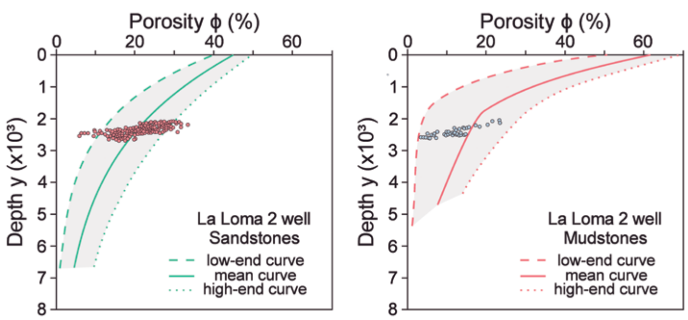

Figure 14. Petrophysical analysis results of porosity and permeability for ANH-La Loma-2 Well.

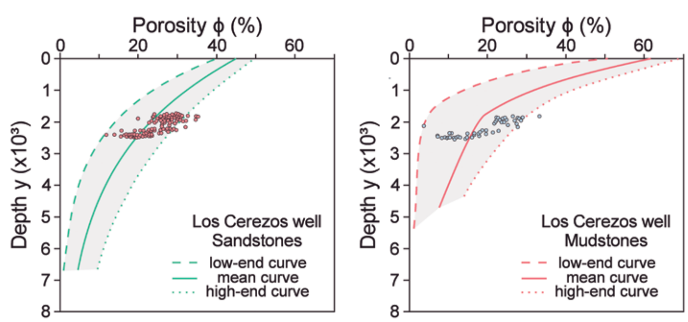

Figure 15. Petrophysical analysis results of porosity and permeability for ANH-CR-Los Cerezos-1X Well.

Acknowledgments

Special thanks to the Agencia Nacional de Hidrocarburos (ANH) from Colombia and the Universidad Industrial de Santander (UIS) for providing the resources and facilities for the development of this research. ANH give permission to show the seismic lines. Thanks to the Petroleum Geochemistry Laboratory (LGP) of the Universidad Industrial de Santander (UIS) for performing the geochemical analysis for this work and to the UIS Petrophysical Analysis Laboratory for performing the petrophysical analysis. Thanks to the style-writer corrector, German Morales. We thank the anonymous reviewers for their valuable contributions, allowing the document to improve substantially.

References

Aguilera, R., Sotelo, V., Burgos, C., Arce, C., Gómez, C., Mojica, J. and Osorno, J. (2010). Organic Geochemistry Atlas of Colombia. Second Edition. *Earth Sciences Research Journal, 14*(Special), 164. https://www.anh.gov.co/Informacion-Geologica-y-Geofisica/Estudios-Integrados-y-Modelamientos/ATLAS_GEOQUIMICO/Atlas_Geoquimico_2010.pdf

American Petroleum Institute (1998). API RP 40. Recommended Practices for Core Analysis. Second edition. American Petroleum Institute, Washington DC. http://w3.energistics.org/RP40/rp40.pdf

ASTM D7708-14. (2014). Standard Test Method for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks, ASTM International, West Conshohocken, PA. www.astm.org

Ayala, R. (2009). *Análisis Tectonoestratigráfico y de Procedencia en la Subcuenca de Cesar: Relación con los Sistemas Petroleros*. MSc. Thesis, Universidad Simón Bolívar, Baruta, Venezuela. http://www.cgares.org/Directorio/Archivos/6276_8%20tesis%20final_cayala.pdf.

Avendaño-Sánchez, G. M. (2019). *Source Rocks and Thermal Maturation in the Southeastern area of the Cesar Sub-Basin, Colombia*. MSc. Thesis, School of Geology, Universidad Industrial de Santander, Bucaramanga, Colombia. http://tangara.uis.edu.co/biblioweb/pags/cat/popup/pa_detalle_matbib.jsp?parametros=188439%7C %7C1%7C1

Barker, C. (1974). Pyrolysis Techniques for source-Rock Evaluation. *AAPG Bulletin, 58(11)*, 2349–2361. https://doi.org/10.1306/83D91BAF-16C7-11D7-8645000102C1865D

Barrero, D., Pardo, A., Vargas, C. A. & Martínez, J. (2007). *Colombian Sedimentary Basins: Nomenclature, Boundaries and Petroleum Geology, a new proposal*. ANH. Bogotá. http://www.anh.gov.co/Informacion-Geologica-y-Geofisica/Cuencas-sedimentarias/Documents/colombian_sedimentary_basins.pdf

Bayona, G., Lamus-Ochoa, F., Cardona, A., Jaramillo, C., Montes, C. & Tchegliakova, N. (2007). Procesos orogénicos del Paleoceno para la Cuenca Ranchería (Guajira, Colombia) y áreas adyacentes definidos por análisis de procedencia. *Geología Colombiana, 32*, 21–46. Retrieved from https://revistas.unal.edu.co/index.php/geocol/article/view/32021/32046

Behar, F., Beaumont, V. & De Penteado, B. (2001). Rock-Eval 6 Technology: Performances and Developments. *Oil Gas Sci. Technol., 56*, 111–134. https://doi.org/10.2516/ogst:2001013

Bermúdez, M. A. (2009). *Cenozoic exhumation patterns across the Venezuelan Andes: insights from fission-track thermochronology.* Ph.D. Thesis, School of Geosciences, Université Joseph Fourier-Grenoble I, Grenoble, France. https://tel.archives-ouvertes.fr/tel-00450838

Bjørlykke, K. (2014). Relationships between depositional environments, burial history and rock properties. Some principal aspects of diagenetic process in sedimentary basins. *Sedimentary Geology, 301*,1-14. https://www.sciencedirect.com/science/article/abs/pii/S0037073813002200?via%3Dihub

Cardona, A., Valencia, V. A., Bayona, G., Duque, J., Ducea, M., Gehrels, G., Jaramillo, C., Montes, C., Ojeda, G. & Ruiz, J. (2011). Early-subduction-related orogeny in the northern Andes: Turonian to Eocene magmatic and provenance record in the Santa Marta massif and Rancheria Basin, northern Colombia. *Terra Nova, 23*, 26–34. https://doi.org/10.1111/j.1365-3121.2010.00979.x

Carr, A. D. (2000). Suppression and retardation of vitrinite reflectance, part 1. *Journal of Petroleum Geology, 23(3)*, 313–343. https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1747-5457.2000.tb01022.x

DiPrimio, R. & Horsfield, B. (2006). From petroleum-type organofacies to hydrocarbon phase prediction. *AAPG Bulletin,* 90, 7, 1031-1058. https://doi.org/10.1306/02140605129

García, M., Mier, R., Arias, A., Cortés, Y., Moreno, M., Salazar, O. & Jiménez, M. (2008). Prospectividad de la Cuenca Cesar-Ranchería. Grupo de Investigación en Geología de Hidrocarburos y Carbones, Universidad Industrial de Santander (UIS). Bucaramanga. http://oilproduction.net/files/cuencas%20petroleras%20de%20colombia-2009.pdf

Guo, Q., Littke, R. & Zieger, L. (2018). Petrographical and geochemical characterization of sub-bituminous coals from mines in the Cesar-Ranchería Basin, Colombia. *International Journal of Coal Geology*, *191*, 66–79. https://doi.org/10.1016/j.coal.2018.03.008

Hernández, M. (2003). Memoria Explicativa Geología Plancha 48, Jagua de Ibirico. Escala 1:100.000, INGEOMINAS. Bogotá. http://recordcenter.sgc.gov.co/B4/13010010020444/documento/PDF/0101204441102000.pdf

Hernández, O. & Jaramillo, J. M. (2008). Reconstrucción de la historia termal en los sectores de Luruaco y Cerro Cansona-cuenca del Sinú-San Jacinto y el piedemonte occidental de la Serranía del Perijá entre Codazzi y la Jagua de Ibirico-cuenca Cesar-Ranchería. Agencia Nacional de Hidrocarburos: Bogotá, Colombia, 58 P. http://www.anh.gov.co/Informacion-Geologica-y-Geofisica/Tesis/Reconstruccion_historia_termal_sector_de_Sinu_San_Jacinto_2009.pdf

Kellogg, J. N. (1984). Cenozoic tectonic history of the Sierra de Perijá, Venezuela-Colombia, and adjacent basins. Geological Society of America, Memoir *162*, 239–262. https://doi.org/10.1130/MEM162-p239

Kim, Y., Lee, C. & Lee, E. Y. (2018). Numerical analysis of sedimentary compaction: Implications for porosity and layer thickness variation. *Journal of the Geological Society of Korea. 54*, 631-640. http://dx.doi.org/10.14770/jgsk.2018.54.6.631

Lee, E. Y., Novotny, J. & Wagreich, M. (2019). *Subsidence Analysis and Visualization - For Sedimentary Basin Analysis and Modelling*. Springer, Cham, 56 p. https://www.springerprofessional.de/subsidence-analysis-and-visualization/15849410

Martínez de Vivas, M., Calderón, W., Zamora, W., Rodríguez, I. & López, E. (2012). Modelamientos Numéricos 3D de Sistemas Petrolíferos en la Cuenca Cesar–Ranchería: Nuevas Ideas Acerca de su Potencial Petrolífero. In: ACGGP (p. 9). https://www.earthdoc.org/content/papers/10.3997/2214-4609-pdb.330.18

Mesa, A. M. & Rengifo, S. (2011). Cesar Rancheria Basin Vol. 6. Medellín, Colombia: ANH-University EAFIT. Department of Geology. https://www.anh.gov.co/Informacion-Geologica-y-Geofisica/Metodos-de-Visualizacion/PETROLEUM%20GEOLOGY%20OF%20COLOMBIA/VOLUMEN_6_CESAR-RANCHERIA_BASINS.pdf

Montes, C., Rodríguez, A., Bayona, G., Hoyos, N., Zapata, S. & Cardona, A. (2019). Continental margin response to multiple arc-continent collisions: The northern Andes-Caribbean margin. *Earth-Science Reviews*, 198. 102903. https://doi.org/10.1016/j.earscirev.2019.102903

Mora, C., Parra, P. & Navas, G. (2007). Caracterización geoquímica de rocas y crudos en las cuencas de Cesar-Ranchería, Sinú-San Jacinto, Chocó y área de Soapaga (Cuenca Cordillera Oriental), Informe Final. Agencia Nacional De Hidrocarburos-ANH, 407. http://www.anh.gov.co/Informacion-Geologica-y-Geofisica/Tesis/CARACTERIZACI%C3%93N%20GEOQU%C3%8DMICA%20DE%20MUESTRAS%20Y%20CRUDO%202007.pdf

Mukhopadhyay, P. K. (1994). Chapter 1. Vitrinite Reflectance as Maturity Parameter, Petrographic and Molecular Characterization and its Applications to basin Modeling. Global Geoenergy Researched Limited, 14 Crescent Plateau, Halifax, Nova Scotia B3M 2V6, Canada. https://pubs.acs.org/doi/abs/10.1021/bk-1994-0570.ch001

Patarroyo, G. D., Torres, G. A. & Rincón, D. A. (2017). Bioestratigrafía e Inferencias de Foraminíferos en las Formaciones Cretácicas La Luna-Colón (Cuenca del Catatumbo, Colombia). *Boletín de Geología*, *39*, 16. https://doi.org/http://dx.doi.org/10.18273/revbol.v39n3-2017002

Patiño, A. M., Parra, M., Ramírez, J. C., Sobel, E. R., Glodny, J., Almendral, A. & Echeverri, S. (2019). Thermochronological constraints on Cenozoic exhumation along the southern Caribbean: The Santa Marta range, northern Colombia. In: *Andean Tectonics* (pp. 103–132). Elsevier Inc. https://doi.org/10.1016/b978-0-12-816009-1.00007-1

Ronderos D., A. (1957). Yacimientos calcáreos del Cerrejón, (intendencia de la Guajira). *Boletín Geológico*, *5(3)*, 63-77. Retrieved from https://revistas.sgc.gov.co/index.php/boletingeo/article/view/349

Sánchez, J. & Mann, P. (2015). Chapter 16: Integrated Structural and Basinal Analysis of the Cesar–Rancheria Basin, Colombia: Implications for its Tectonic History and Petroleum Systems. https://doi.org/10.1306/13531945M1083648

Schumacher, B. A. (2002). Methods for the determination of Total Organic Carbon (TOC) in soils and sediments. United States Environmental Protection Agency. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100S8MB.PDF?Dockey=P100S8MB.PDF

Sieger, R. & Grobe, H. (2013). PanPlot 2 - Software to Visualize Profiles and Time Series; Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research: Bremerhaven, Germany. https://doi.pangaea.de/10.1594/PANGAEA.816201

Shagam, R., Kohn, B. P., Banks, P. O., Dasch, L. E., Vargas, R., Rodríguez, G. I. & Pimentel, N. (1984). Tectonic implications of Cretaceous-Pliocene fission-track ages from rocks of the circum-Maracaibo Basin region of western Venezuela and eastern Colombia, The Caribbean-South American Plate Boundary and Regional Tectonics. William E. Bonini, Robert B. Hargraves, Reginald Shagam. https://pubs.geoscienceworld.org/books/book/165/chapter/3791689/Tectonic-implications-of-Cretaceous-Pliocene

Sweeney, J. J. & Burnham, A. K. (1990). Evaluation of a Simple Model of Vitrinite Reflectance Based on Chemical Kinetics. *American Association of Petroleum Geologist Bulletin*, *74*, 1559-1570. https://www.osti.gov/biblio/5681562-evaluation-simple-model-vitrinite-reflectance-based-chemical-kinetics

Taboada, A., Rivera, L. A., Fuenzalida, A., Cisternas, A., Herve, P., Harmen, B., Olaya, J. & Rivera, C. (2000). Geodynamics of the northern Andes: Subductions and intracontinental deformation (Colombia). *Tectonics, 19*, 787–813. https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2000TC900004

Tissot, B. & Welte, D. (1984). *Petroleum Formation and Occurrence*. Second Edition. Springer-Verlag. 715 pp. https://www.springer.com/gp/book/9783642878152

Vargas, C. A. & Mann, P. (2013). Tearing and breaking of subducted slabs as the result of collision of the Panama Arc-indenter with north-western South America. *Bulletin of the Seismological Society of America, 103*, 2025–2046. https://doi.org/10.1785/0120120328

Villagómez, D., Spikings, R., Mora, A., Cardona, A., Guzmán, G., Ojeda, G., Cortes, E. & Van der Lelij, R. (2011). Vertical tectonics at a continental crust-oceanic plateau, plate boundary zone: Low temperature thermochronology of the Sierra Nevada de Santa Marta, Colombia. *Tectonics*, *30*, TC4004, https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2010TC002835

Wygrala, B. P. (1989). Integrated study of an oil field in the southern Po basin, Northern Italy. Ber. Kernforschungsanlage Jülich, *2313*: 1-217. http://juser.fz-juelich.de/record/153416/files/FZJ-2014-03033.pdf