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Presence of charcoal as evidence of paleofires in the Claromecó Basin, Permian of Gondwana, Argentina: Diagenetic and paleoenvironment analysis based on coal petrography studies

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A B S T R A C T

The PANG0001 well, situated in the Claromecó Basin, Argentina, involves rocks that belong to the Tunas Formation [29], Permian of Gondwana. It is composed of fine to medium sandstones intercalating with black and green mudrocks and three coal seams up to 3 m thick. In the coals, a petrographic analysis was carried out to analyze the depositional environment and the diagenesis level reached by the Tunas Formation. The coals are composed of mono-maceral bands of Collotelinite and Gelinite, from the Vitrinite Group, or Fusinite, from the Inertinite Group. They were deposited in a wet swampy forest with rises and decreases of the phreatic level. The presence of inertinite or charcoal evidence the occurrence of palaeo-fires during the Permian. The vitrinite reflectance values are between 1.3% and 2.38%. The coals classify as semiantracitic to low volatile bituminous, with 10 to 25% of volatile matter. The vitrinite reflectance values indicate temperatures between 140 °C and 190 °C. The Tunas Formation reaches the oil to methane gas window, into a catagenesis to metagenesis range related to the organic matter diagenesis. Coal petrography is a good method for the environment and diagenesis analyses applied to the Tunas Formation.

1. Introduction

The first unequivocal record of Paleozoic charcoal as a direct paleobotanical evidence of palaeo-fires on Gondwana was by Glasspool [25], in the Sydney Basin, Australia. Then several authors have presented new evidence of Permian paleofires based on charcoal or inertinite in different basins, when Earth experienced a global icehouse/greenhouse transition [20,35–40,49,51,60–62,64,69,81,83,88].

The main controls on Permian peat accumulation, distribution and preservation in Gondwana were palaeoclimate and tectonics: widespread glaciations dominated earliest Permian depositional environments throughout the supercontinent so peat began to accumulate in cold, humid climatic conditions in post-glacial fluvial, lacustrine and paralic depositional systems [42]. During the Late-Early Permian, thick peat swamps were present throughout the high-latitude Gondwana supercontinent; these deposits are preserved in a wide range of tectonic and depositional environments. By the Late Permian, coal deposition was generally restricted to eastern Gondwana (Australian, Antarctic, Indian and Brasilian regions) as Gondwana translated to the north [75,76], and aridity increased in the western and central regions of Gondwana [37]. Tectonic subsidence and sedimentation rates, palaeotopography, floral changes, depositional environments, and eustatically controlled changes based on marine transgressions were the dominant factors controlling the thickness, geometry, composition and dimensions of the coal seams [49,65,66].

In this contribution, coal beds are mentioned in the Tunas Formation, in the Claromecó basin, in the cores belonging to the PANG0001 well (37° 34′ 48′′ S, 61° 6′ 57.35′′ W; Fig. 1), situated in the Buenos Aires province, Argentina. Coal samples were taken and analyzed, allowing for the detection the presence of charcoal. The record of cores was donated to the Universidad Nacional del Sur (Bahía Blanca, Argentina) by the Rio Tinto Mining Exploring Company.

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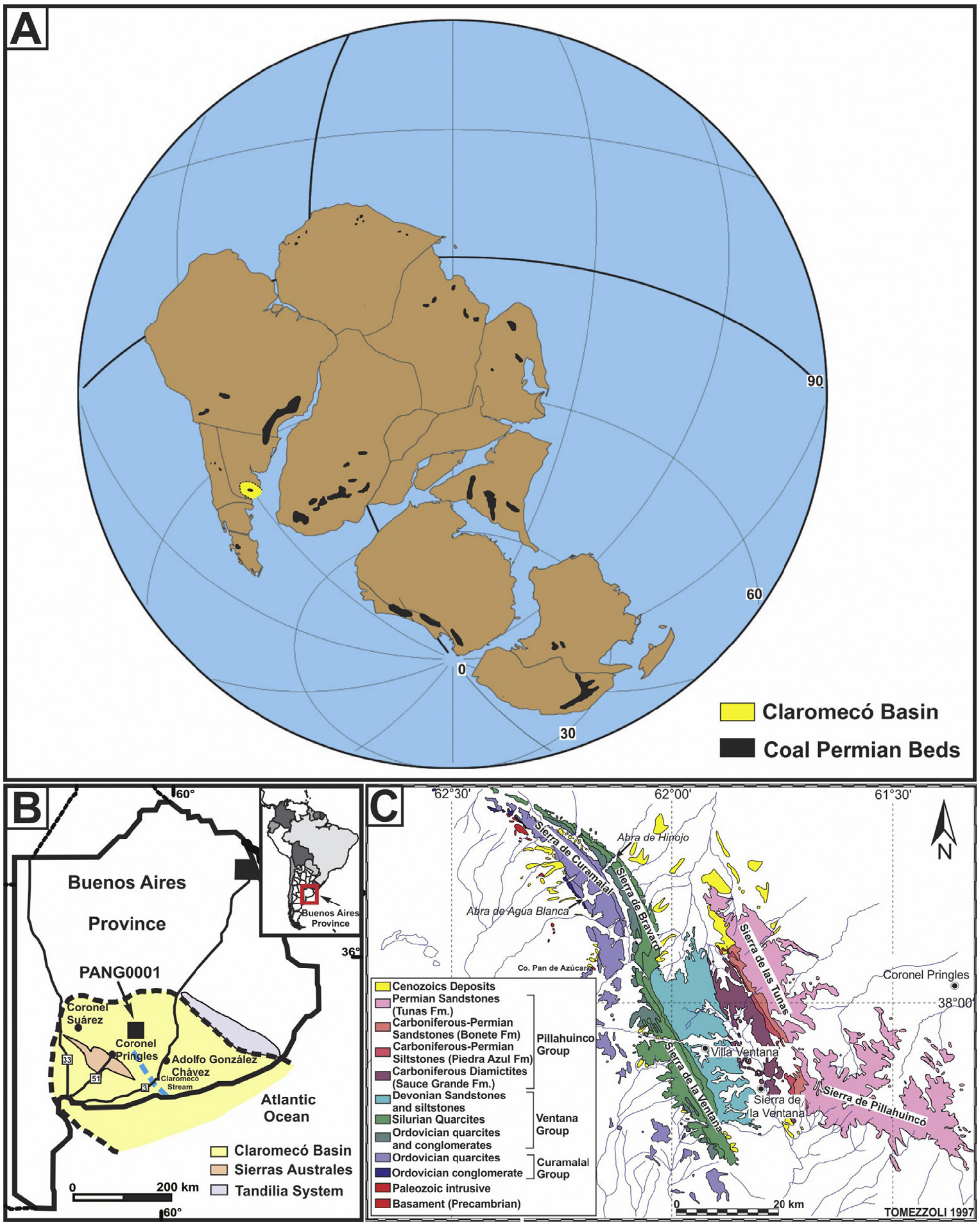

Fig. 1. A: Paleogeographic reconstruction for Gondwana during the Permian and global distribution of the coal beds. Location of the Claromecó Basin (yellow) and its relation with other Upper Palaeozoic basins (based on [42,70,75]). **B:** Location of the PANG0001 well in the Claromecó Basin (dotted line), with limits proposed by Kostadinoff and Font [41], Fryklund et al. [22], Álvarez [1], Zilli et al. [92], Pángaro and Ramos [55]. **C:** Geological map of the Sierras Australes of Buenos Aires Province, pink indicates the outcrops of the Tunas Formation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The analysis of the coal petrography in a formation is important as it indicates the depositional paleoenvironment and the quality and maturity of the organic matter. The quality is defined through the analysis of the original type of organic matter and it is evaluated by the microscopic examination of the coal macerals. The maturity analysis is carried out by measuring the vitrinite reflectance, and it defines the range of the coal which is related to the diagenesis level [28,48,53,71,73,87,94].

2. Methodology

The core records of the PANG0001 well consist of drilling of 958.7 m of depth, with a total extension of the cores of 776 m (information supplied by the Rio Tinto Mining Exploring Company).

At first, a Selley sedimentological log of the cores was made and semi-circular samples of coal and carbonaceous mudrocks were taken (4 cm by 2 cm). Seven (7) of these samples were selected, five (5) of them belonging to the lower part of the log, and two (2) to the upper part (Fig. 2), and polished briquettes were made to carry out the petrographic analysis. The sample preparation was made at first at the Petrotomy Laboratory of the Geology Department of the Universidad Nacional del Sur, and then at the Coal Petrography Laboratory of the Applied Economic Geology Institute (GEA, *Instituto de Geología Económica Aplicada*) at the Universidad de Concepción (Concepción, Chile), where the microscopy analysis was carried out. The samples were prepared following the ASTM D5671-95 and ASTM D 2797-07 norm.

Initially, the macerals were recognized, and with a point counter, the maceral and mineral matter percentages were calculated. In Collotelinite, or in some cases in Gelovitrinite, the vitrinite reflectance was measured. The maceral recognition allows to interpret the depositional environment.

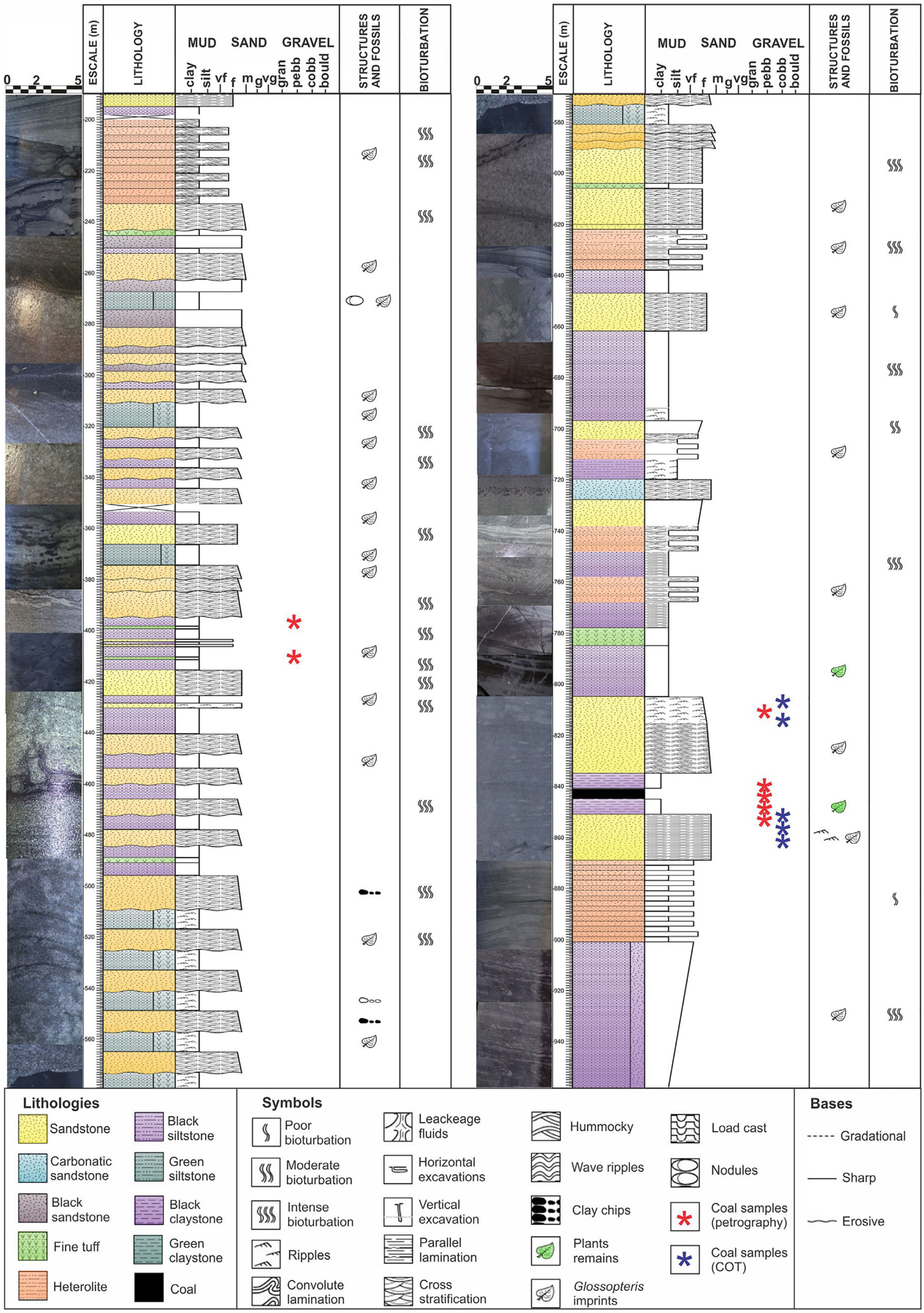

Fig. 2. Sedimentological log of the Tunas Formation in the PANG0001 well, correlated with the outcrops in the Sierras Australes. The lithology, structures, fossils and bioturbation are shown. Left, Photograph of the different lithologies.

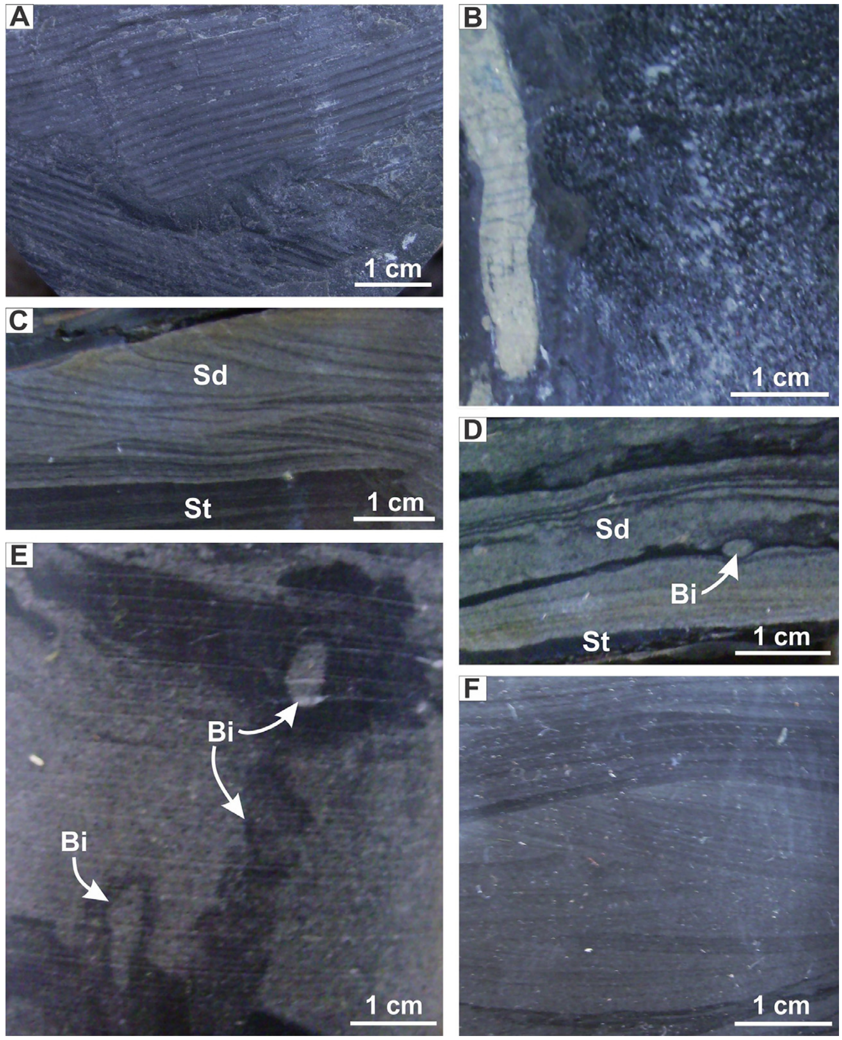

Fig. 3. Fl facies: A: Plant imprints on mudrocks and **B:** pyrite nodules, as fill of the bioturbation. **Hl facies: C:** Heterolite with cross ripple lamination, with light lamina of sandstone (St) and dark lamina of siltstone (St). **D:** intense bioturbation (Bi), obliterating the lamination. **Sr facies**: **E:** Fine sandstones with moderate horizontal and vertical bioturbation (Bi). **F:** Cross ripple lamination.

The International Committee for Coal and Organic Petrology (ICCP) has established standard rules for petrography, in which the description of the maceral must belong to the appearance with incident light using immersion oil (with 25 to 50× magnification). A Leitz ORTHOPLAN-POL microscope with a reticule incorporate was utilized to distinguish the different macerals, with 32× oil objective for immersion oil and Swift automatic counter.

The quantity of organic matter in each sample was analysed by the Total Organic Carbon (TOC). This technique is utilized to measure the amount of carbon of biological origin that has been deposited and then buried and preserved through the geologic time. The method involves gridding 1 g of sample and then removing the inorganic carbon by chemical treatment with hydrochloric acid. The sample is introduced into a LECO equipment in which the carbon is oxidized to carbon dioxide and it is detected by a thermal conductivity detector [95]. The ratio between the weight of CO_2 generated and the original weight of the sample is the percentage of the organic carbon. These analyses were carry out using equipment of the LANAIS CONICET Institute, of the Agronomy Department de of the Universidad Nacional del Sur.

The Vitrinite Reflectance (R_0) was measured with Leitz MPV-Combi equipment, with a Leitz MPV-SP spectral photometer with stable power supply and a control unit MPV COMB. In each sample, 100 points were measured with the automatic counter, using the ASTM D 2798-99 standard.

The R_0 values indicated the range of the coal, the volatile matter contained and the oil generation window into the organic matter diagenesis, using the Teichmüller [71] graphic that shows the medium R_0 related with the coal range (according to the ASTM standard) and the volatile matter contained. The maximum reached temperatures by the samples were estimated using the R_0-temperature graphic of Teichmüller [72]. Using these data, the diagenesis level was estimated.

3. Geological setting

The Claromecó Basin [57], situated in the Buenos Aires province, in Argentina, belonged to the southwest part of Gondwana during the Palaeozoic (Fig. 1). Its limits are not well defined: the Tandilia System is considered the northeast limit (Fig. 1), and it continues toward the west of the Sierras Australes and to the south in subsurface [22]; it extends toward the east including a portion of the argentine marine platform. For this reason, it is defined as a mix basin, with about 45,000 km^2 area on the land and 20,000 km^2 on the platform ([92]; Fig. 1). Pángaro et al. [56] interpreted this basin as part of a large basin, the Hesperides Basin

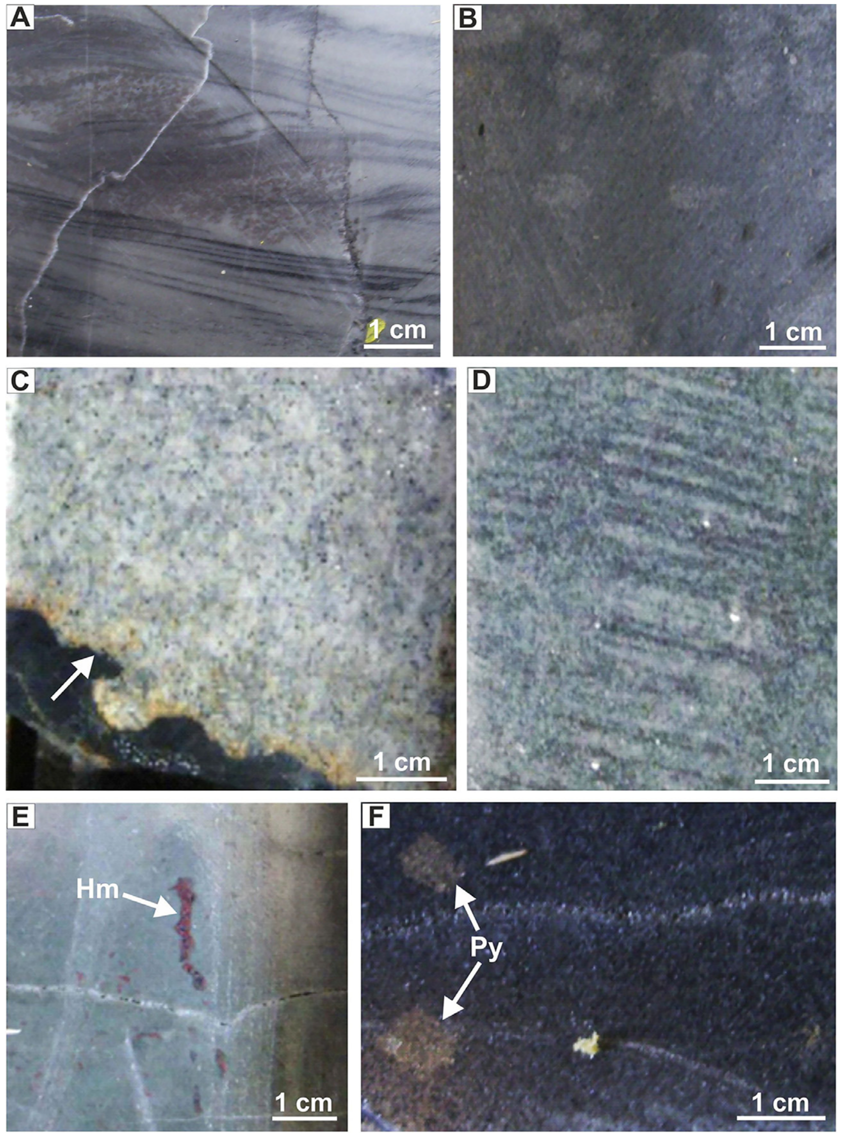

Fig. 4. **A: Tf facies:** Fine tuff of green color with cross and parallel lamination. **B: Src facies:** Carbonaceous medium sandstones. **St facies: C:** Medium sandstone with cross stratification and **D:** erosive base (indicated with an arrow). **E: Fsm facies:** Mudrocks of green color with hematite (Hm) nodules. **F: Sm facies:** Sandstones of black color with pyrite (Py) nodules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

(Pennsylvanian to Early Triassic), that laterally continues the Kalahari, Karoo and Chaco–Paraná Basins, in Africa and South America, with an over 3,000,000 km^2 depocenter.

The Claromecó Basin has the typical *Glossopteris* and *Gangamopteris* Permo–Carboniferous flora from Gondwana ([8,43]; Fig. 1). Lesta and Sylwan [43] mentioned the presence of coal and carbonaceous rocks interbedded in its subsurface Carboniferous-Permian record; there are no outcrop records of coal beds.

The Claromecó Basin [55,57] is known as a folerand basin [57]. Kostadinoff and Font [41] and Introcaso [31] published the first indirect studies about the presence of this basin, using gravimetric methods that show an axis of maximum subsidence lined with the Claromecó stream (Fig. 1). These studies suggest that the sediments have 5–10 km of thickness. Lesta and Sylwan [43] and Fryklund et al. [22] published seismic sections and drilling data were that verify this assessment.

The Claromecó Basin expresses at subsurface the outcropping sequence of the Sierras Australes of Buenos Aires Province in Argentina [58]. The Sierras Australes belongs to a fold and thrust belt that trends northwest-southeast, situated between 37° and 39° south latitude and 61° and 63° longitude west (Fig. 1). Here, outcrop rocks of Cambrian to Permian age, the oldest ones at the west and the youngest at the east, follow the system geometry. These units are covered in discordance by Cenozoic deposits. The general vergency of the system is northeast, diminishing the intensity of the deformation toward the east [13,29]. The Claromecó Basin has units correlated with the lithologies outcropping in the Sierras Australes [2,41,52,89] or in drillings [43]. The strata in the basin do not have an important deformation, as they are in horizontal position; this is corroborated by geophysical studies of anisotropy of magnetic susceptibility [9,10,12,13,78].

The PANG0001 well is situated in the Claromecó Basin and is composed of lithologies that belong to the Tunas Formation [29]. This formation outcrops at the northeast portion of the Sierras Australes, from the north of Sierra de Las Tunas to the south of Sierra de Pillahuincó, with some isolated outcrops in the plain situated at the east, near the Gonzáles Chávez locality, into the Claromecó Basin ([50,78]; Fig. 1). The top of the formation is unknown because it is eroded by an angular discordance. Andreis et al. [7] measured at least 710 m thick at the west outcropping

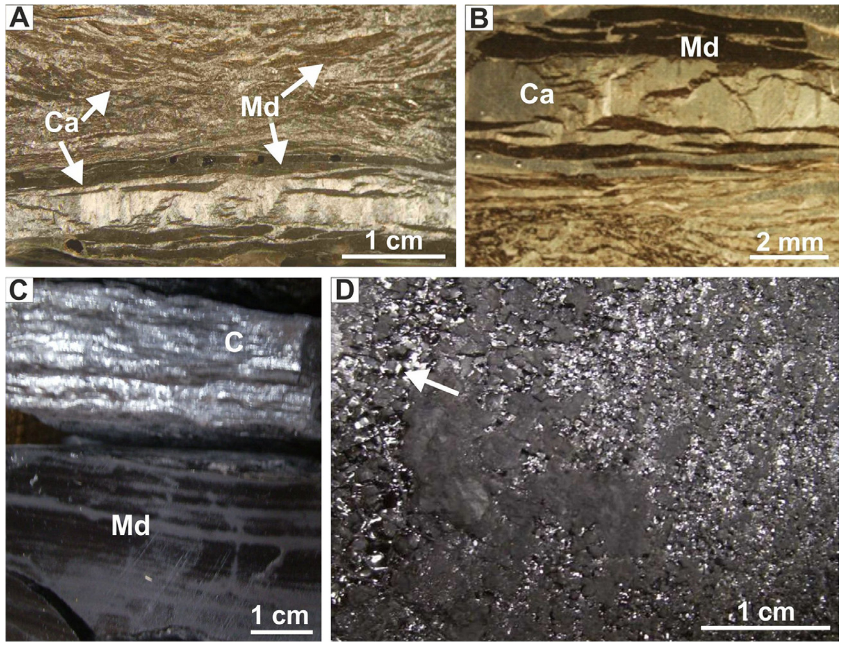

Fig. 5. BO facies: A and **B:** Photograph taken with binocular glass, of sapropelic coal that correspond to microbial algae, composed of bright carbonate laminae (Ca) and dark mudstones laminae (Md). **C Facies: C** Carbonaceous mudstones (Md) with parallel laminae and humic coal on top (C), with major bright. **D:** Humic coal formed by plants material, with the woody structure (indicated with an arrow).

Table 1
COT values in samples taken from the PANG0001 well.

Sample	Lithology	Depth (mbw)	TOC (%)
120 BOX 222	Carbonaceous mudrock	801,68	12,84
111 BOX 226	Coal	813,10	46,08
83 BOX 240	Carbonaceous mudrock	850,33	4,93
79 BOX 242	Carbonaceous mudrock	856,87	6,92
76 BOX 243	Carbonaceous mudrock	858,03	4,11

sector, while Suero [68] measured at least 2400 m and Japas [34] a minimum thickness of 1000 m at the southeast outcropping sector. Lesta and Sylwan [43] measured 600 m of minimum thickness in subsurface.

The Tunas Formation belongs to the upper part of the Pillahuincó Group [29]. This group has been divided into four formations, called from the base to the top: Sauce Grande, Piedra Azul, Bonete and Tunas and has a Carbonic-Permian age [29,43,44]. At the Sierras Australes, fine sandstones of green color integrate the Tunas Formation, with cross lamination, silicified, that alternate with tabular strata of siltstones finely laminated of red color [5,7,29,45]. The sandstones are grey, yellow and reddish mainly fine to medium grain. There are some thin pyroclastic rocks interbedded in the upper part of the outcropping section of Tunas Formation; these levels have been described by the generation of clay minerals as beidelite and vermiculite by diagenesis [33].

The mudrocks of the Tunas Formation have been proportionate Glossopteridales and Lycopsid plants debris [59], and marine remains (mainly bivalves) in a poor state of preservation [24,29]. The *Glossopteris* flora suggests Sakmarian to Artinskian ages [8]. A Lower Permian age to the Tunas Formation is attributed based, among others things, on the finding of *Cristatesporites, Granulosporites, Punctatisporites, Acnthotriletes, Leiotriletes* [43] and the *Tornopollenites toreutos–Reduviasporonites chalastus* (TC) Zones [15,16] in subsurface. The flora associations are typical of the Permian of the West Gondwana [3,4,30,80].

Regarding the age of this formation, several authors made radiometric isotopic dating in tuff outcrops of the upper part and they obtained a lower Permian age of approximately 280 Ma that belong to the Asselian to lower Artinskian [47,79].

Regarding paleoenvironments, the basal part of the Tunas Formation has been considered as the culmination of the regressive cycle characterized by the generation of barrier islands. Towards the middle and top part it has a higher proportion of mudrocks that indicate marine flooding conditions [6]. Zavala et al. [90] reported the existence of fluvial deposits at the upper levels of the outcropping stratigraphic sequence.

Regarding the degree of the diagenesis, there are studies on outcropping samples. Iñiguez Rodriguez and Andreis [32] argue that the Bonete and Tunas formations (Fig. 1), do not reach a state of metamorphism. Buggisch [18] suggests a high diagenesis degree to a very low grade metamorphism for the Piedra Azul and Bonete formations, from illite crystallinity and recrystallization of quartz data. Furthermore, Von Gosen et al. [84] define an ankimetamorphism zone for Bonete and Tunas formations from similar data.

The sequence of the PANG0001 well is composed of different lithologies that belong to the Tunas Formation, between 191 and 958.7 m below the wellhead (mbw). The drilling did not reach the base of this formation, while at 191 mbw, in erosive discordance, there is the youngest material with a possible Cenozoic age. This indicates that the Tunas Formation thickness is greater than 768 m.

The lower part of the well consists of fine sandstones and heterolites, with sharp bases, interbedded with black mudrocks containing pyrite nodules. Four coal beds and carbonaceous mudrocks are interbedded in this section, with an overall thickness of up to 3 m at 780 and 610 mbw. At 850 mbw there are thin levels of microbial algae of 5 cm thickness (Fig. 2). Two tuff levels are observed of 1 m thickness, situated at 780 and 245 mbw (Fig. 2). In the mudrocks *Glossopteris, Gangamopteris, Lycopsid* imprints and some charred woody debris are observed (Fig. 3(A)).

Towards the top of the PANG0001 well, medium sandstones with erosive bases are observed, some of them with carbonate cement, interbedded with black carbonaceous mudrocks and green mudrocks with hematite nodules in the upper part.

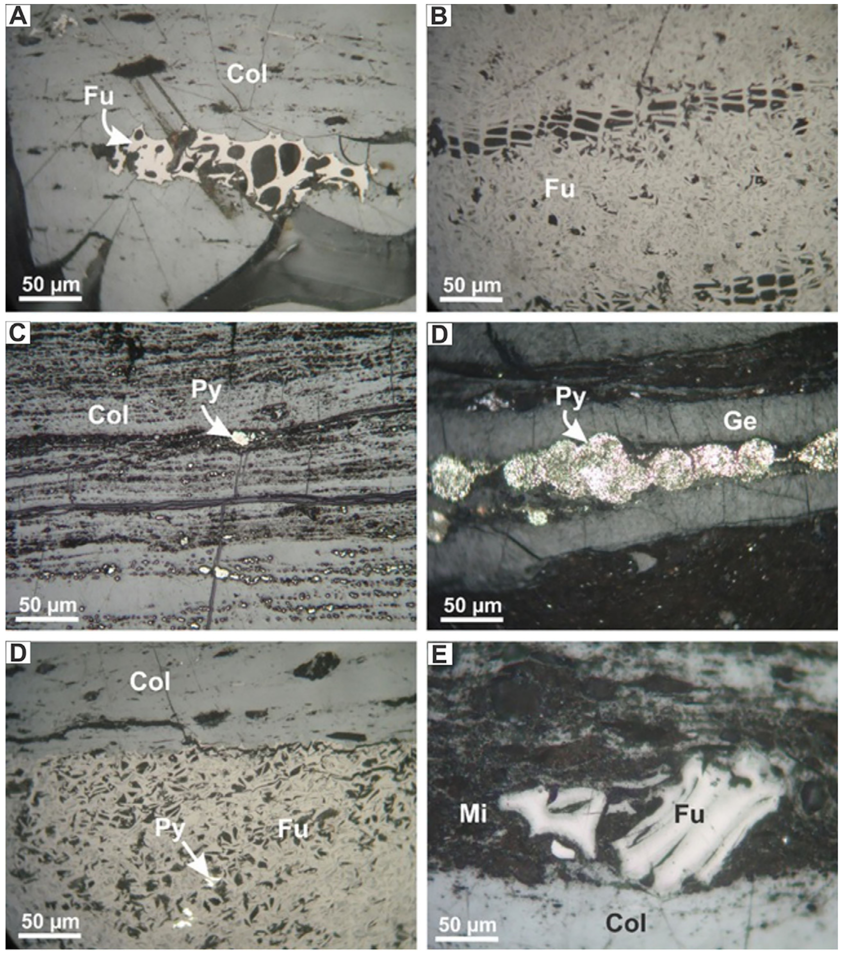

Fig. 6. Micro-photograph, with reflected light, of the samples of the Tunas Formation, belonging to the PANG0001 well, where the different components (macerals, mineral matter and pyrite) are observed. **A:** Collotelinite (Col) and fragment of fusinite (Fu). **B:** fusinite (Fu) where the plant structure is observed. **C:** Collotelinite (Col) with botryoidally pyrite (Py) associated. **D:** Gelinite (Ge) interbeded with mineral matter (Mi) and botryoidally pyrite (Py). **E:** Collotelinite (Co) interbbeded with fusinite (Fu) and pyrite (Py) filling the structure gaps. F: Collotelinite (Co) interbedded with mineral matter (Mi) and fusinite (Fu).

Table 2
Maceral, mineral matter and pyrite percent in the samples of the Tunas Formation, belonging to the PANG0001 well.

Sample	Depth (mbw)	Vitrinite (%)	Inertinite (%)	Mineral matter (%)	Pyrite (%)
433 - BOX 76	396.18	46.63	12.15	40.32	0.90
420 - BOX 81	412.65	55.20	24.17	17.74	2.89
111 - BOX 226	813.10	56.77	28.52	14.70	0.00
A - BOX 237	842.00	58.26	0.00	30.30	11.44
C - BOX 237	842.00	0.83	1.05	98.03	0.09
83 - BOX 240	850.33	64.91	2.11	30.82	2.16
79 - BOX 242	856.87	54.02	13.00	31.72	1.26

The lithologies of the PANG0001 well were grouped in ten different facies:

- **Fl facies**: Mudrocks of black color, with sharp bases, occasionally present parallel lamination. They have intense to moderate horizontal and vertical bioturbation, and plant imprints. They contain pyrite nodules, some of them as fill of the fossil traces (Fig. 3(A) and (B)).
- **Hl facies**: Heterolites of dark grey color, with sharp bases, with intense to moderate bioturbation, horizontal and vertical. In some sections they present cross ripple and hummocky lamination (Fig. 3(C) and (D)).
- **Sr facies**: Fine sandstones of light grey color, with sharp bases. They show parallel and cross lamination and moderate bioturbation, horizontal and vertical (Fig. 3(E) and (F)).
- **Tf facies**: Fine tuff of light green color, with sharp bases. They present parallel and cross lamination (Fig. 4(A)).
- **Src facies**: Medium sandstones with carbonate cement, of light grey color, with sharp bases, massive to cross stratification. (Fig. 4(B)).
- **St facies**: Medium sandstones of light grey color, with erosive bases and cross stratification. They present moderate vertical bioturbation (Fig. 4(C) and (D)).
- **Fsm facies**: Mudrocks of green color, probably with volcanic components, with sharp bases. Toward the top they contain hematite nodules (Fig. 4(E)).
- **Sm facies**: Medium sandstones of black color, with sharp bases, massive. They present pyrite nodules (Fig. 4(F)).
- **BO facies**: Fine levels of boundstones (until 5 cm.), with sharp bases, that correspond to microbial algae. They were identified following the criteria of Noffke et al. [54]: laminae of light color intercalate with laminae of dark color, fine irregular and discontinued lamination, oriented grains and oscillation cracks that

Table 3
Vitrinite Reflectance values of the samples that belong to the Tunas Formation in the PANG0001 well, and its average values, from further depth at the left, to shallower. SD: Standard deviation. Max: Maximum value. Min: Minimum value.

N	R_0 medium						
	79 BOX 242	83 BOX 240	C BOX 237	A BOX 237	111 BOX 226	420 BOX 81	433 BOX 76
1	1.5	2.2	2.2	1.8	2.4	1.5	2.3
2	1.5	2.3	1.9	2.1	2.3	1.6	1.6
3	1.3	2.1	2.2	2	2.6	2	1.4
4	1.7	2.2	1.6	2.1	2.3	1.5	1.2
5	1.7	2.2	2.1	2	2.4	1.9	1.6
6	1.8	2	2.5	2	2.4	2	1.8
7	1.5	1.8	2.1	2.1	2.1	1.6	2.1
8	2	1.7	2.7	2.1	2.3	1.7	1.2
9	1.6	2.1	2.5	2.2	2.4	1.8	1.8
10	2	1.8	2.3	2.2	2.3	1.4	1.4
11	2.3	2	1.6	2.2	2.5	1.9	1.7
12	3.1	2.1	1.8	2.1	2.6	2	1.2
13	2.3	2	1.9	2	2.5	2	3.1
14	2.2	2.1	1.9	1.8	2.2	1.6	1.7
15	1.7	2.4	2.5	2	2.1	1.2	1.5
16	2.1	2.1	1.8	1.9	2.4	1.7	1.7
17	2.4	2.1	1.8	1.9	2.4	1.7	0.9
18	2	2.2	2.1	1.8	2.3	1.8	1.3
19	2.1	2.5	2.1	1.9	2.4	1.6	1.4
20	1.9	1.9	1.9	1.8	2.4	1.3	2
21	2.2	1.9	2	1.9	2.7	1.8	1
22	2.4	2.1	1.6	1.9	2.4	1.4	0.8
23	2.2	2	1.8	2.1	2.6	1.9	1.2
24	2	2.2	1.8	2	2.2	2.1	1.2
25	2.2	2.3	1.7	2.1	2.4	2	1.3
26	2.2	2.1	2	2	2.3	1	1.3
27	2.2	2.1	1.3	2.1	2.4	1.4	0.9
28	1.8	2	1.5	2	2.3	1.5	2.2
29	2.2	2.1	1.7	2	2.3	1.6	1.4
30	2.1	2.1	2.1	2.1	2.4	1.5	1.3
31	1.8	1.9	1.7	2	2.3	1.4	1.2
32	2.2	1.9	2.1	2.1	2.3	1.5	1.2
33	2.4	2.2	2	2.1	2.1	1.4	1.2
34	2.5	1.9	1.9	2.2	2.4	1.9	0.9
35	2.1	2	2.5	2.2	2.5	1.5	1.3
36	2.3	2.2	1.9	1.9	2.3	1.7	1.2
37	2.4	2.2	2	1.8	2.3	0.9	1.8
38	2.1	2.1	2.6	1.8	2.4	1.3	0.8
39	2.5	1.9	1.8	1.8	2.5	1.5	0.8
40	2.1	1.8	2.4	1.8	2.3	1.6	1
41	2.3	2	1.6	1.8	2.4	1.7	1.4
42	2.6	2.2	1.3	1.8	2.4	1.6	2
43	2.2	2	2.1	2	2.8	1.6	1.8
44	2.3	1.9	2.3	1.7	2.9	2	1.7
45	1.9	2	1.6	1.9	2.6	1.6	1.9
46	2.2	1.9	1.3	1.9	2.7	1.7	0.9
47	2	2.1	2.3	2.1	2.5	2.1	1.6
48	2.2	2	1.7	2.1	2.5	2	1
49	1.7	2	2.5	1.8	2.2	1.7	1.4
50	2	2	1.7	2.1	2.5	1.6	1.6
51	2.1	2.1	1.9	2.1	2.5	1.8	1.3
52	2	1.7	1.7	2.1	2.4	1.1	2.8
53	1.7	2.3	2.2	2.1	2.5	1.4	1.2
54	1.3	2	2.7	2.2	2.4	1.6	1.4
55	1.7	2	1.9	1.9	2.5	1.9	1.2
56	1.5	2.1	2.5	1.9	2.5	1.9	1
57	2.2	2	1.8	2.1	2.5	1.9	0.8
58	1.4	2.4	1.8	2	2.3	1.3	1.2
59	1.5	2	2.1	1.9	2.4	1.6	1.1
60	2	2.2	1.8	2	2.4	1.8	1.9
61	1.9	2.1	2.4	1.9	2.2	1.8	0.9
62	1.6	2.1	1.7	2	2.3	0.9	0.9
63	2	2.1	3	2	2.5	1.6	1.3
64	1.7	2	2.4	1.8	2.6	1.6	1.2
65	1.3	2.2	2.2	1.9	2.7	1.6	1
66	1.9	2.2	1.9	1.8	2.5	1.7	1.2
67	2.1	2.2	2.5	1.8	2.4	1.6	1.1
68	2.1	2.3	2.4	1.9	2.4	2	1
69	1.6	2	1.9	1.9	2.5	1.2	1.1
70	1.9	2.1	1.6	2	2.3	1.3	0.9
71	1.7	2.4	3	1.9	2.2	1.7	1.3

(*continued on next page*)

Table 3 (*continued*)

N	R_0 medium						
	79 BOX 242	83 BOX 240	C BOX 237	A BOX 237	111 BOX 226	420 BOX 81	433 BOX 76
72	2	2.1	2	2.1	2.4	1.9	1
73	1.8	2.2	2.1	2.1	2.3	1.3	1.1
74	1.7	2.3	2.1	2.1	2.5	1.8	1.4
75	1.5	2.2	1.7	2.1	2.5	1.9	1.8
76	1.7	1.9	2	2.1	2.4	1.5	1.6
77	1.9	2.1	2.1	2.1	2.4	1.6	1.3
78	2.2	2	2.1	2.1	2.4	1.5	1
79	1.9	2	1.7	2.4	2.3	1.5	1.4
80	1.5	2.1	2.3	2.1	2.5	1.5	1.5
81	1.8	2	2.7	2.1	2.5	1.1	1
82	2	2.2	2.3	2.1	2.3	1.6	1.5
83	1.9	2.2	2.4	1.9	2.7	1.8	1.4
84	1.2	2.2	1.6	1.9	2	2	2.3
85	1.7	2.1	2.3	1.9	2	1.5	1.5
86	1.5	2	1.6	2	2.5	0.9	1.3
87	2.1	2.1	2.3	1.8	2.3	0.9	1.1
88	1.6	1.9	2.1	1.8	2.2	1.3	1.1
89	1.8	2.1	1.6	1.9	2.2	1.2	1.5
90	1.8	1.9	1.8	2.1	2	1.4	1.6
91	2.1	2.1	1.6	2.1	2.3	1.2	1.2
92	2	2	1.2	1.9	2	1.6	1.1
93	1.7	2.2	1.2	2.1	2.2	1	1.2
94	1.8	2.1	2.3	2.1	2.1	1.3	1
95	1.9	1.9	2.8	2.1	2.4	1.9	1
96	1.7	2.1	2.7	1.8	2.3	2	1.2
97	2	1.8	2.6	1.7	2	2	1.3
98	2	2.2	2.4	2	2.4	2.1	–
99	2.2	1.8	2.2	1.9	2.4	1.4	–
100	2.3	1.9	2	2.1	2.3	1.7	–
Average	**1.945**	**2.071**	**2.022**	**1.988**	**2.38**	**1.6**	**1.36**
SD	**0.323**	**0.151**	**0.472**	**0.135**	**0.169**	**0.297**	**0.415**
Max	**3.1**	**2.5**	**3**	**2.4**	**2.9**	**2.1**	**3.1**
Min	**1.2**	**1.7**	**1.2**	**1.7**	**2**	**0.9**	**0.8**

Table 4
Medium values of the vitrinite reflectance (R_0 medium), measured in the samples taken at different depth of the PANG0001 well, belong to the Tunas Formation. Right, values of maximum depth of burial, range of temperature, volatile matter percent, coal range (ASTM standard) and oil window, estimated from medium R_0.

Sample	R_0 medium (%)	Depth of burial (m, [72])	Volatile Matter %	Temperature max. (°C)	Range (ASTM)	Oil window
433 - BOX 76	1.365	1840	25	165–145	Medium volatile bituminous	Wet gas
420 - BOX 81	1.600	1940	19.8	170–150	Low volatile bituminous	Wet gas
111 - BOX 226	2.380	2230	10.5	187–167	Semianthracite	Methane gas
C - BOX 237	2.022	2090	13	180–157	Semianthracite	Methane gas
A - BOX 237	1.988	2060	13.5		Semianthracite	Wet gas
83 - BOX 240	2.071	2125	12.2		Semianthracite	Methane gas
79 - BOX 242	1.945	2020	14		Semianthracite	Wet gas

indicate leakage fluids (Fig. 5(A) and B). These microbial algae levels are interbedded in the sequence at 842 mbw and they are composed of white color laminae of carbonate intercalated with black laminae of carbonaceous mudstones [11].
- **C facies**: Coal and carbonaceous mudrock beds, occasionally with parallel lamination and plant imprints (Fig. 5(C) and (D)).

Zorzano et al. [93] studied the depositional palaeoenvironment of the PANG0001 well facies. They interpret a transgressive-regressive cycle were the facies of the lower part of the sequence represent a marine platform environment and the facies of the upper part represent fluvial and estuary channels.

4. Coal analysis

The organic matter identified in the PANG0001 well corresponds to humic coal (kerogen type III) that is composed by coalified matter from higher plants, in the lower section of the well, between 849.5 and 836 mbw. There are four humic coal beds of 0.5–1.5 m thickness, interbedded with carbonaceous mudrocks with a total thickness of 13.5 m. In the upper section, between 412 and 396 mbw, there are thin coal laminae, less than 2 cm (Fig. 2). In these levels the vegetal structure that corresponds to *Glossopteris, Gangamopteris, Lycopsids* and woody tissues (Fig. 5(C) and (D)) can be distinguished.

In five samples that contain humic coal, the Total Organic Carbon (TOC) was estimated; in seven samples of humic coal, petrographic analyses were carried out to determine the quality and the maturity of the coal.

4.1. TOC analysis

In samples of carbonaceus mudrocks the TOC values are between 4,11 and 12,84%, while in a coal sample the obtain value is 46,08% (Table 1).

4.2. Microscopy analysis

The microscopy analysis was carried out in seven samples of humic coal, and corresponds to the quality of the organic matter (maceral analysis) and the maturity of the organic matter (vitrinite reflectance).

4.2.1. Quality of the organic matter: Analysis of macerals

Microscopically, the coals of the Tunas Formation are represented by monomaceralic bands of up to 2 cm thick, composed of macerals that belong to the Vitrinite Group or to the Inertinite Group, with complete absence of macerals of the Liptinite Group. Pyrite is in the coals generally as nodules.

- In the *Vitrinite* Group, the Collotelinite and Gelinite macerals predominate. Sometimes it is not possible to distinguish the maceral (Fig. 6).
- In the *Inertinite* Group, only the Fusinite maceral was observed (Fig. 6).

The counting shows a predominance of macerals belong to the Vitrinite Group in all the samples (up to 64.9%) followed by Fusinite, of the Inertinite Group (up to 28.5%). The mineral matter is very variable with values between 14–40%, indicating that the coal grade (mineral matter percent) varies between Medium Grade (<20% mineral matter), Low Grade (between 20 and 30%) and Very Low Grade (between 30 and 50%). The C-BOX 237 sample contains little quantity of coal: it has 98% of mineral matter. The pyrite percentages vary from 0.1 to 11.4% (Table 2).

The inertinite coal correspond to charcoal, based on the Scott [60,62] criteria: black color and streak, silky luster and well-preserved anatomical details (Figs. 5(D), 6(A), B, E and F).

4.2.2. Maturity of the organic matter: Vitrinite reflectance

The reflectance was measured mainly in collotelinite, however in some samples it was not possible to distinguish this maceral from the gelinite; therefore, the values obtained could be a bit higher than they should, resulting in some errors of minor significance.

The obtained values of vitrinite medium reflectance (R_0 medium) are around 2% in the samples of the lower part of the PANG0001 well sequence (at approximately 850 mbw) and have values of 1.36% in the samples of the upper part (at 396 mbw); thus can be observed a decrease of the vitrinite reflectance values in the samples of the upper part of the sequence (Table 3). According to these results, the coal samples taken from the lower section of the PANG0001 well classify as semianthracitic, with a volatile matter of 10–14%, and the samples from the upper part classify as medium to low volatile bituminous, with a volatile matter of 19–25% (Fig. 7; Table 4).

According to data obtained in the PANG0001 well log, the lower part of the Tunas Formation reached equivalent stage of methane oil window during the late catagenesis [71], whereas the upper part reached the condensed and wet gas oil window (Fig. 7, Table 4). The temperature obtained from R_0 shows values between 145 and 187 °C, according to the graphic of Teichmüller [72] (Fig. 8; Table 4).

5. Diagenetic and palaeoenvironment considerations

The results suggest that the Tunas Formation reached, during its burial, a catagenesis to metagenesis stage, according to the organic matter maturity and a mesogenesis to mature mesogenesis stage, with respect to the mineral diagenesis ([74,96].

Previous studies of diagenesis in outcrops of the Tunas Formation in the Sierras Australes, obtained by mineralogical methods (illite crystallinity and recrystallization of quartz) show a high diagenesis degree [18,32,84]. These results are well correlated with the results here obtained by the R_0 values: the metagenesis stage coincides with the high diagenesis degree. However, it must be considered that the Sierras Australes is a thrust and fold belt and

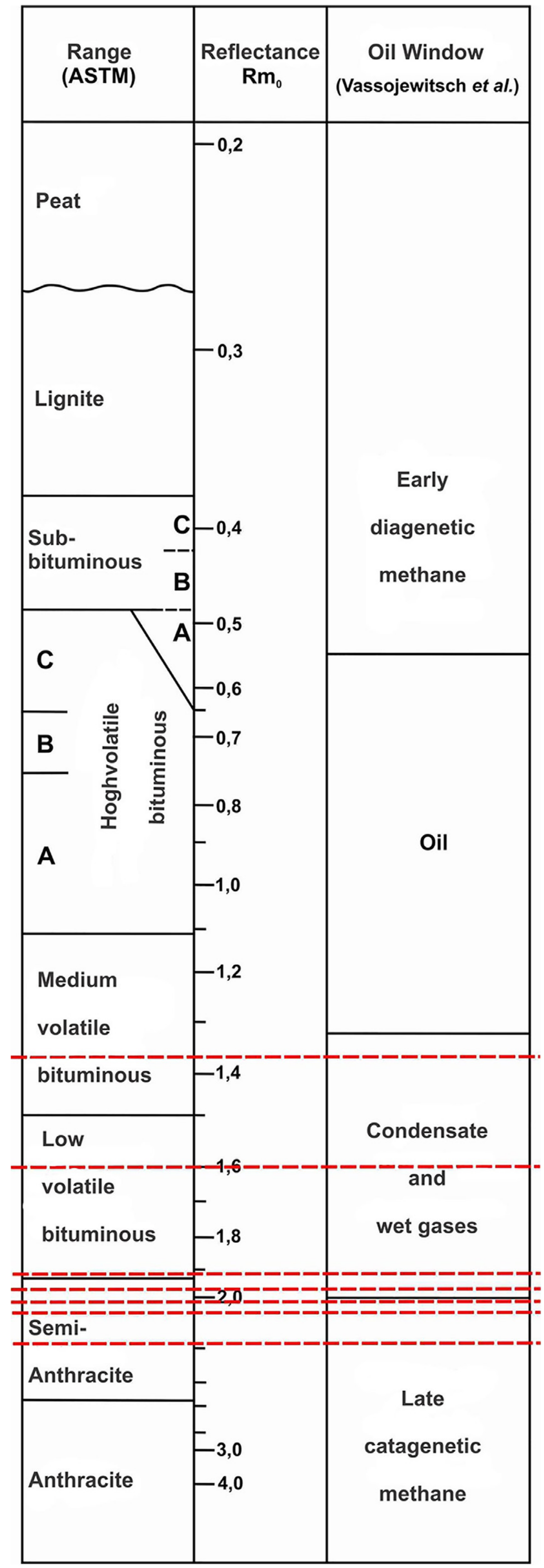

Fig. 7. Graphic that shows the medium values of the vitrinite reflectance (Rm_0) of the coals belonging to the Tunas Formation (in red spotted line), its range (based on ASTM standard) and the oil window [71]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

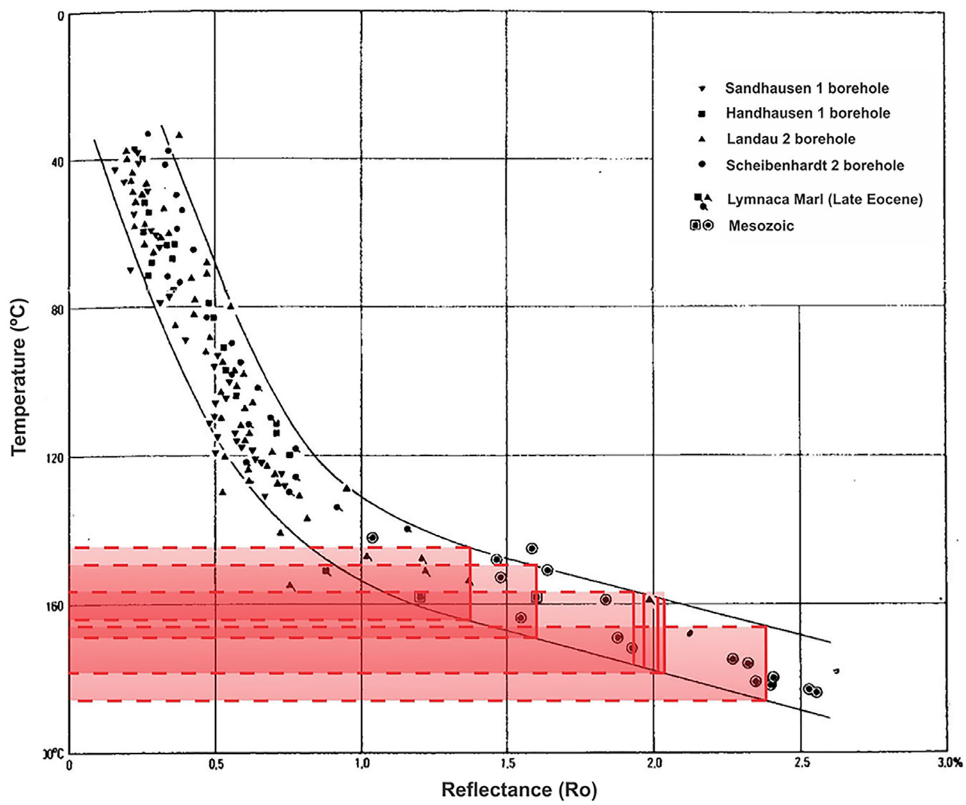

Fig. 8. Graphic that shows the ratio between the vitrinite reflectance and the maximum temperature to which the different coal samples of Germany were subjected [72]. The red areas correspond to the samples of the Tunas Formation.

here the deformation could be an important factor in the diagenesis degree, compared with the strata in the Claromecó Basin that are practically undeformed ([9,10,13,14]).

According to Tissot et al. [74], the temperatures reached for the R_0 values obtained in the Tunas Formation are between 140 and 160 °C and this is coincident with the range of temperature obtained using the graphic of Teichmüller [72].

The fluids associated with the algal mats of the Tunas Formation and its diagenesis stage, were analyzed by Arzadún et al. [11,13] by the study of fluid inclusions in carbonate samples associated with microscopic algae, taken from the PANG0001 well at 842 mbw. These studies found that the formation reached temperatures from 126 to 152 °C and a metagenesis stage into the organic matter diagenesis. These data are concordant with the results obtained in this paper.

The coal of the Tunas Formation (Permian age), found in subsurface in the Claromecó Basin, is of a humic type (from superior plants: Type III kerogen); these are composed by monomaceralic bands of collovitrinite and gelovitrinite, of the Vitrinite Group and Fusinite, of the Inertinite Group.

The laminae composed of vitrinite derived from woody tissues such as stems, branches and roots, correspond to an environment of swampy forest. The laminae composed of fusinite are the result of fires and they probably represent periods in which the phreatic level descend and the swamp surface gets dry ([19,61,62,91,97]); this controlled the early diagenetic conditions, evidenced by the presence of framboidal pyrite related to the maceral predominance. The presence of this mineral indicates an anoxic environment during the early diagenesis, and it reaches 11.44% in absence of inertinite (BOX237 sample). This can be attributed to periods in which the phreatic level rises with no registered fires, inhibiting the oxidation of pyrite and the development of inertinite. The other samples have a minor presence of pyrite, related to the major values of inertinite, corresponding to periods in which the phreatic level descends (Fig. 9). This indicates that the Tunas Formation was originally deposited in an environment of wet swampy forest, alternate with periods in which the swamp got dry and experienced fire. These paleoenvironment interpretations are consistent with previous studies in the area (Ruiz and Bianco, 1985; [43,93]) and with the facies described here. The existence of fires during the Permian of Gondwana is registered, in base to the Inertinite or charcoal studies, in different basins, such as the Paraná Basin in Brazil, the Karoo Basin in South Africa, the Damodar Basin in India and in the Mar Muerto area [20,36–40,42,49,51,61,62,88], Saar-Nahe basin in SW Germany [83], in Northern America [21,60], in China [69,85] and in Jordan [82] (Fig. 1(A)).

The rest of plants founding in the coals and in the carbonaceous mudrocks are not clearly in situ but the structure has a good preservation of the charcoal in some levels and a bad preservation (as fragments) in other ones. Thus, indicate an autochthonous origin for the material and then it was transported, thus the fires occurred not far from the place of deposition.

Several authors argue that the high concentrations of Gondwanan inertinites have a pyrogenic origin with high atmospheric oxygen; in these conditions even wet vegetation may burn frequently and intensively [27,63,81]. According to Bowman et al. [17], combustion occurs when atmospheric O_2 concentrations are above 13%, and variation in O_2 levels correlates with fire activity throughout Earth history; at levels mayor than 30% even plants and fuels with high moisture contents would burn easily, even without a distinct dry season [27]. Reconstructions of palaeo-atmospheric composition based on inertinite percent, demonstrated that during the Permian the concentration of pO_2 was globally high, between 28 and 30% [26,27,86]. However, the record of charcoal in the Permian is minor than in the Carboniferous, maybe because of climate deterioration and tectonic reorganization of landscapes [81,83]. Dur-

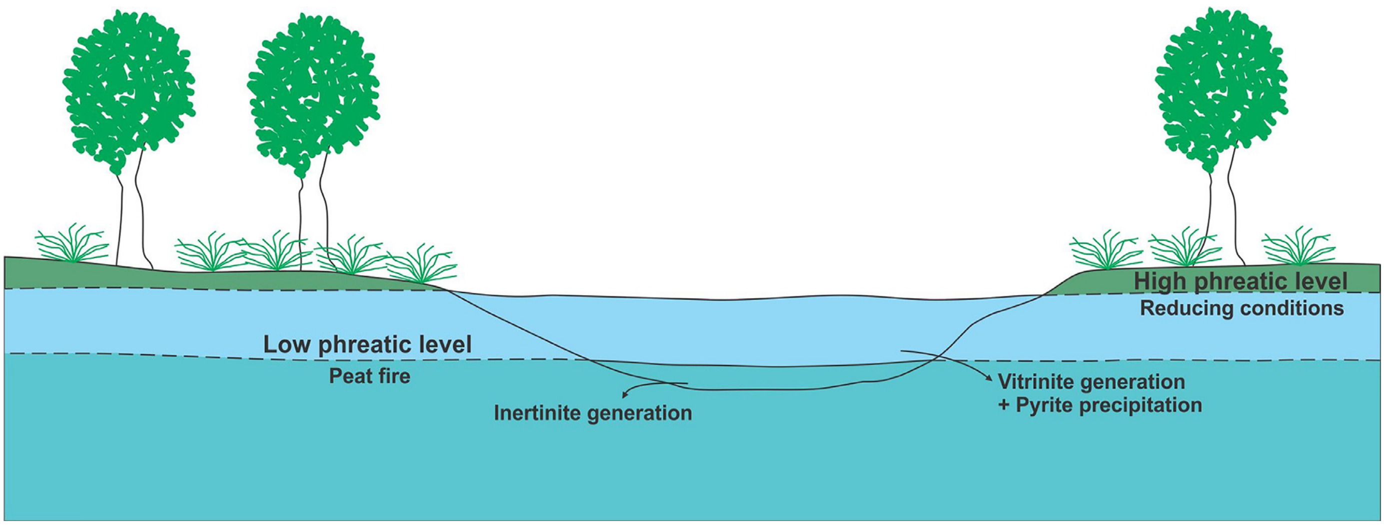

Fig. 9. Diagram of the original environment of the Tunas Formation, interpreted by coal analysis. It consists of a wet swamp forest, alternating with periods where the swamp became dry, due to the lowering of the water table.

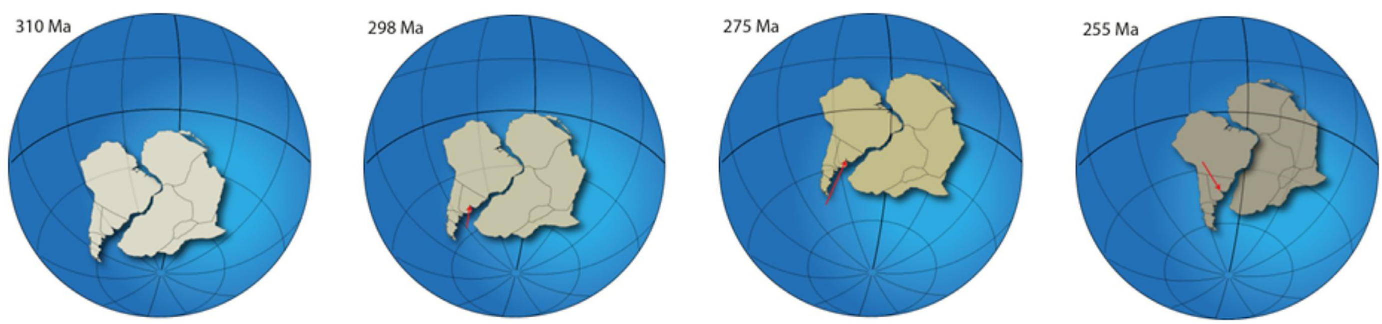

Fig. 10. Paleogeographic reconstruction of Gondwana that shows the latitudinal movements of the continents toward the Equator during the Permian, based on paleomagnetic poles of Tomezzoli [75].

ing the Permian, the continents were assembling, forming the Pangea with a movement of 9 cm per year toward the Equator [75] (Fig. 10). This produced a generalized volcanism in different regions (for example the Choiyoi volcanism at the San Rafael Basin and in the Karoo Basin in South Africa) and the closure of several basins with its consequent continentalization [23,46,67,77]. These changes could led the decreased of the potential amount of available fuel for wildfires on a large scale, and may taphonomic filters has not been preserved due the degradation under the semi-arid and arid conditions prevailing during the Permian [81,83].

6. Conclusions

The data provided in this paper confirm the presence of Permian coals in the sub-surface of the Claromecó Basin, in the Tunas Formation, coeval with outcrops in the near area of the Sierras Australes. The coal petrographic analysis suggests interpreting the paleoenvironment and the diagenesis conditions, contributing important information about this basin, and determines:

- The presence of humic Permian coal in the Claromecó Basin, which implies a type III kerogen (from plant material).
- The humic coals are composed of Collotelinite and Gelinite that are macerals of the Vitrinite Group, and Fusinite that are macerals of the Inertinite Group.
- The humic coals classify as semianthracitic (in the lower part) and low volatile bituminous (in the upper part).
- The temperature reached by the Tunas Formation is between 150 and 190 °C.
- The diagenesis reaches a catagenesis to metagenesis stage respect to the organic matter diagenesis and a mesogenesis to mature mesogenesis respect to the mineral matter diagenesis.
- The fine-grained carbonaceous facies of the Tunas Formation were deposited in a wet swampy forest environment, with increases and decreases of the phreatic level.
- The presence of inertinite or chacoal is product of Permian fires in the Claromecó Basin, as in other Permian basins. This is related to the high concentration of O_2 in this period and maybe with climatic and tectonic changes.

The petrographic analysis of the Permian coals in the Claromecó Basin (Argentina), and in particular the vitrinite reflectance, was an efficient method to determine the diagenesis level reached in the Tunas Formation and its depositional environment characteristics

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