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RESEARCH PAPER

Geochemical Characterization of Coal Deposits of Candiota Coalfield Rio Bonito Formation (Eo-Permian) of Paraná Basin, South Brazil*

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Abstract

This work integrates organic geochemistry (total organic carbon - TOC, total Sulphur - S and Rock Eval pyrolysis data) and detailed organic petrography results of the Eo-Permian interval (Rio Bonito Formation, Paraná Basin) in the Grande Candiota area, Rio Grande do Sul State (RS), where the largest Brazilian coalfield is located. Samples were collected along the SVH-07 well and in front of the open-pit mine at Seival. The organic petrography analysis allowed to characterize the coals composition and to classify the stage of coalification. The results reveal that the Grande Candiota coals were deposited in a stormy coastal environment. As the samples present high percentage of inorganic material, the Seival coals must be considered more appropriately as coaly shales. The highest percentage of TOC was observed at the base of the coal Seams. The Upper Seam 7(US7) presents the highest average organic matter content and the Lower Candiota Seam (LCS) the lowest one. The sampled coals can be classified as humic coal due to the predominance of vitrinite, followed by liptinite and inertinite maceral groups. Analyzing each coal Seam individually, it is observed that vitrinite and organic carbon contents are higher in the base of Rio Bonito Formation, whereas inertinite and liptinite contents increase upwards. These variations encompassed a parasequence scale whose base is represented by the carbon Seam deposited at higher humidity conditions, whereas the top paleo soils are associated to longer dry periods. Considering the coal Seams as a whole, it is observed an upward decreasing of the vitrinite content and an increase of inertinite and liptinite, as well as the Hydrogen Index values. These data should be related to a retro gradational system in a transgressive context of the Rio Bonito Formation. The significant increase of sulfur content in Banco Louco Seam also suggests a greater influx of seawater into the depositional system. The Hydrogen Index values show that the coal of US7 has the highest volatile ratio. This behavior is related to the higher liptinite group content in these strata, diminishing the calorific power of this coal. Data from the organic petrography analyzes of the Seival coals were compared with those of the Candiota coalfields, for Lower Candiota and Upper Candiota Seams; it is observed that they have a certain similarity. In addition, the Seival coal organic composition was compared with other South Hemisphere Gondwanan coals, for which they have significant differences related to the higher proportions of liptinite and smaller of inertinite. The coalification stage (rank) for the Seival coals, on the basis of the vitrinite reflectance, ranged from peat to a sub-bituminous B type.

Keywords: Coal. Organic Geochemistry. Organic Petrography. Rio Bonito Formation. Eo-Permian interval. Paraná Basin. Brazil.

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1 Introduction

The largest known Brazilian coal reserve, estimated in 8 billion tons is located in southeast of Paraná Basin, in the region of Grande Candiota, Rio Grande do Sul State (RS), where the study area is located (Cientec, 1980). The coals occur in the lithostratigraphic unit called the Rio Bonito Formation, of Eo-Permian age (Sakmarian/Artinskian), as the other coalfields of Paraná Basin.

The open-pit mine of Seival, currently inactive, is owned by COPELMI MINERAÇÂO Ltda. The total reserves of Seival coals are about 223,393,000 tons, according to COPELMI internal report of November 1998. Its location is at the southern end of Brazil, in the Rio Grande do Sul State, at the Grande Candiota region, near the Bagé city (Fig. 1).

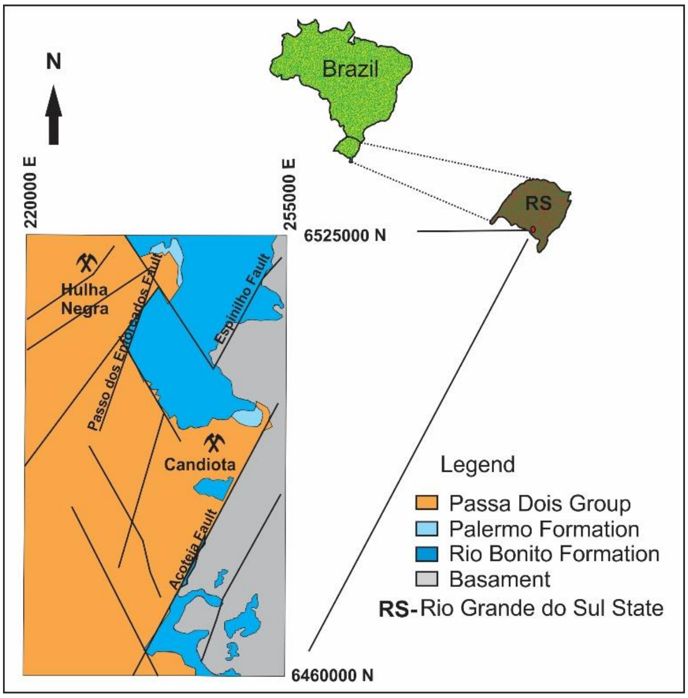

Fig. 1. Location map of the study area.

1.1 The main goals

The main goals of this study are to characterize the petrochemical and geochemical characteristics of the Seival coal, in association with the depositional environment related to the peat formation, in addition to determine the carbonization stage of these coals. Based on organic geochemistry and organic petrography data, the geological integration with several stratigraphic and faciological aspects of Seival coals was carried out according to the depositional model proposed by Della Favera et al. (1997), extended to the region of Grande Candiota. The petrographic analyzes also allowed the comparison between the obtained data in Seival Coalfield with those of previous works, carried out in the Candiota mine and in other Gondwanan coals of the South Hemisphere.

2. Study Area: Geological Context

The Paraná Basin is located in the central/southeast region of South America (covering parts of Brazil, Argentina, Paraguay and Uruguay), with a total extension of about 1,500,000 km^2, of which approximately 1,000,000 km^2 are located, in the southern region of Brazil (Fig. 1). This basin consists of a large intracratonic syneclisis, filled by sedimentary rocks, from the Neo-Ordovician to the Neo-Cretaceous, as well as records of magmatic events. The maximum thickness of the sedimentary-igneous fill is about 8,000 meters in the geometric center of the basin (Zalan et al., 1990).

The origin, evolution and filling of Paraná Basin is extensively discussed in the works of Cordani et al. (1984), Aborrage and Lopes (1986), Zalan et al. (1990), Milani et al. (1994, 2007) and Milani (1997). The stratigraphic studies of the Paraná Basin began in 1908 with the work of White and was followed by several other researches. Based on the existing knowledge Schneider et al. (1974) published the stratigraphic column of the basin that was improved by Zalan et al. (1990) and later by Millani et al. (2007).

Milani et al. (2007) recognized six second-order allostratigraphic units, representing cycles of subsidence and sediment accumulation, limited at a basin scale by non-conformities, called Rio Ivaí (Neo-Ordovician-Eo-Silurian), Paraná (Devonian), Gondwana I (Carboniferous-Eo-Triassic), Gondwana II (Middle and Upper Triassic), Gondwana III (Eo-Jurassic/Eo-Cretaceous) and Bauru (Upper Cretaceous) supersequences. The interval studied is inserted in the Gondwana I sequence (Fig. 2).

The study area, Seival, at Rio Grande do Sul State, is located in the Candiota Depression, on the southern border of the Riograndense Shield, located at southeast of Paraná Basin (Fig. 1). Since the beginning of 20th century, several researches have been developing at Grande Candiota region. Della Favera et al. (1992) studied it for the first time, based on a conceptual basis of sequence stratigraphy. Della Favera et al. (1997) applied, the sequence stratigraphy perspective to study the Seival area too.

The Grande Candiota region presents low tectonic disturbance, being its structure an inheritance of Pre-Cambrian and Eo-Paleozoic tectonism, with NNE/SSW and NW/SE preferential structural directions: Espinilho Fault, near Seival, to the east; Açoteia Fault to the southeast and; Passo dos Enforcados Fault to the northwest (Fig. 1). For the most part, these preexisting directions underwent episodic tectonic reactivations throughout the depositional history of Candiota depression.

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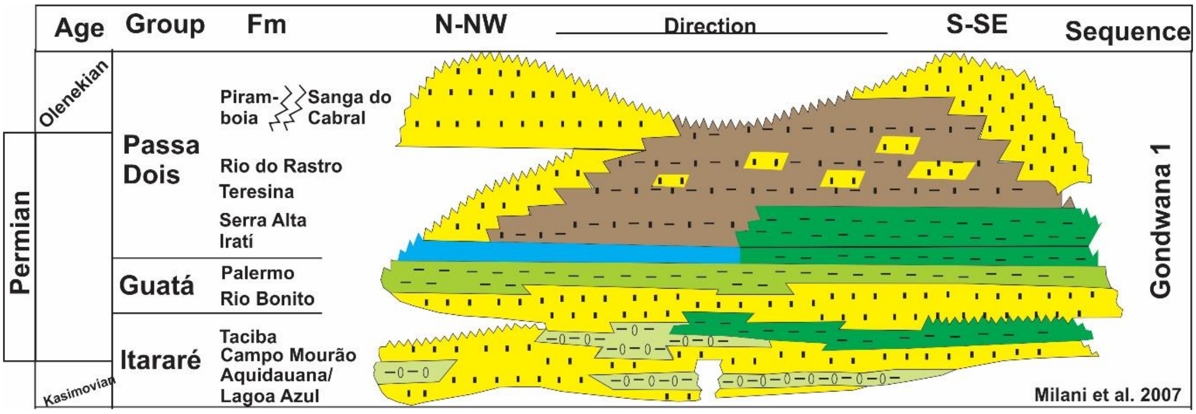

Fig. 2. Stratigraphic column of the Paraná Basin (according to Milani et al., 2007).

However, the most significant reactivation occurred later, in the Mesozoic (Jurassic/Cretaceous), accompanied by magmatism and causing some minor faults, related to the South Atlantic Ocean rifting. The sedimentation phase was apparently a period of calm tectonic activity and the sedimentary Seams are almost in their original dispositions (Della Favera et al., 1992).

In Seival, the stratigraphic sections based on gamma ray profiles shows erosion in the high blocks, usually in the extreme northeast of the area, suggesting the occurrence of normal faults stablished after all the sedimentary deposition.

It is conspicuous the presence of growth faults, acting during the Permian sedimentation. These faults have sin-depositional and non-tectonic character, caused by intense deposition of coarse-grained clastic sediments on more plastic materials (in this case, probably the coals).

These structures are characterized by a listric fault configuration, creating space for the accommodation of large volumes of coarse sediments and resulting in a local sandy section with thickness greater than are commonly found (Della Favera et al., 1997) (Fig. 3).

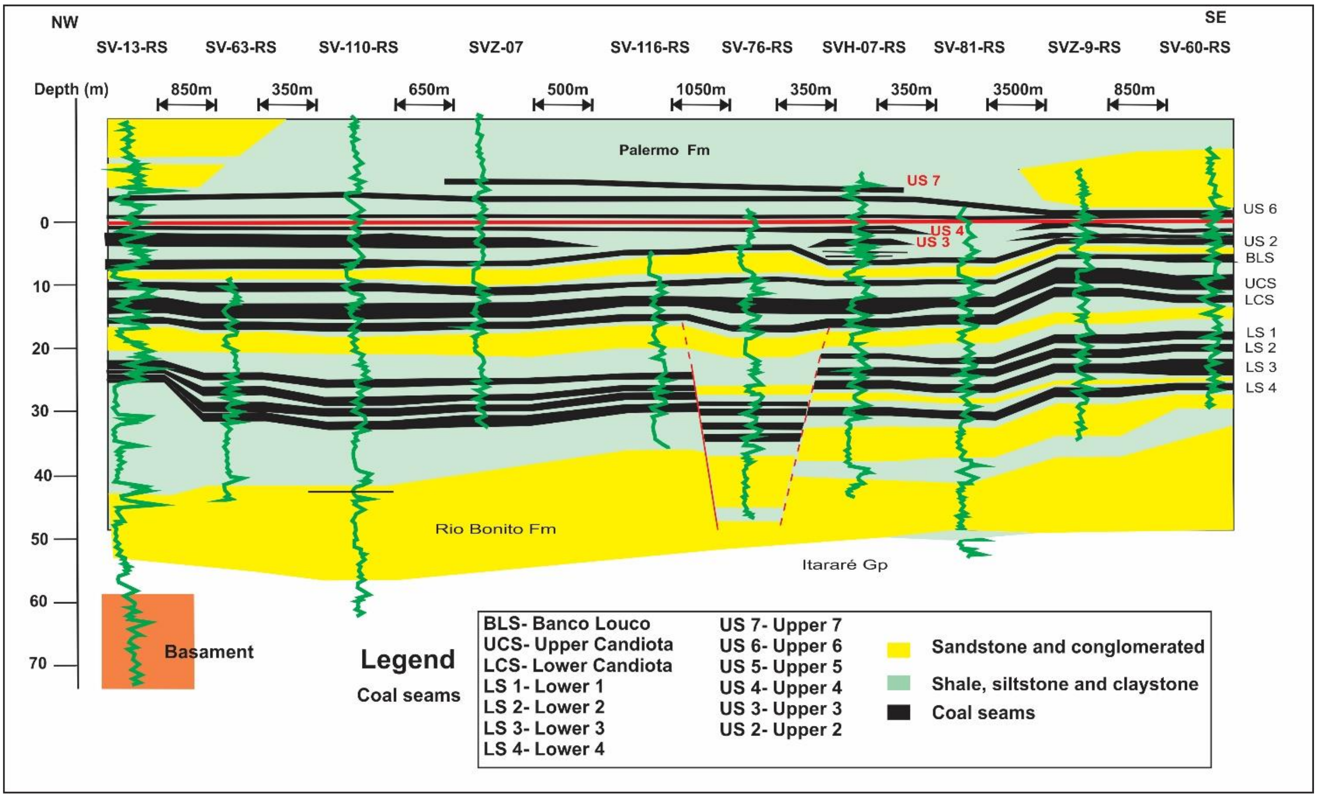

Fig. 3. Stratigraphic section correlative to the Seival area, containing the SVH-07-RS well (adapted from Della Favera, 1997).

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Medeiros (1996), based on Holz (1996) and Della Favera et al. (1992) considered that the paleogeography of the region of Grande Candiota, in the interval between Itararé and Rio Bonito formations, as an archipelago formed by structural highs isolated from the basement, such as Porto Alegre and Uruguay highlands (Fig. 4).

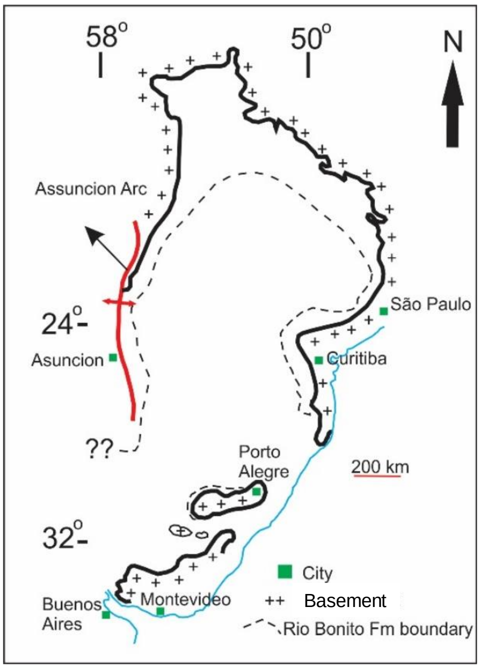

Fig. 3. Area of occurrence of Rio Bonito Formation in the Parana Basin (in Rio Bonito time). We can note the absence of Porto Alegre-Uruguay highlands (adapted from Della Favera, 1997).

According to Della Favera (1997), the basement in Seival is formed by metasedimentary units of the Camaquã Group, filling, the Camaquã Basin, characterized by a molassic foredeep depozone of Eo-Paleozoic age. The Itararé Group stands discordantly on the paleo-valleys filling. The sedimentation of this unit occurred in a periglacial context resulting generally in marine continental deposits with diamictite, tilite and varvite main facies. During the deposition of much of the Itararé Group, the region of Grande Candiota was a topographical elevation. Consequently, only the upper portion of this group occurs in the area.

The Rio Bonito Formation rests concordantly on the Itararé Group and contains the coal section. In the other southern regions of Brazil, coal is also found in this formation. According to Della Favera et al. (1997), the Rio Bonito Formation can be subdivided into two parts:

1 - The basal portion is sandy, with medium to thick sandstones, with festoon structures and sigmoids, as well as some conglomerates. This lower section is related to lagoonal deposits influenced by fluvio-deltaic systems. These deltas should be classified as braid-delta type and are probably associated to a postglacial environment with high gradient (as interpreted also in Candiota-RS, Criciuma (Santa Catarina State- SC), Recreio and Guaiba-RS, by Della Favera et al. (1992, 1996, 1998).

2 - The upper portion is essentially silty, consisting of siltstone, claystone and intercalations of coal Seams (Fig. 5).

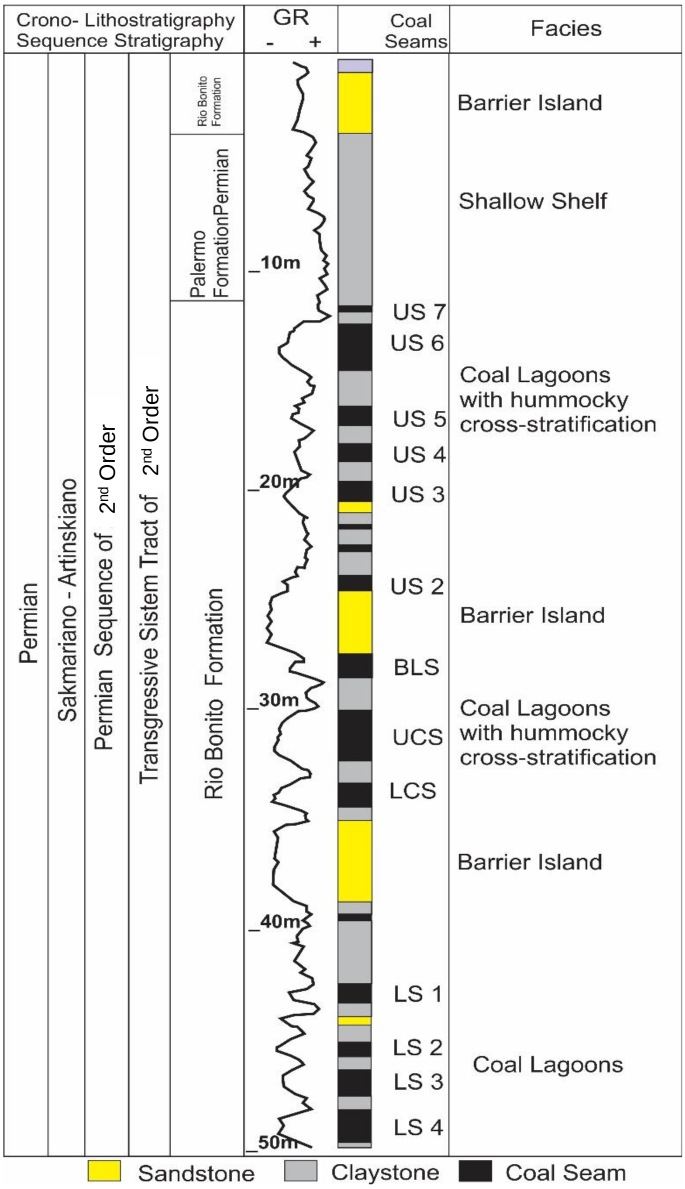

Fig. 5. Stratigraphic reference profile of the Seival area, based on the well SVZ-07-RS (Della Favera et al., 1997).

This second portion was deposited in lagoonal and shallow marine environments. All the coals seams observed in Seival, from the Upper Candiota Seam (UCS) to the Upper Seam 7 (US7) present hummocky cross stratification, produced by the action of storm waves and characterized by beach facies. The presence of this structure implied a new faciological characterization and a new positioning of the coal in the parasequence. In the Rio Bonito Formation, thin

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layers (with a maximum of 6 cm of thickness) of the so-called tonsteins, rocks rich in kaolinite, also reported in the coal deposits of Rio Grande do Sul. These rocks are interpreted as altered volcanic ash. The top of the Rio Bonito Formation gradates vertically for the Palermo Formation. This contact represents a change of facies from the coal of Rio Bonito Formation to siltstones of Palermo Formation, characterizing a diachronic contact. The Palermo Formation is essentially silty and, in the Seival area, only the lower portion occur. The rest of Gondwana I sequence (in the lithostratigraphic framework named Passa Dois Group) are not present in Seival region.

3. Materials and Methods

Samples for analysis were collected at Seival open pit coal mine and in the cores of the SVH-07 well. Coals were sampled in Lower Candiota Seam (LCS), Upper Candiota Seam (UCS), Banco Louco Seam (BLS) and Upper Seam 3-7 (US3, US4, US5, US6 and US7) and shales above and below these carbonaceous Seams, with spacing of 20 cm between the samples. The collected material was submitted to organic petrography in reflected light, total organic carbon (TOC), total sulfur (S) and Rock Eval pyrolysis.

The organic petrography study of the coals was performed in polished sections and analyzed in reflected light. After the plugs confection, they were sanded and then polished with alumina. In the Zeiss MPM 400 microscope the groups of macerals and minerals in white light were identified and quantified with a 50x objective, 10x ocular and immersion oil (with a refractive index of 1.518 at 23ºC). The vitrinite reflecting power was determined in vitrinite particles in the colotelinite maceral with the equipment previously calibrated with synthetic sapphire standard.

For the other analyzes, 25g of each sample (rock) were pulverized, acidified (20% HCl) for 24h, washed three times with distilled water, the first boiled and the next two with water at room temperature. After drying, prepared samples were weighed. The percentage of the insoluble residue was determined by difference of dry weight. With the remaining material after acidification and drying, the TOC and S analyzes were performed simultaneously on the LECO SC-444 equipment.

Pyrolysis was performed on Rock Eval II equipment from pulverized sample; variable amounts of sample were used depending on TOC content (Espitalié et al., 1977).

4. Results and Discussion

4.1 Organic Petrography of Coals

Sixteen samples were analyzed in the eight mentioned coal Seams: Lower Candiota Seam (LCS), Upper Candiota Seam (UCS), Banco Louco Seam (BLS) and Upper Seam 3-7 (US3, US4, US5, US6 and US7). The obtained results are presented in Table 1.

Tab. 1. Average percentage, by volume, of the maceral groups and mineral matter in the Seams of coal of Seival Mine. Legend: LCS - Lower Candiota Seam; UCS - Upper Candiota Seam, BLS - Banco Louco Seam; Upper Seam 3-7 (US3, US4, US5, US6 and US7).

Seams	**Maceral groups**			**Mineral Matter**		
	Vitrinite	Inertinite	Liptinite	Clay	Pyrite	Carbonate
US7	40.58	10.54	37.65	11.23	-	-
US6	33.75	8.79	23.31	32.79	0.43	0.93
US5	17.89	17.88	9.58	54.1	0.27	0.27
US4	21.79	12.01	17.77	46.75	0.84	0.84
US3	29.02	37.89	10.24	22.37	0.24	0.24
BLS	19.9	8.78	15.64	54.52	0.61	0.5
UCS	49.62	14.71	15.24	19.27	0.39	0.77
LCS	35.68	7.45	8.31	47.36	0.72	0.48

The results show that the coals usually present a predominance of the vitrinite group, followed by the liptinite and inertinite groups, in the organic portion. The highest vitrinite contents were recorded in the UCS (49.32%), US7 (40.58%), LCS (35.38%) and US6 (33.75%). The coals US7 and US6 are quite rich in the liptinite group (37.65% and 23.31%, respectively). The US3 Seam is an exception. It shows a predominance of inertinite (37.89%), followed by vitrinite and liptinite. The US5 Seam had similar values of vitrinite (17.89%) and inertinite (17.88%), followed by liptinite. The predominance of vitrinite in the coal of the Seival Mine, allows classifying it as humic coal, according to Hunt (1982).

Relatively high amounts of inertinite (oxidized organic material) in the US3 and US5 suggest relatively drier climatic conditions in the depositional environment during the organic matter sedimentation. These arid conditions should have caused a lowering in the level of the peat bogs water, damaging the preservation of the organic material.

Another factor that can cause inertinite rise, in the coals, is the amount of organic material transported to the peat site.

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Several authors mention that also spontaneous fires should have contributed to a greater accumulation of oxidized vegetal matter in the peat bogs. In addition, the distribution of barrier islands and growth faults should have conditioned some restrictions on the peat bogs, facilitating the subaerial exposures and, consequently, the oxidation of the organic matter.

The average inorganic content of the coals, considering all the Seams, is very high, reaching 36.91%. This inorganic portion consists almost entirely of clay and, secondarily, of pyrite (in granular and sometimes with framboidal form) and carbonates. The highest percentages of mineral matter were found in BLS (54.2%) and US5 (54.1%). High mineral matter contents were also found in LCS (47.06%), US4 46.75%) and US6 (32.79%). In these carbonaceous intervals, clay is the predominant constituent, and in the Seam US6 its percentage is equivalent to that of vitrinite. This large volume of minerals is common in Gondwanan coals of the South Hemisphere, which are mainly related to transition depositional environments.

The association of clay with sub-autochthonous macerals (Correa da Silva, 1991) resulted probably from the stormy reworking of these peats in the depositional site, a fact evidenced by the presence of hummocky cross stratifications in the coals.

Through the average contents of the maceral groups and minerals, a comparison can be made between the LCS, UCS and BLS of Seival Mine and those of the Candiota Coalfield, analyzed in previous works (Table 2).

Tab. 2. Comparison between the mean values of the maceral groups and the minerals of the coals of the Seival Mine and the Candiota. Legend: BLS- Banco Louco Seam; UCS-Upper Candiota Seam; LCS - Lower Candiota Seam; V- Vitrinite; I- Inertinite; L- Liptinite; M-Minerals.

Seams	Candiota Coalfield												Seival Mine			
	Corrêa da Silva and Marques-Toigo ()				Ade (1993)				Silva (1994)				This work			
	V	I	L	M	V	I	L	M	V	I	L	M	V	I	L	M
BLS	-	-	-	-	8	40	14	38	10	36	10	44	19.5	8.8	15.2	55.3
UCS	40	16	8	36	38	17	9	36	29	21	9	41	49.3	14.7	15.2	20.4
LCS	39	16	4	40	39	18	7	36	30	20	7	43	35.4	7.4	8.3	48.3

In general, the results are well-matched, with the predominance of the vitrinite group (except in the BLS of Candiota Coalfield) and large amounts of minerals which are sometimes the main constituents. However, it is observed that for the three correlated Seams, the values of the liptinite group are always higher in Seival Mine than in Candiota Coalfield. Despite the methodological differences in the acquisition and preparation of the samples between different studies, it is possible that these higher percentages are due, at least in part, to the counting done with fluorescence microscopy methods, only in Seival (in this work).

For the LCS, the most striking difference is the mean value obtained for the group of the inertinite in Seival, corresponding approximately to half of that in Candiota. In the UCS of Seival, liptinite occurs with double of the contents and the mineral concentration represents about half of that found in Candiota. In relation to the BLS, Ade (1993) and Silva (1994) point out that the Candiota Coalfield is an exception, being the only seam among those studied that presented predominant levels of inertinite. In Seival, the BLS shows the same compositional behavior of the other Seams, not presenting this anomaly.

Table 3 presents the relative contents of the maceral groups (expressed in 100%, not accounting the minerals) for the analyzed samples, and the mean for each Seam of coal at the Seival Mine.

The predominant maceral in the studied coals is vitrinite, followed by liptinite and inertinite. The only exception is the US3 in which the inertinite is the main organic constituent. The highest average contents of each maceral group are distributed as follows: the vitrinite group in the LCS (83.21%), the liptinite group in the US7 (42.41%) and US3 (49.11%). Considering all the coal Seams and the average contents of the maceral groups, it is observed that: vitrinite presents decreasing contents from the LCS to the US3 and from there occur alternating low and high percentages up to the US7; the inertinite occurs with increasing values of the LCS to the US3 and decreasing from the US5 to US7. The US4 is out of these tendencies; the inertinite occurs with increasing values from the LCS to the US3, decreasing from the US5 to US7. The US4 exhibits different trends; liptinite shows a cyclic trend of growth towards the upper Seams (LCS, UCS, BLS and US3-US7).

Based on Table 3, Figure 6 shows the triangular diagram illustrating the above-mentioned behavior and the relationships between several coal Seams. The analysis of this diagram shows that the vitrinite content in the UCS and LCS Seams are relatively higher than in the other Seams. The

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inertinite group presents markedly higher values in the US3 and US5 coals. The liptinite levels show a general tendency of growth toward the upper Seams, which stand out from the US4. A high value is also observed in the BLS.

Tab. 3. Mean percentage by volume of the maceral groups (expressed in 100%, not accounting the minerals), for the Seams at the Seival Mine. Legend: US - Upper Seam; BLS- Banco Louco Seam; UCS-Upper Candiota Seam; LCS - Lower Candiota Seam.

Seams	Mean values of Maceral Groups (%)		
	Vitrinite	Inertinite	Liptinite
US7	45.7	11.9	42.4
US6	49.9	13.0	37.1
US5	39.4	39.4	21.2
US4	42.2	23.3	34.5
US3	37.6	49.1	13.3
BLS	44.7	20.2	35.1
UCS	60.8	19.2	20.0
LCS	83.2	7.3	9.5

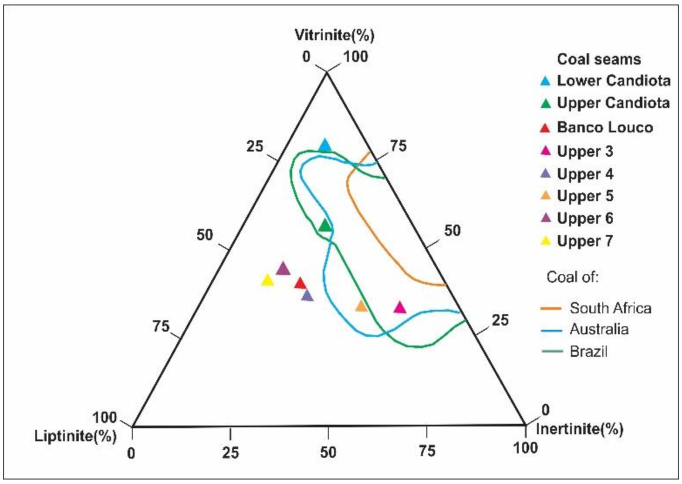

Fig. 6. Triangular diagram of the maceral groups (100%) of the studied coal Seams of the Seival Mine and the comparison with the Gondwanan coalfields of South Africa and Australia (according to Mackowsky, 1975) and Brazil (according to Corrêa da Silva, 1989).

The organic composition of some Gondwanan coals of the South Hemisphere was compared to that of Seival coals. Petrographic data (maceral groups) are related to the coals of South Africa and Australia, according to Mackowsky (1975), and from Brazil, including the coals of Santa Catarina (Barro Branco Seam), Rio Grande do Sul (Morungava coalfield) and Paraná (Ribeirão Novo and Marins coalfields), according to Correa da Silva (1989).

The coalfields delineated for the mentioned Gondwanan coal generally show high proportion of inertinite (>50%), low liptinite and varying vitrinite contents (mean ≈50%). These coalfields differ from Seival organic matter, where the relative amounts of inertinite are not as expressive, except in the Seams US3 and US5 that have rather higher liptinite content. In general, the results obtained for the Seival coal are not similar to the other Gondwanan coals, being several plotted Seams outside the fields delimited for these coals. Seival coals are markedly different of data obtained by Silva (1994) in Candiota (Fig. 7).

The Seams used in the comparison between these coals were the LCS, UCS and BLS. The main differences observed in Seival were: higher vitrinite contents; in particular in the LCS and BLS; higher liptinite contents, especially in the BLS coal; and lower inertinite levels, more markedly in BLS coal.

4.1.1 Degree of carbonification (rank)

The carbonification of organic matter is a geological process that occurs due to factors such as burial, temperature and time. Vitrinite is a product of the carbonification essentially of woody parts of plants and its reflectance is one of the parameters used to determine the degree of carbonification of organic matter (rank). The progressive increase in rank of a coal produces an increase in the reflecting power of vitrinite. The random reflector power of vitrinite (Rm%) was determined in all the Seams analyzed in this work and the average results per Seam are presented in Table 4.

Tab. 4. Mean vitrinite reflecting power values (Rm%) and the standard deviation of the analyzed coal from the Seival Mine, according to Costa (1999). Legend: US - Upper Seam; BLS - Banco Louco Seam; UCS - Upper Candiota Seam; LCS - Lower Candiota Seam.

Seams	Mean Values	
	Rm%	Standard Deviation
US7	0.217	0.024
US6	0.413	0.038
US5	0.459	0.035
US4	0.325	0.028
US3	0.339	0.047
BLS	0.270	0.032
UCS	0.377	0.033
LCS	0.427	0.047

The measured values of the reflectance are low, probably due to the methodology used in the measurements, which were mainly accomplished in the maceral desmocolinite since the telocolinite is in general rare in the samples. The comparison between the Seival data and the mean values of Rm% for the LCS, UCS and BLS obtained in previous works, are presented in Table 5.

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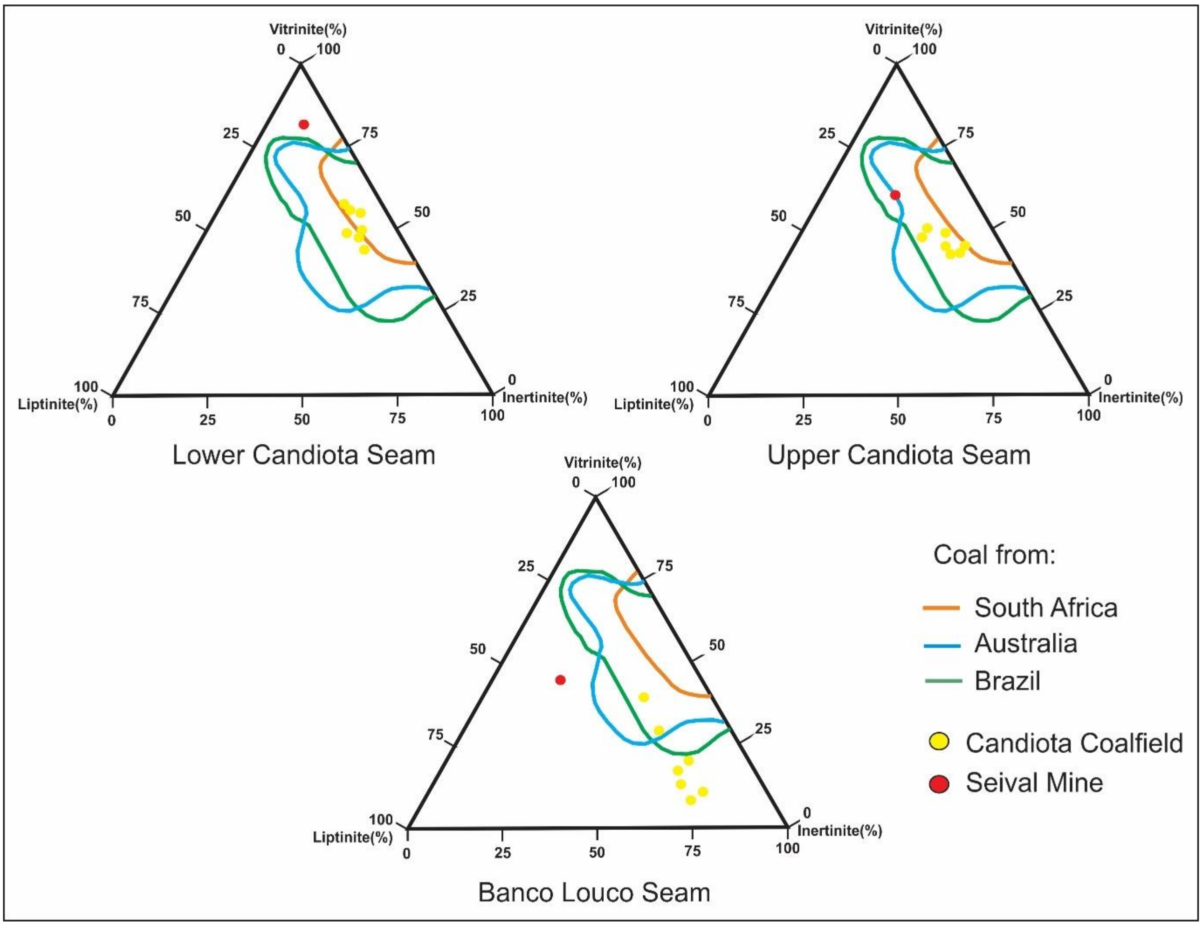

Fig. 7. Triangular diagram of maceral groups (to 100%), comparing the coal Seams of Seival Mina and seven cores of Candiota coalfields (Silva, 1994) and Gondwanan coalfields of South Africa and Australia (Mackowsky, 1975) and Brazil (Corrêa da Silva, 1989).

Tab. 5. Mean vitrinite reflectance (Rm%) values between the coal Seams of the Seival Mine and the Candiota Coalfield. Legend: BLS-Banco Louco Seam; UCS-Upper Candiota Seam; LCS - Lower Candiota Seam.

Seams	Nahuys and Camara (1972)	Cientec (1980)	Corrêa da Silva and Marques-Toigo (1985)	Silva (1994)	This work
	Rm%	Rm%	Rm%	Rm%	Rm%
BLS	-	-	-	0.40	0.27
UCS	-	0.51	0.40	0.41	0.38
LCS	-	0.46	0.40	0.41	0.43
UCS + LCS	0.47	-	-	0.41	-

The values of Rm% for Candiota vary between 0.40% and 0.46% for the LCS, between 0.40% and 0.51% for the UCS and with a value of ≈0.40% for the BLS (Table 5). The results obtained in the Seival Mine are reasonably compatible to those of Candiota for the first two Seams. The BLS and US7 have lower values (0.270% and 0.217%, respectively).

According to the International Committee for Coal Petrology (ICCP 1963-1975), coalification is the process by which the organic matter deposited in the bog is transformed into lignite and then into coal. This process takes place under reducing conditions and is a function of temperature, time and pressure.

Several parameters for determining the degree of coalification (rank) and classification according to American (ASTM) and German (DIN) standards can be observed in Figure 8 together with the positioning of the coal Seams of Seival and Candiota Coalfield. In this table, the vitrinite reflectance data for the coal Seams of the Seival Mine and more complete analyzes for the Candiota coalfield (Silva, 1994) are plotted.

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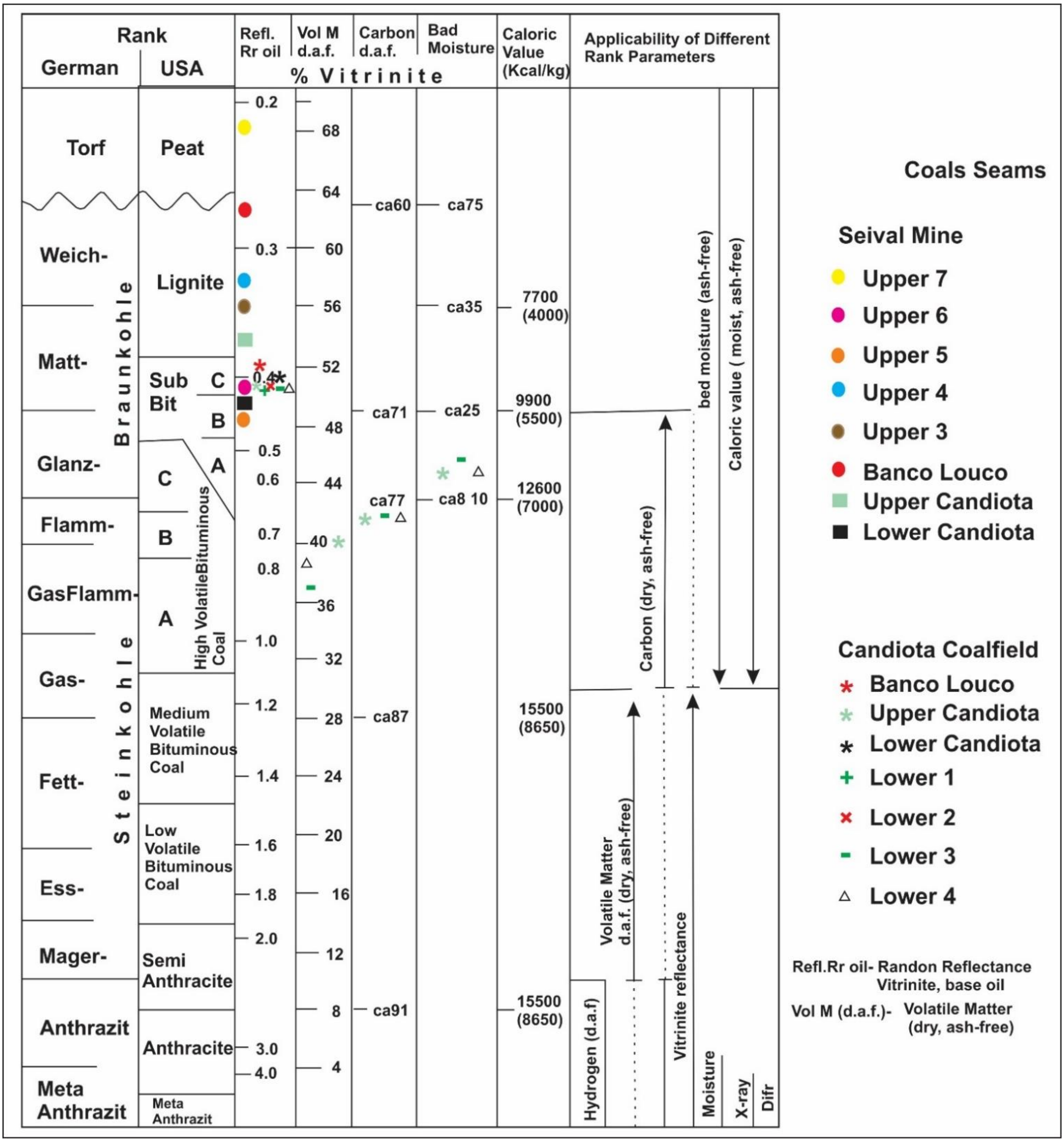

Fig. 8. Classification of the carbonization degree of the Seival and Candiota coalfields (Silva, 1994) based on the vitrinite reflectance.

As observed by Silva (1994), it is difficult to find a perfect connection between the several parameters used in the classification of the South-Brazilian Gondwanan coals and the international norms used for coals in the Northern Hemisphere. Differences found in the positioning of the considered parameters do not allow an alignment of data, which hinders the classification. This fact probably occurs due to faciological variations during the coal formation process.

In relation to the vitrinite reflectance (Rm%), the coal of the Candiota (UCS and LCS) is in the sub-bituminous C stage (ASTM). Using the results of moisture and vitrinite content, the classification of the coal of the UCS, is in the sub-bituminous A/bituminous high volatile C and bituminous high volatile B (ASTM), corresponding to Glanzbraunkohie - Gasflammsteinkohie (DIN, Germany classification).

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The rank classification for the coal Seams of the Seival Mine, according to Figure 9 were: LCS (sub-bituminous coal B), UCS (lignite), BLS (lignite), US3 and US4 (lignite), US6 (sub-bituminous C) and US7 (peat) (ASTM). It is observed that the depth increase of the coal Seams does not determine increasing in the rank rise, as expected, showing the fragility of this technique when a single parameter for the classification is used. This situation was verified and discussed by Corrêa da Silva (1989).

4.2 Geochemical Analysis

4.2.1 Total Organic Carbon (TOC)

The TOC values vary between 6.23% and 50.1%, in the analyzed Seival Mine coals samples. Only a sample of the base of the UCS reached the maximum percentage mentioned above, the other values range between 20% and 40%. In terms of the mean TOC, the only coals with values >30% are UCS (31%), US3 (33%) and US7 (39%). These Seams constitute the relatively purest coals in Seival, especially the US7.

The lowest mean TOC values (about 20%) were obtained in the LCS and BLS, in extremely impure Seams. The low concentrations of TOC show that most of these rocks are formed of inorganic material (ashes), identified petrographically as mainly clay-minerals. Large volume of terrigenous materials should have been incorporated, to a great extent, during the reworking of the turfs by stormy events. In this way, the Seams of coal should in fact be considered more as carbonaceous shales than as coals in a narrow sense.

The distribution figures of the TOC x depth values of each Seival coal Seam show that they are heterogeneous and show significant internal variations in organic content (Fig. 9).

The TOC values tend be higher at the bottom of the Seams, and tend to decrease toward the top. Thus, the purer portions of the coals are located at the base Seams, where the highest concentrations of organic matter occur. The UCS also presents this behavior but shows a smaller variation of TOC contents towards the top, pointing that it is more homogeneous in TOC content than the other Seams (Fig. 9).

The US7 coal, although not thick, also have low variable TOC values from the base to the top of the Seam (Fig. 9). The BLS includes two distinct Seams, with high content of inorganic material, intercalated with a clayey silt level, very well marked by low organic contents (<8%; Fig. 9). The US6 coal is also composed by two sub-Seams, with TOC values also decreasing toward the top. As a whole, this coal has significantly higher TOC contents in the lower Seam, meaning a lower proportion of impurities at the base (Fig. 9).

According to organo-petrographic data, the maceral group of vitrinite is the main constituent of most of the studied coals in Seival. The exceptions occur in the Seams: US3, where inertinite prevails; US5, where vitrinite and inertinite values are similar and US7, where the contents of vitrinite and liptinite are quite similar (Table 5).

TOC contents and vitrinite values are directly related, especially in the LCS, UCS and BLS (Fig. 10). Thus, these Seams show an inverse relation to inertinite and to liptinite (Fig. 10). In US3 and US5, the high TOC contents are more related to the inertinite group. In US6, TOC and inertinite are correlated. This Seam and the US7 have the highest organic contents distributed predominantly by vitrinite and liptinite maceral groups (Fig. 10).

4.2.2 Total Sulfur (S)

Total sulfur (S) contents are very low. Using the graph of TOC x S (Fig. 11A), it can be observed that, in general, sulfur concentrations follow the organic matter contents, but with values markedly lower than those observed in marine environments (Fig. 11B). For the coal Seams, this interaction is best visualized by comparing the graphs of TOC x depth and S x depth in Figure 11 (A and B).

The values of S x depth for the Seival coals show that the LCS and UCS are quite homogeneous and have average sulfur contents of 0.34% and 0.52%, respectively (Fig. 11A). These values are relatively low when compared to other coals. In BLS, sulfur concentrations increase to mean levels of 1 to 3%, showing larger variation than in the other Seams (Fig. 11A). This sulfur increasing trend indicates probably a greater influx of sea water in the bog depositional site. The relative abundance of sulfates contained in seawater provides a greater amount of sulfur to the sedimentary environment, through sulfate-reduction promoted by anaerobic organisms. This greater influx of sea water, suggested by the increase of sulfur concentration in the sediments, is related to the regional transgression toward the Palermo Formation.

In addition, the sedimentological data from the Seival area indicate the presence of a last barrier island just above the BLS (Della Favera et al., 1997). The barriers should have probably protected the lagoons where the peatlands were forming. The characteristics of the BLS indicate a shallow continental shelf environment and a more direct interaction of the sea water in the peatbogs.

The only exception to the increase in sulfur content mentioned above is the coal of US4, whose average sulfur content is 0.43% and corresponds to a very impure coal, with an average organic matter concentration of about 24% (Fig. 11B). The low sulfur content present in this Seam, along with the high inertinite content, suggests restriction of the sea water entrance during the peat accumulation.

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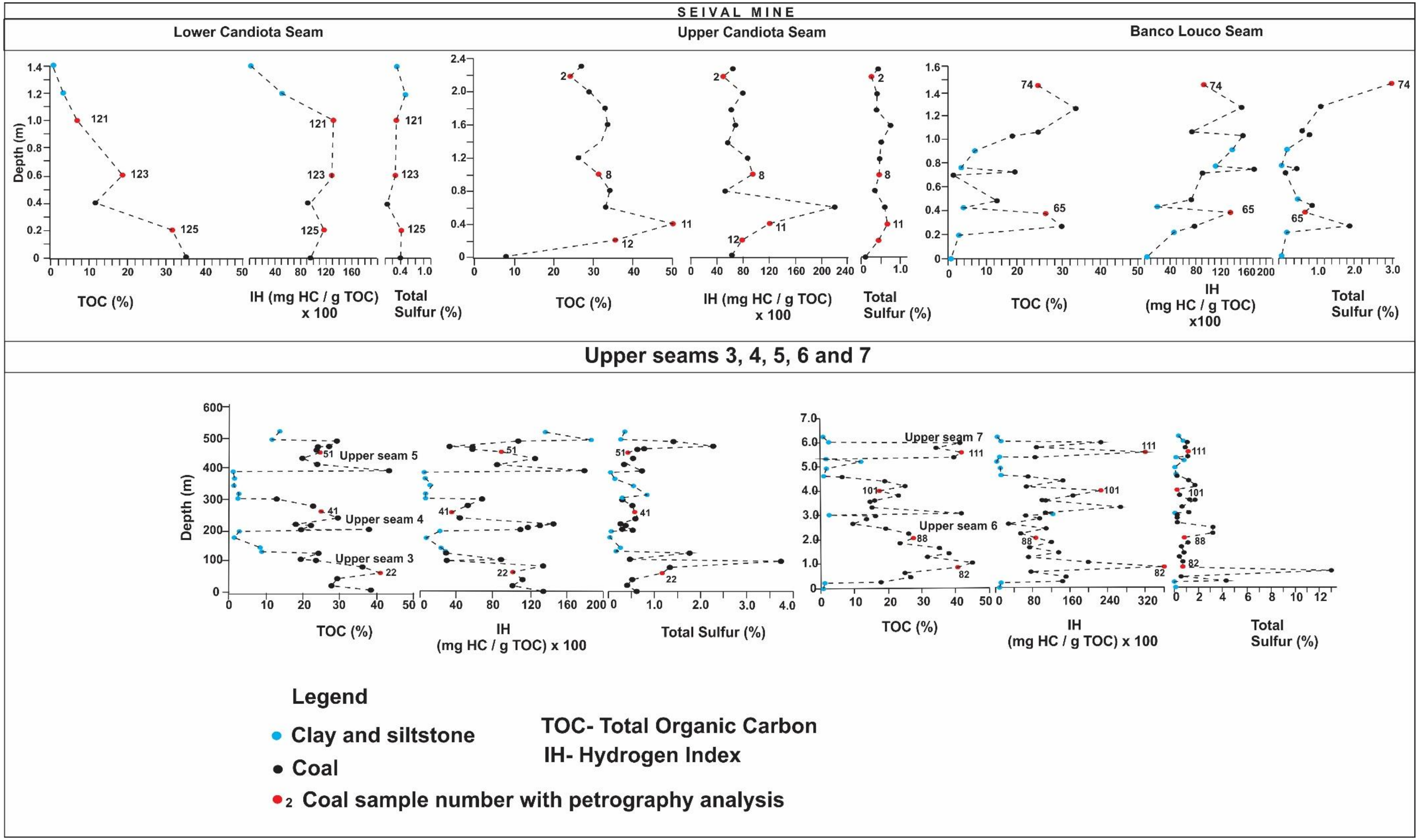

Fig. 9. TOC, Hydrogen Index and Total Sulfur contents in LCS, UCS, BLS, US3,5,6 and 7 coal seams versus depth (m).

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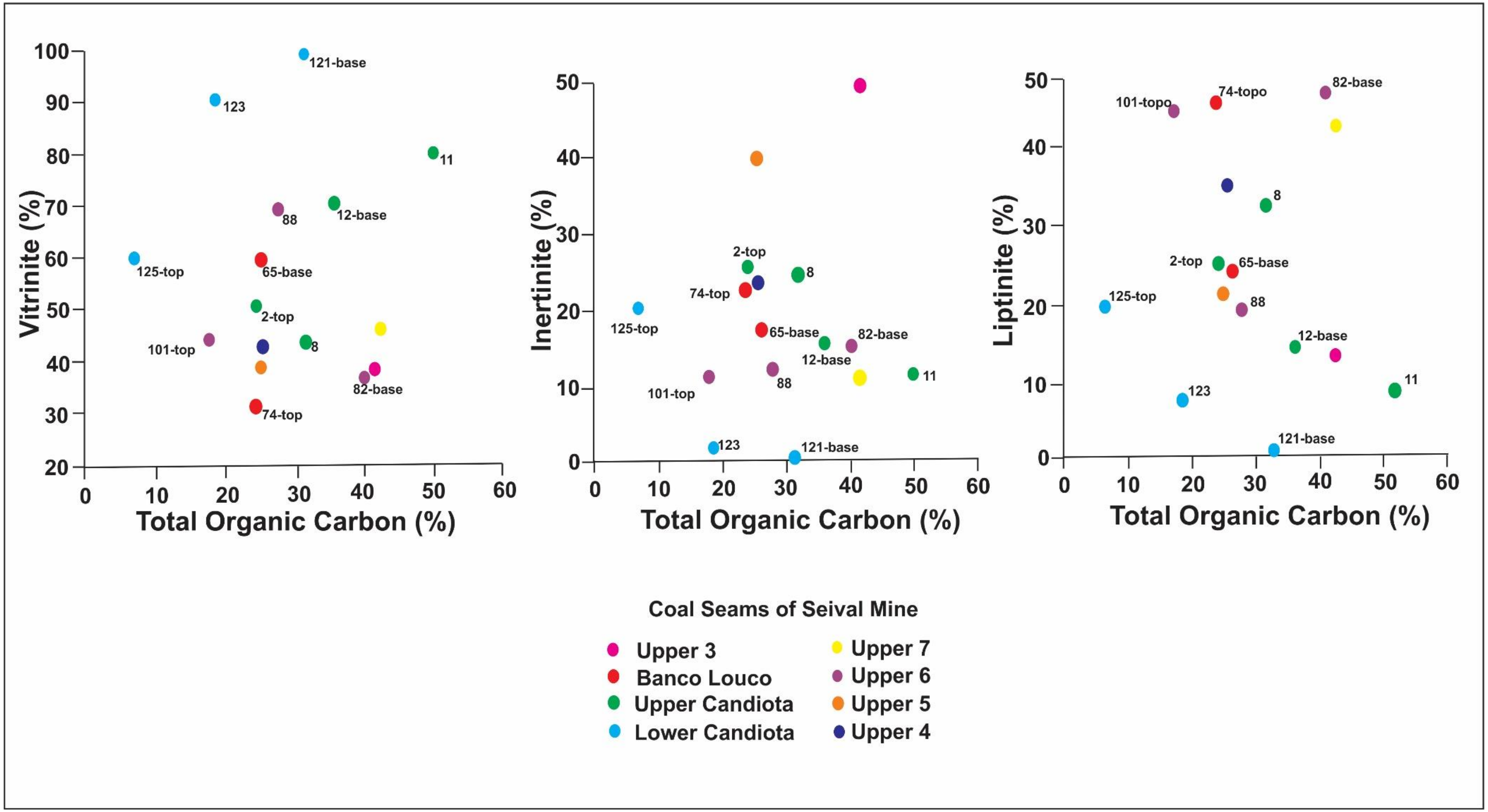

Fig. 10. TOC versus vitrinite, inertinite and liptinite contents in Seival Mine coal seams.

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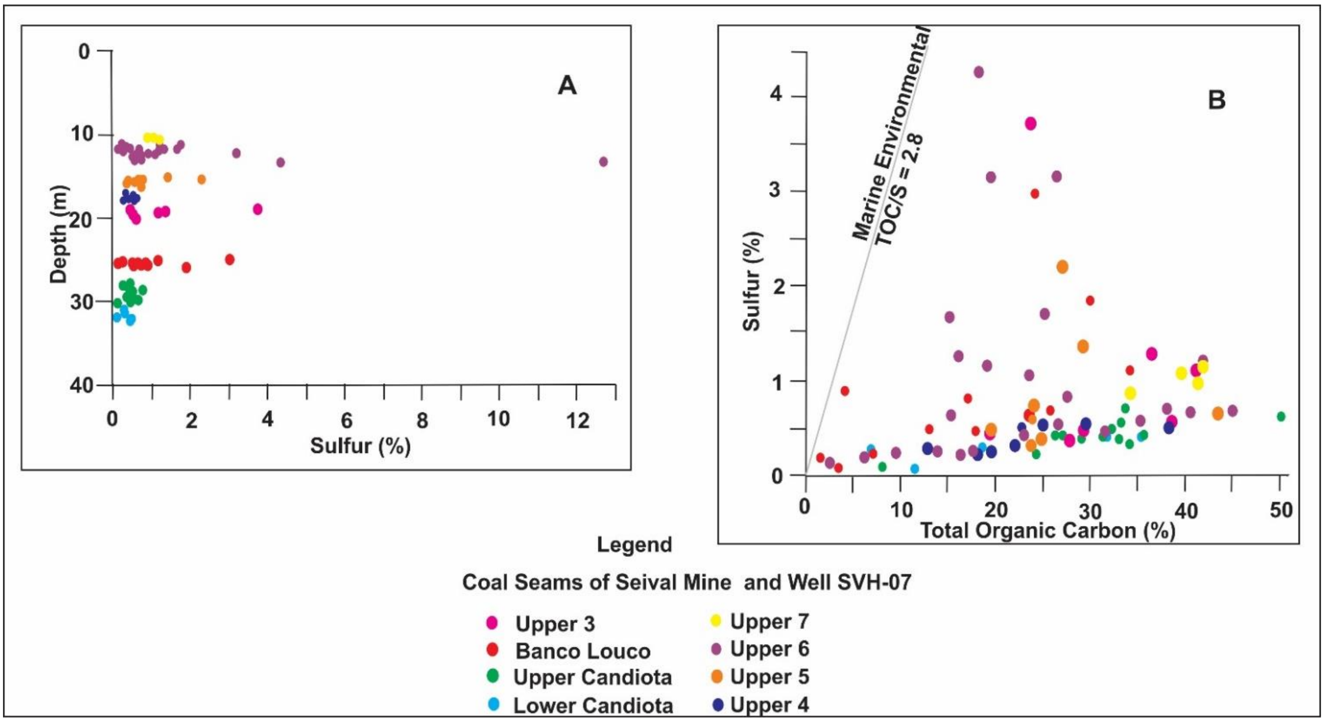

Fig. 11. (A) S versus depth and (B) S versus TOC values for coal seams from the SVH-07 well and Seival Mine.

4.2.3 Pyrolysis: Hydrogen Index

In the relationship between depth and the hydrogen index (HI), it can be observed that, in general, the HI increases towards the top suggesting an increase of hydrogen in this sense (Fig 12).

In the coal Seams, a trend of hydrogen enrichment towards the top can be observed from the LCS. This tendency is associated with the liptinite group increase in the upper Seams (Tab. 3 and Fig. 12).

The HI represents essentially the volatiles amount still present in organic matter. In this way, it has a direct implication in the quality of coals evaluation. As the volatiles content increases, the calorific value of coal decreases, which is one of the most important industrial properties. Thus, the BLS, US6 and mainly US7, which show the highest values of HI, are the coals with the highest volatile organic matter contents (Fig. 12). In this way, these Seams should represent coals with lower relative quality, due to their lower calorific value.

The results of organic petrography and organic geochemistry of the analyzed samples in each Seam of coal (Table 3), evidences that:

- In the LCS, although the contents of liptinite increase to the top, the amounts of inertinite also increase significantly in the same direction, which compensates the HI, resulting in a small increase of this index values towards the top, since the inertinite is a maceral that contains very small amount of hydrogen in its composition (Fig. 9);
- The coal of the UCS presents a slight tendency of decreasing in the HI values to the top; the simultaneous increase of the liptinite and inertinite contents in this direction also explain the slight variation of the HI values (Figure 9).
- In the coal of BLS, the HI values have a general increasing tendency to the top, but a slight decrease of this index values is observed in the upper portion of this Seam. Although a marked enrichment in liptinite occurs at the top of BLS, the HI values also reflect the increase of inertinite and the marked decrease of vitrinite (Fig. 9).
- The coals of US6 and US7 have the highest percentages of liptinite among all Seival Seams. In addition, these Seams have low and relatively constant ratio of inertinite, so that the values of the Hydrogen Index are directly related to the highest content of this maceral group (Fig. 9). Thus, the organic composition of the US6 and US7 are consistent with the context of greater drowning in which these two coals were deposited.

4.3 Integration of the Organic Petrography and Geological Evolution of the Study Area

The set seams of LCS up to US5 presents a tendency to reduction of vitrinite and rise the liptinite and inertinite contents. The US6 and US7 show a different behavior: the former tendency is slightly altered with respect to vitrinite,

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which returns to higher values; the inertinite proportion shows a sharp decrease; and the liptinite content keeps the rising pattern towards the upper coal seams (Table 3).

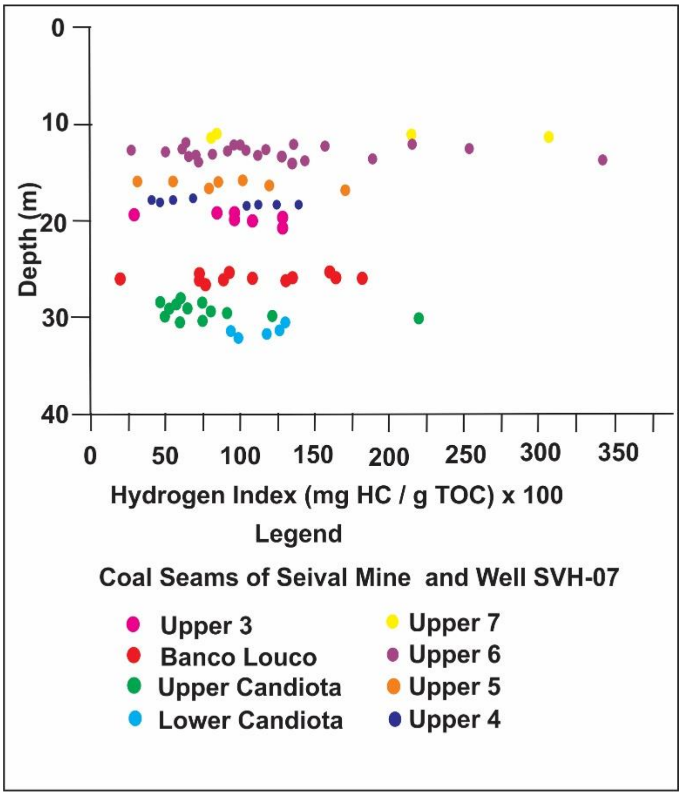

Fig. 12. Values of the Hydrogen Index versus depth, of samples from the SVH-07 well and the Seival Mine.

These data indicate that the evolution of the paralic depositional environment, with vegetation development and formation of peat bogs, in the appropriate places, would be characterized by: a continuous decrease in the contribution of woody plant material, expressed by vitrinite; a lower occurrence of subaerial exposures of the peat bogs in the upper most seams, indicated by the decrease in the proportion of inertinite; and by the increase in the amount of lighter materials in the depositional system, shown by the higher levels of liptinite.

These results obtained in Seival characterize a typically retrogradational system, consistent with the continuous regional drowning of the Grande Candiota area, at the time of the coals deposition. The sulfur distribution (Fig. 11) shows an increase from the BLS Seam. These data suggest the presence of transgressive system and, thus, a greater marine influence in the coals sedimentation of the upper section of the Rio Bonito Formation.

Studies done by Della Favera et al. (1997) indicate that the Seams of coal represent the basis of the parasequences, superimposed by silty-clayey paleosoils, which should mean climatic 5th order regressions, concluding the parasequences.

During the driest cycles, the coals would be covered by soils and the site of peatlands formation should have been situated in a relatively more distal area. This more arid climatic condition is also suggested by the increase of inertinite in relation to that of vitrinite towards the top (up to US5), indicating a greater subaerial exposure suffered by the peat bog which should have allowed the oxidation of the deposited organic matter. During these regressive phases, there should also have been a greater contribution of already oxidized organic material from the continent, which should also have contributed to the enrichment in inertinite.

During stormy events, some incorporation of organic material from plants also should have occurred. Most of the siliciclastic materials present in the coal esams would have been incorporated to the organic material during this peat remobilization (Fig. 13).

5. Conclusion

The TOC data of the Seival coal present average values between 20 and 40%. The seam richest in organic content is the US7 (TOC mean value of 39%) and that with the lowest organic content is the LCS (TOC mean value of 21%).

The most homogeneous coals are the UCS and US7. The average content of inorganic material in Seival coals is quite high, with a value of 35%, being mainly composed of clay-minerals. From these results, the coals can be considered more appropriately as carbonaceous shales. The high amount of inorganic material present in the coals depicts the reworking in the depositional environment, possibly submitted to storm episodes, in which much of the inorganic material would be incorporated into the peat. The reworking occurred in the peat is evidenced by the presence of the hummocky cross stratifications in the coal seams.

The geochemical analyzes show that the total sulfur content in Seival is generally low. The sulfur content is higher in the BLS than in the LCS and UCS, suggesting a greater seawater entrance into the depositional system during the deposition of Banco Louco Seam. The results are consistent with the context of marine transgression at a basin scale in the Grande Candiota region and with the presence of the last barrier island just above the BLS, from which the coals depositional environment can be considered as a shallow continental shelf.

The organic petrography study of the coal seams allowed the identification of macerals of the vitrinite, inertinite and liptinite groups, and clay-minerals, pyrite and carbonates. The macerals present in general a detrital aspect, resultant of the reworking by stormy events. Most of the coals present in their organic composition a predominance of macerals of the vitrinite group, followed by the groups of liptinite and inertinite, and thus can be considered as humic carbons.

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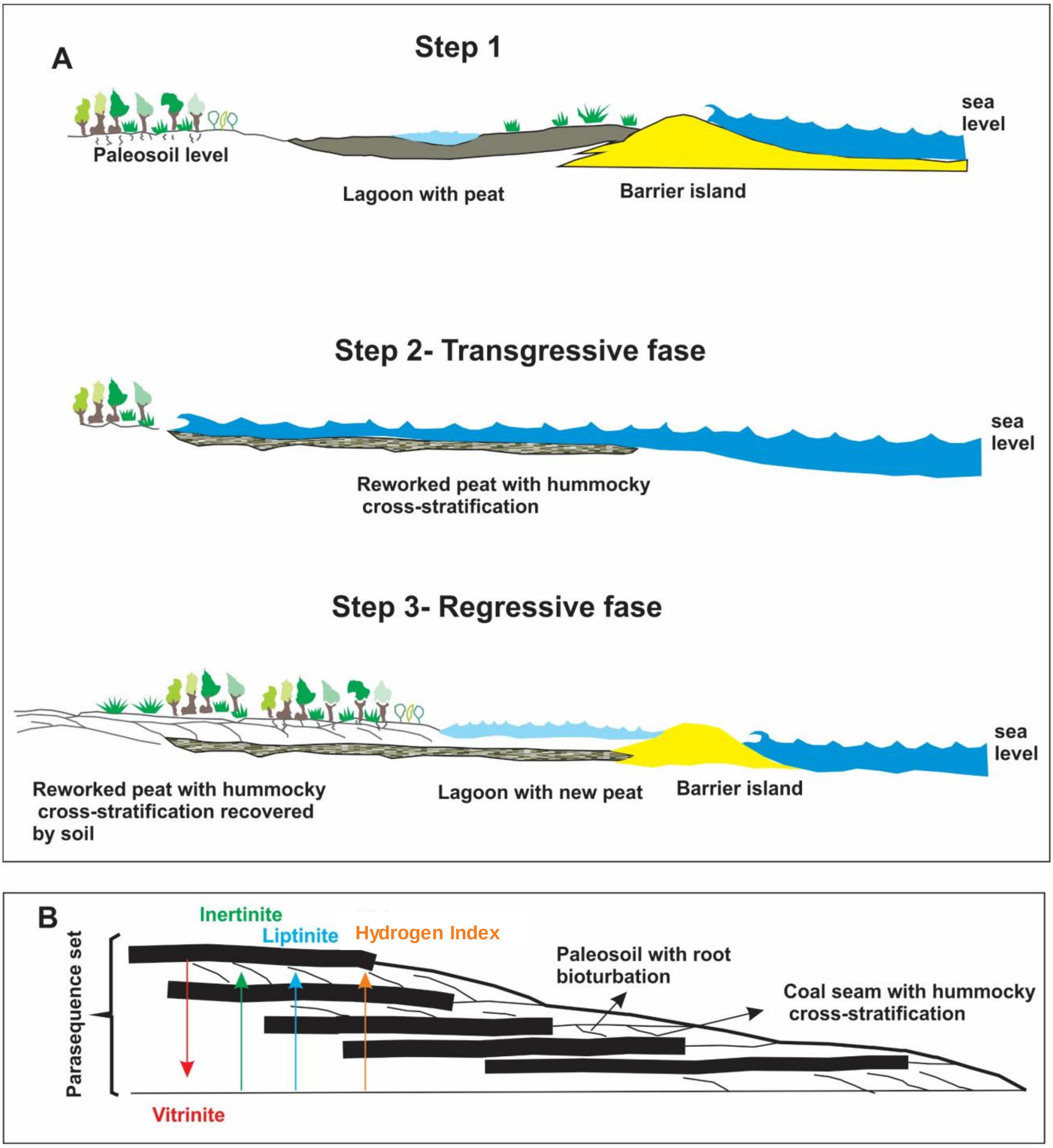

Fig. 13. A: Schematic profile showing the formation of parasequences in the Seival area, in which the coals represent the base and the soil, the top of the parasequence. B: Schematic section of the retrogradational parasequence set within the transgressive system tract, and the general variation trends of the vitrinite, inertinite and liptinite maceral groups and the Hydrogen Index.

The US3 coal is an exception because it presents a predominance of inertinite, which should indicate drier climatic conditions, causing a greater subaerial exposure of the peat and oxidation of the accumulated organic material. In general terms, the pattern found for all coals towards the US7, is a decrease in the mean contents of vitrinite and an increase in the inertinite and liptinite contents. This pattern is typical of a retrogradational system, with a reduction of woody plant matter, an increase in the contribution of lower density organic matter and lower subaerial exposure of peat bogs. These conclusions coincide with those suggested by the total sulfur content.

The comparison between the composition of the Seival coals organic matter and other Gondwanan coals from Australia, South Africa and Brazil shows that there is a considerable difference. In Seival, the contents of inertinite

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are lower and of liptinite much higher. The comparison between the organic compositions of the Seival coals and those of the Candiota Coalfield, for the LCS, UCS and BLS, reveals a similarity of the predominance of vitrinite (except in the BLS) and high inorganic content. The liptinite contents in Seival are comparatively higher, probably due to the counting of the macerals carried out with fluorescence in this work, which caused a considerable increase in the relative content of this maceral group.

The values of the Hydrogen Index of the coal seams present in general an increase trend towards the top, accompanying the liptinite contents. The US6 and especially the US7 are the richest in hydrogen and, therefore, have the highest proportion of volatiles, representing the seams with lower calorific value.

The base of each parasequence is represented by the coal seams with hummocky structures.

Vitrinite data show that the coals of Seival have low degree of carbonification. The mean reflectance values of vitrinite allow ranking these coals from peat to sub-bituminous B, although it is not advisable to use a single parameter for coals classification.

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