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Chemistry

Chemical evaluation of carbonized logs from Araucariaceae species: characterization of materials associated to multivariate analysis for environmental inferences

Avaliação química de lenhos carbonizados de espécies de Araucariaceae: caracterização de materiais associados à análise multivariada para inferências ambientais

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ABSTRACT

The main objective of this study was to develop a methodology to evaluate, by physical and chemical methods, artificially charred logs from three species of Araucariaceae, and compare them fossil charcoal collected in the Faxinal and Belvedere outcrops for possible paleoenvironmental inferences. The species studied were *Araucaria angustifolia, Araucaria bidwillii* and *Araucaria columnaris.* For fossil charcoal analyses we used samples from the Mina do Faxinal and samples from the Curva do Belvedere Outcrop. The carbonization process from species of Araucariaceae were Thermogravimetric Analysis (TGA) associated to the techniques of Fourier Transform Infrared Spectroscopy (FTIR) and multivariate analysis. The Principal Component Analysis (PCA) showed that it is possible to describe 90,9% of the data, grouping the samples into two main clusters. Both samples of fossil charcoal from Belvedere and Faxinal showed charring characteristics above 400ºC. Results showed that technical associations, such as TGA, FTIR and multivariate analysis may help to characterize the natural carbonization process and contribute to important paleoenvironmental and archaeological information and inferences.

Keywords: Fossil charcoal Belvedere; Fossil charcoal Faxinal; Principal component analysis; Thermogravimetric analysis; Mid-infrared

RESUMO

O principal objetivo deste estudo foi desenvolver uma metodologia para avaliar, por métodos físicos e químicos, lenhos carbonizados artificialmente de três espécies de Araucariaceae, e compará-los com amostras de carvão fóssil de Belvedere e Faxinal para possíveis inferências paleoambientais. As espécies estudadas foram *Araucaria angustifolia*, *Araucaria bidwillii* e *Araucaria columnaris*. Para as análises de carvão fóssil foram utilizadas amostras da Mina do Faxinal e amostras do Afloramento da Curva do Belvedere. O processo de carbonização das espécies de Araucariaceae foram Análise Termogravimétrica (TGA) associada às técnicas de Espectroscopia de Infravermelho por Transformada de Fourier (FTIR) e análise multivariada. A Análise de Componentes Principais (ACP) mostrou que é possível descrever 90,9% dos dados, agrupando as amostras em dois agrupamentos principais. Ambas as amostras de carvão fóssil de Belvedere e Faxinal apresentaram características de carbonização acima de 400ºC. Os resultados mostraram que associações técnicas, como TGA, FTIR e análise multivariada podem ajudar a caracterizar o processo de carbonização natural e contribuir para importantes informações e inferências paleoambientais e arqueológicas.

Palavras-chave: Carvão fóssil Belvedere; Carvão fóssil Faxinal; Análise de componentes principais; Análise termogravimétrica; Infravermelho médio

1 INTRODUCTION

One of the greatest challenges of human beings, discussed in different fields of science, is the modification in natural environments (CHAMLEY, 2003). Explaining the modifications through which the planet has already passed is one of the ways to establish future environmental scenarios. This can be done by studying past events and focusing on its causes and consequences to understand the contemporary scenario (JASPER; UHL, 2011).

Plants are sensitive organisms to climate change (PIRES *et al.*, 2011), as well as extraordinary environmental markers. They help to understand structural changes related to environmental events that have affected and continue to affect (GASTALDO; DIMICHELE; PFEFFERKORN, 1996).

Conifer trees, specifically species from the Araucariaceae family, share adaptation characteristics to environmental conditions, making them valuable to geologists and paleobotanists (DUTRA; STRANZ, 2003).

Scott and Stea (2002) believe that fire, being an important agent in the dynamics of a large number of ecosystems, must have acted in a similar way throughout the history of the Earth. In this sense, the analysis of vegetation fires is important to evaluate the relation among climate, weather, fuel and people, since they play a major source of interaction within modern ecosystems (BOWMAN *et al*., 2009; FLANNIGAN *et al*., 2009).

The occurrence of paleo fires, as evidenced by macroscopic charcoal analysis in many geologic sites, are stated in several studies, such as: Falcon-Lang (2000); Uhl *et al*., (2004); Uhl *et al*. (2008); Uhl *et al*. (2010); Scott (2000); Scott (2010); Jasper *et al*. (2008); Manfroi *et al*. (2015); Jasper *et al*. (2016); Dos Santos *et al*. (2016); El Atfy *et al*. (2016). These studies show the anatomy of the charcoal and infer on possible paleoenvironmental reconstructions. They may define and guide conservation actions and recovery of current environments, contributing as a tool to understand environmental issues of contemporaneity (SCOTT, 2000; UHL; KERP, 2003; UHL *et al*., 2004).

Some studies associate the chemical characterization of materials, using infrared and thermogravimetric analysis techniques, coupled with multivariate analysis. Research showed satisfactory results using physical and chemical techniques, such as the studies by O'Keefe *et al*. (2013), Zodrow *et al*. (2012), D'Angelo *et al*. (2011), D'Angelo *et al*. (2012) e Ascough *et al*. (2010). From physical and chemical analyses, they developed important contributions on (paleo)environmental and archaeological issues. Even so, few studies describe the chemical characteristics of macroscopic charcoal and how it varies according to its own formation process.

Fourier transform infrared spectroscopy (FTIR) analysis is a rapid and non-destructive technique of qualitative and quantitative determination of biomass components in the mid-infrared region (Tucker *et al*., 2001). This technique permits to evaluate the changes that occur in the log components (MOORE; OWEN, 2001; CHANG; CHANG, 2001; COLOM *et al*., 2003; SCHWANNINGER *et al*., 2004).

However, due to the acquisition of a large amount of spectral data by FTIR, it is necessary to use chemometric methods. These allow the construction of models based on the relation between the spectral characteristics and chemical components present in the analyses. Chen *et al*., (2010) showed a successful application of chemometric analysis (for example, Principal Component Analysis (PCA) and Partial Least Squares (PLS) on determining biomass components.

In this sense, the present study aims to contribute to the recognition of paleoenvironmental conditions, using physical and chemical methodology to identify artificial charcoal of three species of Araucariaceae and compare them to fossil charcoal collected in the Faxinal and Belvedere outcrops. The study was carried out by infrared and thermogravimetric analysis, and associated to multivariate analysis techniques to obtain chemical signatures of different types of artificial charcoal and fossil charcoal.

1.1 Geological and Paleontological Context

Covering ~1,500,000 km2 of south-eastern and southern Brazil, the Paraná Basin is an intracratonic basin that comprises six sedimentary supersequences Milani *et al*. (2007). From the base to top: 1) Rio Ivaí (Ordovician–Silurian); 2) Paraná (Devonian); 3) Gondwana I (Carboniferous–Lower Triassic); 4) Gondwana II (Upper Triassic), 5) Gondwana III (Jurassic–Lower Cretaceous) and; 6) Bauru (Upper Cretaceous). The Late Paleozoic strata are related to the Gondwana I Supersequence and were deposited under a second-order transgressive-regressive cycle discontinuously preserved in the basin (HOLZ *et al*., 2010).

In summarizing the lithostratigraphy of Gondwana I Supersequence, Milani *et al*. (2007) and Holz *et al*. (2010) reinforced that the package is divided into three groups, as also suggested by Schneider *et al*. (1974). At the base, the Itararé Group exposes diamictites, sandstones, siltstones and mudstones deposited by periglacial systems related to “multi-lobe glaciers” occurring in the area at the end of the Late Paleozoic Ice Age (LPIA). The middle Guatá Group, where coal-bearing strata are common, comprises successions representing fluvio-paralic, lagoon back-barrier and maximum flooding associations from a transgressive pulse. The uppermost Passa Dois Group shows a regressive process and continental trends are preserved.

2 MATERIAL AND METHODS

By evaluating the physical and chemical changes that occur during the carbonization process of logs *in natura* at different temperatures, as well as its influence on significant chemical characteristics, we intend to use the applied variables as a basis for possible (paleo)environmental inferences involved in natural processes.

2.1 Sample identification

Log fragments of three Araucariaceae species were collected in different localities of Rio Grande do Sul, Brazil. They were extracted from specimens that fell down for various reasons in areas of the municipalities of São José dos Ausentes (28º47'06,56" S e 49º58'50,85" L – *Araucaria angustifolia*), Novos Cabrais (29º47'3,48" S e 52º58'14,59" L – *Araucaria bidwillii*) and Colinas (29º32'28,84" S e 51º50'28,35" L – *Araucaria columnaris*).

The samples were obtained in the form of discs at a height of 1.50 m, measuring 8 cm of thickness and 18 to 35 cm of diameter.

For fossil charcoal analyses, samples stored in the paleobotanical collection of the Science Museum of UNIVATES (*Museu de Ciências da Univates)* were used. Samples from *Mina do Faxinal* were previously studied using standard methods for charcoal analyses, by Jasper and Uhl (2011). Samples from the Curva do Belvedere Outcrop were studied by multiple methods by Kubik *et al*. (2020).

The samples for the three species evaluated were identified as artificial charcoal, and the (paleo)environmental samples were identified as fossil charcoal. All analyzes were performed at the Research and Food Production Technology Center (CTPPA) - Science and Technology Park (Tecnovates) /UNIVATES.

2.2 Carbonization process by thermogravimetric analysis

The thermogravimetric analyzer Perkin Elmer TGA-4000 model was used for the carbonization process. Thermogravimetric analyses were performed under nitrogen gas atmosphere (heating in the absence or scarcity of oxygen) at a constant flow rate of 20 mL min^{-1} using 20 mg (± 2 mg) of samples for each charring temperature, at room temperature - approximately 25ºC. mention that charcoal is generated by pyrolysis. Charring temperatures of logs *in natura* were 50°C in 50°C, in a range of 50°C to 995°C. Analyzes were performed on 3 replicates for each charring temperature. The heating ramp was 25°C min^{-1} until obtaining the desired temperature.

The log fragments were dry and did not receive thermal treatment prior to chemical and physical analyses. Similarly, the samples of fossil charcoal from Belvedere and from Faxinal were analyzed as withdrawn from the outcrops.

2.3 Obtaining infrared spectra

Spectra were obtained on the SHIMADZU spectrophotometer, IR Affinity-1 model. Preceding spectra readings, samples of artificially charred logs were prepared with a KBr tablet (Potassium Bromide). Subsequent to tablet preparing, spectra were obtained in the infrared spectrophotometer, in a range between 1900 and 650 cm^{-1}, resolution of 4 cm^{-1} and 64 scans. Spectra for each sample were obtained in triplicate.

2.4 Multivariate data analysis

Obtained spectra were processed through computational tools of multivariate analysis, using the Principal Component Analysis (PCA) with the computer program Chemostat@. Prior to multivariate analysis, spectra were smoothed using the method *Savitzky-Golay* (with derivative order: 0; polynomial order: 1 and 5 for number of points per window), normalized in the range between 0 and 1, applied "*mean center*" and first derivative with 5-point window.

2.5 Statistical analyses

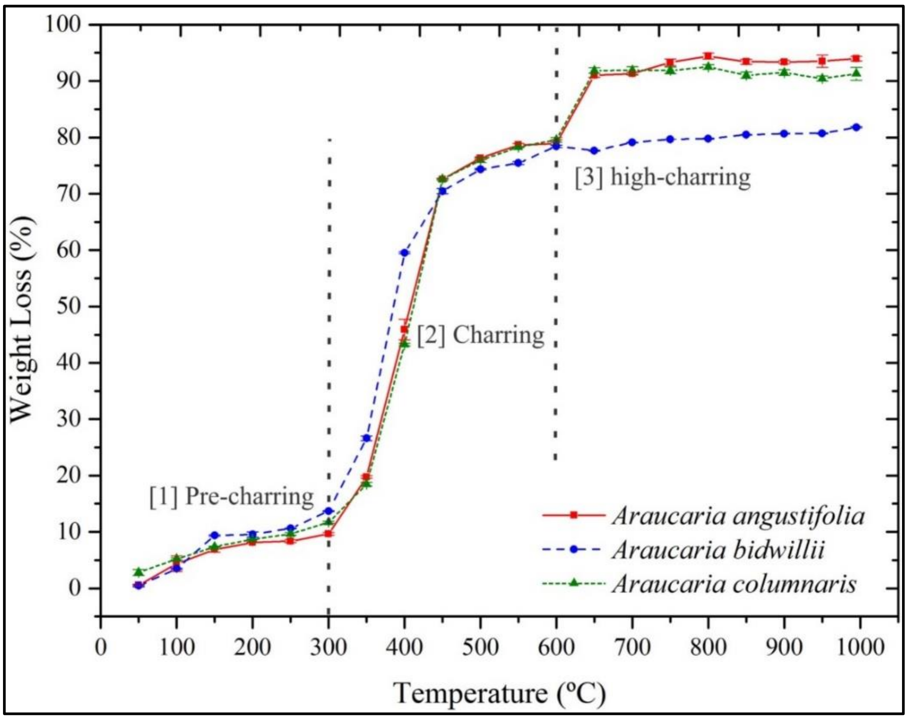
Data referent weight loss from the carbonization process by TGA were subjected to analysis of variance factor (one-way ANOVA) using Prism@ software and, in case of significant differences, the treatments were compared with each other using the Tukey test for significance levels of 5% ($p < 0.05$).

3 RESULTS

3.1 Characterization of log fragments by thermogravimetric analysis

Figure 1 displays the amounts of sample weight loss (%) of the three analyzed species, evaluated by TGA with temperature range from 50 °C to 995 °C. The information " Zones 1, 2 and 3 highlighted" were determined from the similar thermal events for the 3 samples evaluated.

Figure 1 - Dynamic thermal degradation curves of *Araucaria angustifolia, Araucaria bidwillii* and *Araucaria columnaris* at the heating rate of 50 ºC/min



Source: Authors' (2021)

It is possible to observe that for the three species evaluated by TGA, the thermodegradation of the logs occurs in similar thermal events until reaching the temperature of 600ºC. From 600ºC, thermal stability occurs for the species of *Araucaria bidwillii.* However, for the species *Araucaria angustifolia* and *Araucaria columnaris*, thermal stability occurs only from 650ºC.

Furthermore, for the three species evaluated by TGA, the thermodegradation of the logs occurs in similar thermal events (Figure 1, pre-charring) until reaching a temperature of 600ºC. From 600ºC (Figure 1, high-charring) thermal stability occurs for the species of *Araucaria bidwillii*. However, for the species *Araucaria angustifolia* and *Araucaria columnaris,* the thermal stability occurs only from 650ºC.

During the thermodegradation process at 995°C, the three species showed average weight loss of 93.98%, 81.80%, and 91.28% for *Araucaria angustifolia, Araucaria bidwillii* and *Araucaria columnaris*, respectively, with statistically significant differences ($p<0.05$) among them.

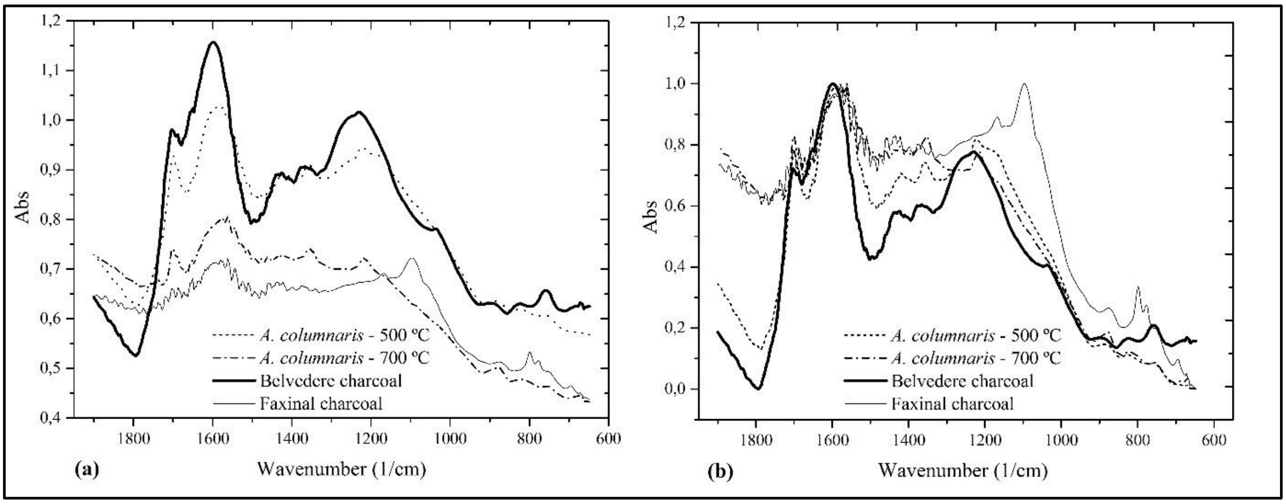
In the initial range, from 300ºC to 600ºC (Figure 1, charring), the logs showed the greatest mass loss. The average results for mass losses were 69.24% for *Araucaria angustifolia*, 64.71% for *Araucaria bidwillii* and 67.87% for *Araucaria columnaris*, with no significant differences among them.

In the range of 600ºC to 995ºC (Figure 1, high-charring) the average results of mass loss were 15.08% for *Araucaria angustifolia*, 3.37% for *Araucaria bidwillii* and 11.72 % for *Araucaria columnaris*. After being submitted to the maximum value of thermal degradation (995ºC), the residual mass for the species *Araucaria angustifolia, Araucaria bidwillii* and *Araucaria columnaris* were 6.02%, 18.20%, and 8.72%, respectively.

3.2 Representation of functional groups by FTIR

The temperatures with the most significant alterations in spectra by temperature range were chosen, in addition to the fossil charcoal samples of both, Belvedere and Faxinal. In the spectral range of 1900 and 650 cm^{-1}, 4 spectra are shown in Figure 2a and Figure 2b.

Figure 2 - Spectral representation of logs charred artificially at temperatures of 500 ° C and 700°C for the *Araucaria columnaris* species and the samples of charcoals from Belvedere and from Faxinal. They were tested by thermogravimetric analysis for the spectral range between 650 and 900 cm^{-1}: (a) original data and (b) after baseline normalization



Source: Authors' (2021)

Figure 2a shows two different temperatures, 500°C and 700°C, representing *A. columnaris* and the spectral samples of the fossil charcoals from Belvedere and from Faxinal. When assessing the set of spectra by species, after baseline normalization (Figure 2b), species with a characteristic spectral similarity can be observed by temperature range.

Jung *et al*. (2018) describes that the FTIR spectroscopy offers a simple, efficient and non-destructive method for identifying and distinguishing materials analyzed. In this study, the representation of charred wood at 500°C can be seen in the spectra of

A. columnaris in Figure 2b. The representative peaks in this temperature range are: 1701 cm-1 and 1688 cm-1 belonging to the vC = O functional group, 1591 cm-1, 1580 cm-1, 1562 cm-1, 1545 cm-1 and 1512 cm-1 assigned to the absorption of aromatic compounds (vC = C, vC = N, vC = O,), 1474 cm-1 related to δCH2 absorption, 1458 cm-1 and 1420 cm-1 assigned to the δCH3 vibrational group and 1221cm-1, assigned to the γC-H group (BARBOSA, 2007).

The representative peaks at 700°C for the charred wood of the species A. columnaris are: 1871 cm-1, 1846 cm-1, 1775 cm-1, 1751 cm-1, 1751 cm-1, 1738 cm-1, 1701 cm-1, 1688 cm-1, 1545 cm-1, 1524 cm-1, and 1512 cm-1 belonging to the functional group (vC=C, vC=N, vC=O,), 1493 cm-1, 1462 cm-1, 1437 cm-1 and 1422 cm-1 assigned to the vibrational group δCH3 and δCH3 , 1354 cm-1 and 1215 cm-1 listed to the functional group assigned to the group vS=O and vC=O (BARBOSA, 2007).

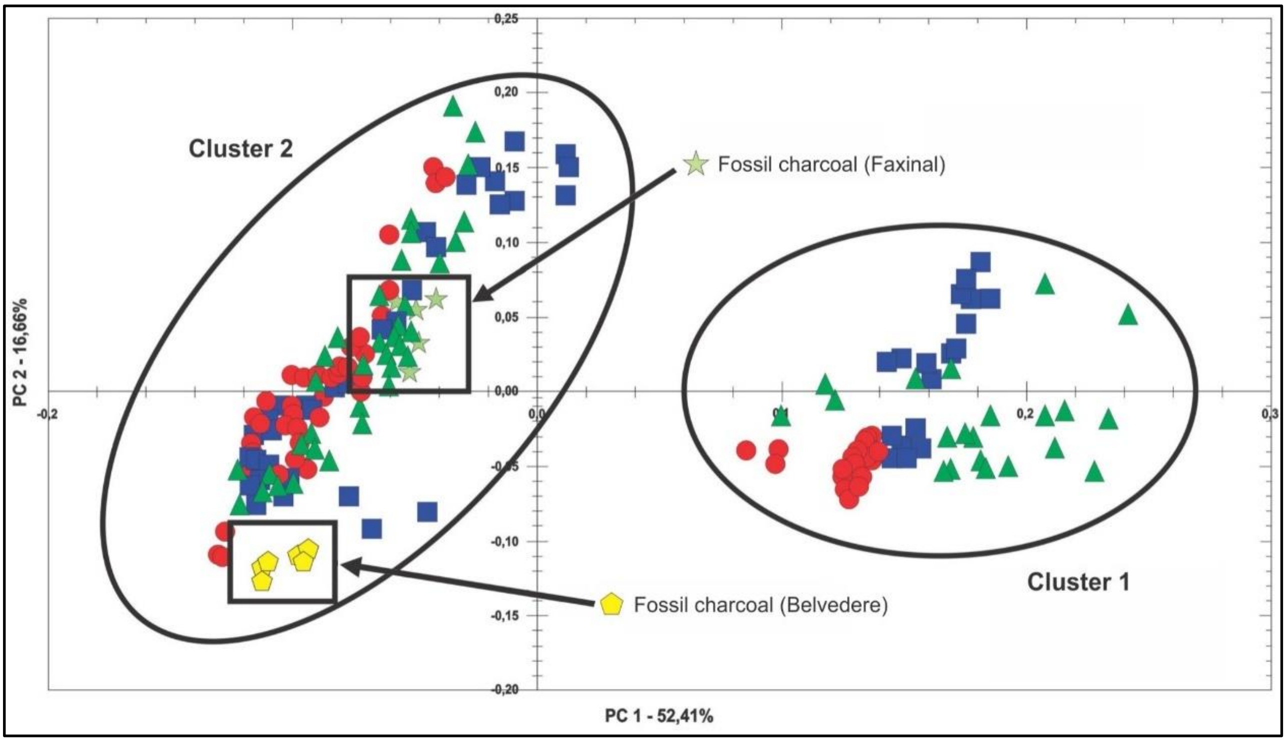
Spectra obtained for samples charred at 500° C have a spectral similarity with the fossil charcoal of Belvedere. Similarly, the spectra from logs charred at 700ºC have spectral similarities to the spectral samples of the fossil charcoal from Faxinal. Main peaks detailing present in the spectra of Figure 2b can be seen in Table 1S (additional material).

Even with a wide-ranging and full discussion, it is not possible to characterize the exact nature of the log components tested using only the FTIR technique. In order to obtain more information, the multivariate analysis was used, considering the amount of spectral information between 1900 and 650 cm^{-1}.

3.3 Characterization by principal component analysis

A PCA was used to focus on the similarity of data obtained from the FTIR analyses. The PCA showed that with six main components it is possible to describe 90.09% of the data. Thus, the graph of scores (Figure 3) contains most of the explained variance (52.41%), grouping the samples into two main groups.

Figure 3 - Representation of PC1 *versus* PC2 scores for log samples of artificial charcoal by TGA for *A. angustifolia* (red circle), *A. bidwillii* (green triangle) and *A. columnaris* (blue square), and for fossil charcoal samples from Belvedere (yellow pentagon) and fossil charcoal from Faxinal (light green star), highlighted in the picture.

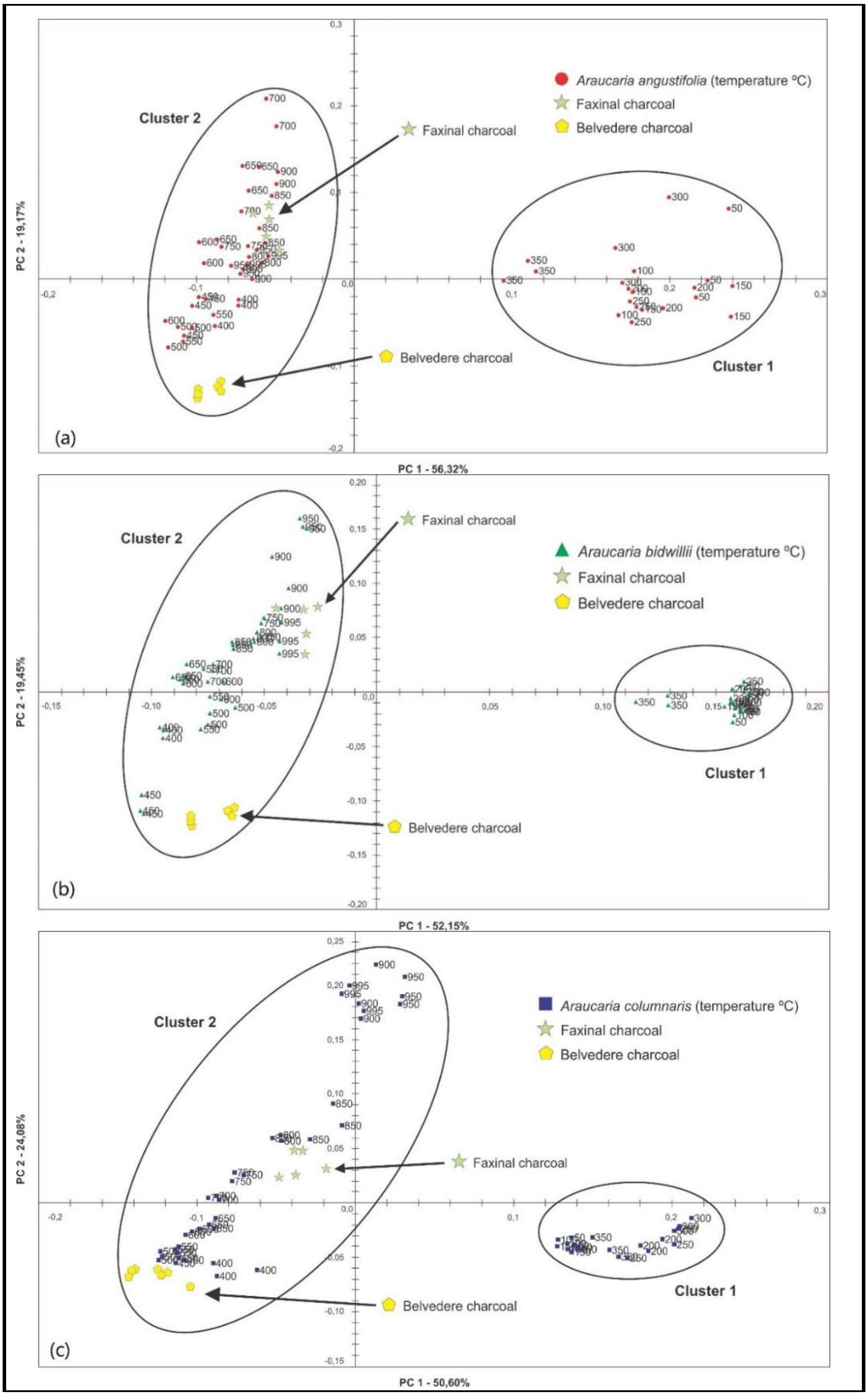


Source: Authors' (2021)

The analysis of the graphic representation of the scores (Figure 3) shows the samples separated into different groupings: PC1 separates samples with charring temperatures below 350°C (group 1), and positive numbers along the vector, from samples whose charring was performed above 400°C (group 2), and negative numbers along this PC (Main Component). The fossil charcoal samples from Belvedere and Faxinal are located in the set of samples charred above 400°C (group 2).

By individually evaluating the artificial charcoal samples from the species of *A. angustifolia, A. bidwillii* and *A. columnaris*, and with the fossil charcoal samples from Belvedere and Faxinal (Figure 4), two main groups can be observed.

Figure 4 - Representation of scores for PC1 *versus* PC2 for log samples of artificial charcoal by TGA for (a) *A. angustifolia, (b) A. bidwillii* and *(c) A. columnaris* and for the fossil charcoal samples from Belvedere and from Faxinal, highlighted in the figure



Source: Authors' (2021)

Analyses of the graphic representation of the scores of Figure 4 show the samples separated into different groupings: PC1 separates samples with charring temperatures below 350ºC (group 1) and positive values along the vector, and from samples whose charring was performed above 400ºC (group 2), and negative numbers along this PC. The fossil charcoal samples from Belvedere and Faxinal are located in the set of samples charred above 400°C (group 2).

The formation of clusters is also evidence of the proximity of the fossil charcoal samples from Belvedere with the lowest charring temperatures (400ºC to 550ºC). The samples from the fossil charcoal of Faxinal, on the other hand, are close to the highest charring temperatures (between 650ºC and 995ºC).

The formation observed in the analyses of principal components (PCs) in Figure 3 and Figure 4 is in line with what was observed in Figure 1, which depict significant physical changes concomitantly with the chemical changes of the logs.

4 DISCUSSION

Braadbart and Poole (2008) point out that differences in log morphology may have an influence on physical and chemical changes. Scott and Glasspool (2007) state that there is a relation between natural fires and (paleo)environmental factors and that assessing them can represent important interpretation tools of different periods in the planet's history.

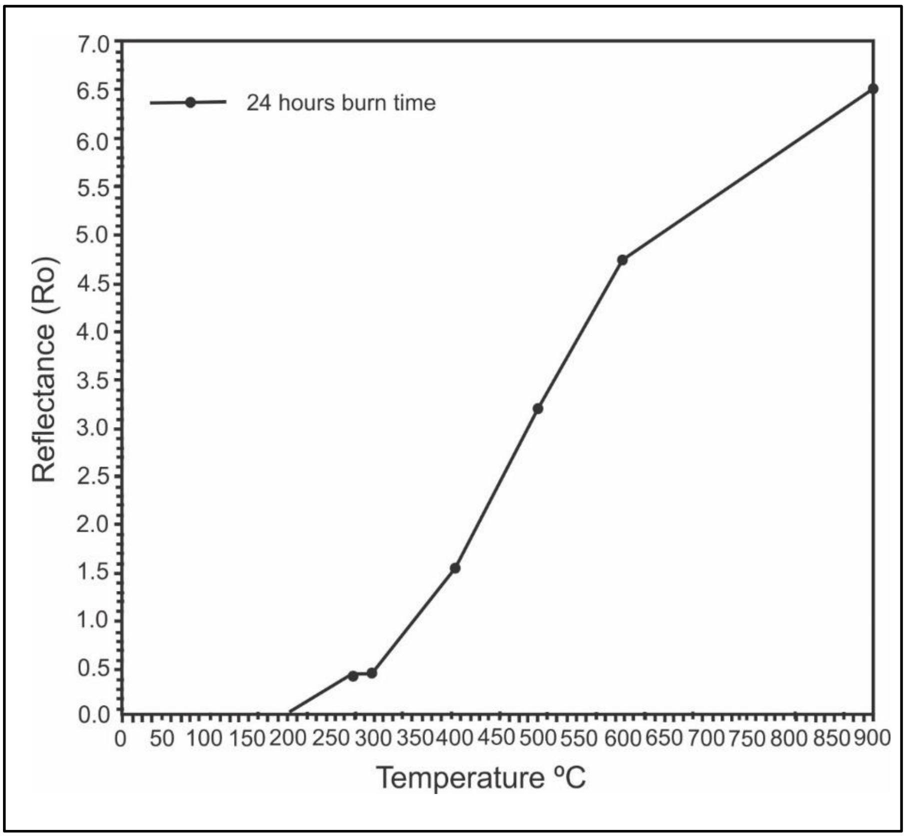
Scott and Glasspool (2007) mention that charcoal is generated by pyrolysis (heating in the absence or scarcity of oxygen), and, therefore, not being an oxidation product. For the combustion of materials to occur, the action of three basic elements is essential: sufficient concentration of atmospheric oxygen (oxidizing), occurrence of ignition sources (energy) and availability of combustible material (SCOTT, 2010).

Ignition of fire on vegetation is directly related to atmospheric oxygen levels (WATSON; LOVELOCK; MARGULIS, 1978) and, according to Bowman *et al*. (2009) and Scott and Glasspool (2007), charring only occurs when oxygen concentration is greater than 13%.

The results of Diessel (2010) on the analysis of the distribution of coal macerals generated in an interval of almost 70 million years (from the Pennsylvanian age to the end of the Permian age), show a universal pattern of increase and decrease in the percentages of inertinite. This pattern, observed in Paleozoic coals on different continents, suggests that the formation of inertinite, as a consequence of fire prevention, responded to global influences far beyond to just responding to local environmental influences and their specific flora, with emphasis on elevation of atmospheric oxygen concentration (pO_2) among the analyzed variables.

Based on this information, Hudspith *et al*. (2012) mention that the amount of inertinite in coal can be used to interpret the history of paleofires at a local scale. Studies performed by McParland *et al*. (2009) related a positive correlation between the cell wall reflectance value (inertinite) and the charcoal formation temperature, allowing the correlation of the charcoal charring temperature. Guo and Bustin (1998) and Scott and Glasspool (2007) presented this study in an experimental way, as shown in Figure 5.

Figure 5 - Relation between charring temperature and reflectance. Results obtained in a controlled experiment of the relations between reflectance values (in oil) and temperature in the formation of charcoal in a 24-hour charring period



Source: Scott (2010, p. 18)

According to Figure 5, coals with reflectance below 1% Ro may have been formed at temperatures between 300ºC and 400ºC. On the other hand, charcoal with reflectance values greater than 5% Ro require high firing temperatures or prolonged exposure to heat. Temperatures of many types of fires are present in this range, concluding that the coals produced by lower temperatures will have lower reflectance values in the semifusinite range. So, the reflectance of the fusinite is acquired before the carbonization process, regardless of age, lithology or diagenesis/geological environment (SCOTT, 1989).

Studies performed by Schmidt *et al*. (2015) used the relation between charring temperature and reflectance in blocks polished by oil from large-scale charred log scraps, occurring at the base of a layer of volcanic ash interspersed with a layer of coal from Mina do Faxinal. The standards established by Jones *et al*. (1991), (Figure 5) were followed to determine charcoal charring patterns and intensity. According to this methodology, charring temperatures between 330º C and 460 ºC were used. Characteristics evidenced in SEM indicated that the cell walls were completely homogenized, signalizing a charring temperature above 325ºC.

The organic petrographic analyzes of the charred stem scraps showed the presence of fusinite in the superficial parts of the log, as well as a transition to semi-fusinite and, finally, to vitrinite, in the internal portions of the log. These evidences reflect charring processes in the external portion of the log, while the internal parts not affected by the charring, later evolved to vitrinite, characterizing what Jones *et al*. (1993) call “transitional fossils”.

Schmidt *et al*. (2015), mention that small and thin charcoal scraps from the upper limit of the volcanic ash layer displayed the same results regarding reflectance values, being the entire material preserved, as inertinite. These scraps showed a complete homogenization of cell walls in SEM.

Still Schmidt *et al*. (2015), the set of evidences show that the fires that occurred at the base of the volcanic ash level, where a large association of charred stems is observed, were only on the surface. So, they affected the logs when they were still in a living position. It was a low temperature event, and the transport of charcoal was practically non-existent on that horizon. On the other hand, the recurrence of small charcoal scraps at the upper boundary of the volcanic ash bed with the coal layer, indicates recurrent fires in the lowlands surrounding the peat bog, and subsequent transport of these materials to the areas near to the peat bog.

Bica (2014) infers a probable charcoal charring temperature in the Belvedere outcrop, which is also found in the Rio Bonito Formation, even though in different faciology, with the exclusive use of Jones and Chaloner's (1991) criteria. Jones and Chaloner established that different levels of homogenized cell walls in fossil charcoal could directly reflect the charring temperature the logs were subjected to at the time of combustion. In the analyzed material, all samples of fossil charcoal had cell walls completely homogenized in SEM. Consequently, Bica (2014) suggested a charring temperature between 340ºC and 600ºC.

Such assumptions were raised in the article by Jones and Chaloner (1991), who use Figure 5 for inferences on charring temperatures. However, Scott and Glasspool (2007) and Glasspool and Scott (2013), based on laboratory experiments in low oxygen ingress systems, argue that phases, such as cell wall cracking, may not occur, even at constant temperatures of 900°C for 24 hours.

In this study, the fossil charcoal samples from Belvedere and from Faxinal showed charring characteristics above 400ºC. This statement is in agreement with studies carried out by Schmidt *et al*. (2015) and Bica (2014). Furthermore, it was possible to observe that the fossil charcoal samples from Belvedere are located in the temperature cluster above 400ºC, tending to lower temperatures in the PCA. The samples of the fossil charcoal from Faxinal are also located in the cluster of temperatures above 400ºC, but tend to higher temperatures in the PCA, showing a different behavior from fossil charcoal samples of Belvedere.

Kubik *et al*. (2020) presented studies of fossil charcoal samples collected from the outcrops of Quitéria and Belvedere curve, both from the same origin of sedimentary deposition in the Paraná Basin, and related to the Permian Period. The result of the study, which was carried out by chemical characterization of biomaterials, inferred on analyzed samples regarding the environment of the deposition, origin of the organic matter and possible type of forest fire. The authors point out that, in addition to the samples presenting a mix in the organic composition, the concentrations of Polycyclic Aromatic Hydrocarbons (PAH) were high, indicating a charring temperature between 400°C and 500°C. These numbers were an estimation based on inertinite reflectance, which showed slightly lower values, ranging between 375°C and 440°C.

In this study, the results indicated that the charring temperatures without absence of oxygen, by TGA, reached higher temperatures than those presented by

Schmidt *et al*. (2015). Nevertheless, the parameters of pressure, temperature and the absence or restricted presence of oxygen in the thermodegradation process must be taken into account. So, considering that the methodology was developed in restricted absence of oxygen, if the amount of oxygen present in the (paleo)environment is greater than this study, the carbonization temperature of the log can be anticipated.

5 CONCLUSION

Based on the data here presented and on the discussion points, it is possible to come to the following conclusions:

1) TGA is a simple tool which enables the analysis and comprehension of problems involving physical and chemical changes and its mechanisms, depending on the temperature and weight.

2) Weight loss increases with the increasing of carbonization temperature.

3) FTIR is a valuable tool to characterize and identify substances due to its good sensitivity and accuracy, as well as low analysis cost, easy operation and minimum quantity of samples.

4) PCA is a supervised method that provides good indicators of chemical similarity among analyzed samples.

5) FTIR, associated to multivariate analysis, is a useful tool because it allows the analysis of carbonized logs based on the search for similarities or sample clustering, as from the similarity between the tested species and their respective temperature ranges.

6) In this study, the samples of the fossil charcoal from Belvedere and the fossil charcoal from Faxinal, showed charring characteristics above 400ºC for the samples of artificial charcoal logs in TGA.

7) It is worth highlighting that the fossil charcoal from Belvedere had lower charring temperatures than the fossil charcoal from Faxinal. However, the parameters of pressure, temperature and the absence or restricted presence of oxygen in the thermodegradation process must be taken into account.

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REFERENCES

ALZATE, S.B.A.; FILHO TOMAZELLO, M.; PIEDADE, S.M.S. Variação longitudinal da densidade básica da madeira de clones de *Eucalyptus grandis* Hill ex Maiden, *E. saligna* Sm. e *E. grandis x urophylla.* **Scientia Forestalis**, n. 68, p. 87-95, 2005.

ASCOUGH, P.L.; BIRD, M.I.; SCOTT, A.C.; COLLINSON, M.E.; WEINER, S.; COHEN-OFRI, I.; SNAPE, C.E.; LE MANQUAIS, K. Charcoal reflectance: implications for structural characterization. **Journal of Archaeological Science**, v. 37, n.7, p. 1590-1599, 2010.

BAKER, T. R.; PHILLIPS, O. L.; MALHI, Y.; ALMEIDA, S. et al. Variation in wood density determines spatial patterns in Amazonian. **Global Change Biology**, v. 10, n. 5, p. 545-562, 2004.

BARBOSA, L. C. **Espectroscopia no Infravermelho na Caracterização de Compostos Orgânicos**. Viçosa: Ed. da UFV, 2007, 189p.

BEAUMONT, E. Industrial charcoal making. **FAO Forestry Paper**, Rome-Italy, v. 63, 1985.

BICA, J. B. **Investigação de paleoincêndios vegetacionais permianos no afloramento Curva do Belvedere**: Significado paleoambiental para o paleozoico superior da bacia do Paraná. 2014. 104f. Dissertação (Mestrado em Ambiente e Desenvolvimento) – Centro Universitário UNIVATES, Lajeado, 2014.

BOWMAN, D. M. J. S. *et al*. Fire in the Earth system. **Science**, v. 324, n. 5926, p. 481-484, 2009.

BRAADBAART, F.; POOLE, I. Morphological, chemical and physical changes during charcoalification of wood and its relevance to archaeological contexts. **Journal of archaeological science**, v. 35, n. 9, p. 2434-2445, 2008.

CHAMLEY, Hervé (Ed.). **Geosciences, environment and man**. Elsevier, 2003, 527p.

CHANG, S. T.; CHANG, H. T. Comparisons of the photostability of esterified wood. **Polymer Degradation and Stability**, v. 71, n. 2, p. 261-266, 2001.

CHEN, H.; FERRARI, C.; ANGIULI, M.; YAO, J.; RASPI, C.; BRAMANTI, E. Qualitative and quantitative analysis of wood samples by Fourier transform infrared spectroscopy and multivariate analysis. **Carbohydrate polymers**, v. 82, n. 3, p. 772-778, 2010.

COLOM, X.; CARRILLO, F.; NOGUES, F.; GARRIGA, P. Structural analysis of photodegraded wood by means of FTIR spectroscopy. **Polymer degradation and stability**, v. 80, n. 3, p. 543-549, 2003.

CONESA, J. A.; CABALLERO, J. A.; FONT, A. M. R. Analysis of different kinetic models in the dynamic pyrolysis of cellulose. **Thermochimica Acta**, v. 254, p. 175-192, 1995.

D'ANGELO, J. A.; ESCUDERO, L. B.; VOLKHEIMER, W.; ZODROW, E. L. Chemometric analysis of functional groups in fossil remains of the Dicroidium flora (Cacheuta, Mendoza, Argentina): implications for kerogen formation. **International Journal of Coal Geology**, v. 87, n. 2, p. 97-111, 2011.

D'ANGELO, J. A.; ZODROW, E. L.; MASTALERZ, M. Compression map, functional groups and fossilization: a chemometric approach (Pennsylvanian neuropteroid foliage, Canada). **International Journal of Coal Geology**, v. 90, p. 149-155, 2012.

DIESSEL, C. F. K. The stratigraphic distribution of inertinite. **International Journal of Coal Geology**, v. 81, n. 4, p. 251-268, 2010.

DOS SANTOS, Â. C. S.; CELESTINO HOLANDA, E.; DE SOUZA, V.; GUERRA-SOMMER, M.; MANFROI, J.; UHL, D.; JASPER, A. Evidence of palaeo-wildfire from the upper lower Cretaceous (Serra do Tucano Formation, Aptian–Albian) of Roraima (North Brazil). **Cretaceous Research**, v. 57, p. 46-49, 2016.

DUTRA, T. L.; STRANZ, A. História das Araucariaceae: a contribuição dos fósseis para o entendimento das adaptações modernas da família no Hemisfério Sul, com vistas a seu manejo e conservação. **Tecnologia, diagnóstico e planejamento ambiental**. São Leopoldo: Ed. da UNISINOS, p. 293-351, 2003.

EL ATFY, H.; SALLAM, H.; JASPER, A.; UHL, D. The first evidence of palaeo-wildfire from the Late Cretaceous (Campanian) of North Africa. **Cretaceous Research**, v. 57, p. 306-310, 2016.

FALCON-LANG, H. J. Fire ecology of the Carboniferous tropical zone. **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 164, n. 1-4, p. 339-355, 2000.

FLANNIGAN, M.; KRAWCHUK, M.; DE GROOT, W.; WOTTON, M.A.; GOWMAN, L.M. Implications of changing climate for global wildland fire. **International Journal of Wildland Fire**, v. 18, n. 5, p. 483-507, 2009.

GASTALDO, R. A.; DIMICHELE, W. A.; PFEFFERKORN, H. W. Out of the icehouse into the greenhouse: a late Paleozoic analogue for modern global vegetational change. **Gsa today**, 1996.

GLASSPOOL, I.J.; SCOTT, A. C. Identifyingpast fire events. In: Belcher, C.M. (ed.). **Fire Phenomena and the Earth System**: An Interdisciplinary Guide to Fire Science. Oxford: John Wiley&Sons, p. 177-206, 2013.

GUO, Y.; BUSTIN, R. M. FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals. **International Journal of Coal Geology**, v. 37, n. 1-2, p. 29-53, 1998.

HAYKIRI-ACMA, H.; YAMAN, S.; KUCUKBAYRAK, S. Comparison of the thermal reactivities of isolated lignin and holocellulose during pyrolysis. **Fuel Processing Technology**, v. 91, n. 7, p. 759-764, 2010.

HOLZ, M.; FRANÇA, A. B.; SOUZA, P. A.; IANNUZZI, R.; ROHN, R. A stratigraphic chart of the Late Carboniferous/Permian succession of the eastern border of the Paraná Basin, Brazil, South America. **Journal of South American Earth Sciences**, v. 29, n. 2, p. 381-399, 2010.

HUDSPITH, V. **The Palaeoecological and Industrial Significance of Inertinite (Charcoal) in Late Permian Coals from the Kuznetsk Basin, Russia**. 2012. 326f. Tese (Doutorado em Filosofia) - Royal Holloway, University of London, London, 2012.

JASPER, A.; UHL, D. Using the Late Paleozoic/Early Mesozoic icehouse/greenhouse transition to understand the actual climate change. *In*: **GOAL Meeting**, v. C538, p. 95-99, 2011.

JASPER, A.; UHL, D.; AGNIHOTRI, D.; TEWARI, R.; PANDITA, S. K.; BENICIO, J.R.W.; PIRES, E.F.; DA ROSA, A. A. S.; BHAT, G. D.; PILLAI, S. S. K. Evidence of wildfire in the Late Permian (Lopingian) Zewan Formation of Kashmir (India). **Current Science**, 110(3):419-423, 2016.

JASPER, A.; UHL, D.; GUERRA-SOMMER, M.; MOSBRUGGER, V. Palaeobotanical evidence of wildfires in the late palaeozoic of South America–early permian, rio bonito formation, Paraná basin, Rio Grande do Sul, Brazil. **Journal of South American Earth Sciences**, v. 26, n. 4, p. 435-444, 2008.

JONES, T. P.; CHALONER, W. G. Fossil charcoal, its recognition and palaeoatmospheric significance. **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 97, n. 1-2, p. 39-50, 1991.

JUNG, M. R.; HORGEN, F. D.; ORSKI, S. V.; RODRIGUEZ, V.; BEERS, K. L.; BALAZS, G. H.; ... LYNCH, J. M. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. **Marine Pollution Bulletin**, v. 127, p. 704-716, 2018.

KUBIK, R.; MARYNOWSKI, L.; UHL, D.; JASPER, A. Co-occurrence of charcoal, polycyclic aromatic hydrocarbons and terrestrial biomarkers in an early Permian swamp to lagoonal depositional system, Paraná Basin, Rio Grande do Sul, Brazil. **International Journal of Coal Geology**, v. 230, p. 103590, 2020.

LARA, D. M.; BRESCIANI, L.; OSTERKAMPC, I. C.; HILGEMANNB, M.; ETHUR, E.; JASPER, A.; FERRÃO, M. F.; UHL, D.; STÜLP, S. Avaliação de fragmentos de lenhos carbonizados de araucariaceae por meio de termogravimetria e infravermelho associadas à análise multivariada. **Química Nova**, v. 40, n. 8, p. 895-901, 2017.

MANFROI, J.; UHL, D.; GUERRA-SOMMER, M.; FRANCISCHIN, H.; MARTINELLI, A. G.; SOARES, M. B; JASPER, A. Extending the database of permian palaeo-wildfire on Gondwana: charcoal remains from the Rio do Rasto Formation (Paraná Basin), middle permian, Rio Grande do Sul State, Brazil. **Palaeogeography, palaeoclimatology, palaeoecology**, v. 436, p. 77-84, 2015.

MCPARLAND, L. C.; COLLINSONN, M. E.; SCOTT, A. C.; CAMPBELL, G. The use of reflectance values for the interpretation of natural and anthropogenic charcoal assemblages. **Archaeological and Anthropological Sciences**, v. 1, n. 4, p. 249-261, 2009.

MILANI, E. J.; MELO, J. H. G.; SOUZA, P. A.; FERNANDES, L. A.; FRANCA, A. B. Bacia do Paraná. **Boletim de Geociências da Petrobrás**, v. 15, n. 2, p. 265-287, 2007.

MOORE, A. K.; OWEN, N. L. Infrared spectroscopic studies of solid wood. **Applied Spectroscopy Reviews**, v. 36, n. 1, p. 65-86, 2001.

O'KEEFE, J. M. K.; BECHTEL, A.; CHRISTANIS, K.; DAI, S. D.; WILLIAM, A.; EBLE, C. F.; ESTERLE, J. S.; MASTALERZ, M.; RAYMOND, A. L.; VALENTIM, B. V.; WAGNER, N. J.; WARD, COLIN, R., HOWER, J.C. On the fundamental difference between coal rank and coal type. **International Journal of Coal Geology**, v. 118, p. 58-87, 2013.

PERES, M. L.; GATTO, D. A.; STANGERLIN, D. M.; CALEGARI, L.; BELTRAME, R.; HASELEIN, C.; SANTINI, R. E. J. Idade de segregação do lenho juvenil e adulto pela variação da massa específica de açoita-cavalo. **Ciência Rural**, v. 42, n. 9, p. 1596-1602, 2012.

PINHEIRO, PC da C.; FIGUEIREDO, F. J.; SEYE, O. Influência da temperatura e da taxa de aquecimento da carbonização nas propriedades do carvão vegetal de Eucalyptus. **Biomassa e Energia**, v. 2, n. 2, p. 159-168, 2005.

PIRES, E. F.; GUERRA-SOMMER, M.; SCHERER, C. M. S.; DOS SANTOS, A. R.; CARDOSO, E. Early Cretaceous coniferous woods from a paleoerg (Paraná Basin, Brazil). **Journal of South American Earth Sciences**, v. 32, n. 1, p. 96-109, 2011.

ROWELL, R. M.; PETTERSEN, R.; HAN, J. S.; ROWELL, J. S.; TSHABALALA, M. A. In: ROWELL, R. M. **Handbook of wood chemistry and wood composites**. Boca Raton: CRC press, 2005.

SCHMIDT, I. D.; SOMMER, M. G.; MENDONÇA, J. D. O.; MENDONÇA FILHO, J. G.; JASPER, A.; KLEPZIG, M. C.; IANNUZZI, R. Charcoalified logs as evidence of hypautochthonous/autochthonous wildfire events in a peat-forming environment from the Permian of southern Paraná Basin (Brazil). **International Journal of Coal Geology**, v. 146, p. 55-67, 2015.

SCHNEIDER, R. L.; MÜHLMANN, H.; TOMMASI, E.; MEDEIROS, R. A.; DAEMON, R. F.; NOGUEIRA, A. A. Revisão estratigráfica da Bacia do Paraná. *In*: **Anais Cong. Brasil. Geol**, n. 28, p. 41-65, 1974.

SCHWANNINGER, M.; RODRIGUES, J.C.; PEREIRA, H.; Hinterstoisser, B. Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. **Vibrational spectroscopy**, v. 36, n. 1, p. 23-40, 2004.

SCOTT, A. C. Charcoal recognition, taphonomy and uses in palaeoenvironmental analysis. **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 291, n. 1-2, p. 11-39, 2010.

SCOTT, A. C. Observations on the nature and origin of fusain. **International Journal of Coal Geology**, v. 12, n. 1-4, p. 443-475, 1989.

SCOTT, A. C. The Pre-Quaternary history of fire. **Palaeogeography, palaeoclimatology, palaeoecology**, v. 164, n. 1-4, p. 281-329, 2000.

SCOTT, A. C.; STEA, R. Fires sweep across the Mid-Cretaceous landscapes of Nova Scotia. **Geoscientist**, v. 12, n. 1, p. 4-6, 2002.

SCOTT, A. C.; GLASSPOOL, I. J. Observations and experiments on the origin and formation of inertinite group macerals. **International Journal of Coal Geology**, v. 70, n. 1-3, p. 53-66, 2007.

SHEN, D. K.; GU, S.; BRIDGWATER, A. V. The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose. **Carbohydrate Polymers**, v. 82, n. 1, p. 39-45, 2010.

TREUSCH, O.; HOFENAUER, A.; TROGER, F.; FROMM, J.; WEGENER, G. Basic properties of specific wood-based materials carbonised in a nitrogen atmosphere. **Wood science and technology**, v. 38, n. 5, p. 323-333, 2004.

TREVISAN, R.; HASELEIN, C. R.; SANTINI, E. J.; SCHNEIDER, P. R.; MENEZES, L. F. Efeito da intensidade de desbaste nas características dendrométricas e tecnológicas da madeira de Eucalyptus grandis. **Ciência Florestal**, v. 17, n. 4, p. 377-387, 2007.

TREVISAN, R.; HASELEIN, C. R.; SANTINI, E. J.; SCHNEIDER, P. R.; MENEZES, L. F. Efeito da intensidade de desbaste nas características dendrométricas e tecnológicas da madeira de Eucalyptus grandis. **Ciência Florestal**, v. 17, p. 377-387, 2007.

TUCKER, M. P.; NGUYEN, Q. A.; EDDY, F. P.; KADAM, K. L.; GEDVILAS, L. M.; WEBB, J. D. Fourier transform infrared quantitative analysis of sugars and lignin in pretreated softwood solid residues. In: Twenty-Second Symposium on Biotechnology for Fuels and Chemicals. **Humana Press**, Totowa, p. 51-61, 2001.

UHL, D.; KERP, H. Wildfires in the Late Palaeozoic of Central Europe -The Zechstein (Upper Permian) of NW-Hesse (Germany). **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 199, n. 1-2, p. 1-15, 2003.

UHL, D.; JASPER, A.; HAMAD, A. M. B. A.; MONTENARI, M. Permian and Triassic wildfires and atmospheric oxygen levels. **Ecosystems**, v. 9, p. 179-187, 2008.

UHL, D.; JASPER, A.; SCHINDLER, T.; WUTTKE, M. First evidence of palaeo-wildfire in the early Middle Triassic (early Anisian) Voltzia Sandstone Fossil-Lagerstätte - the oldest post-Permian macroscopic evidence of wildfire discovered so far. **Palaios**, v. 25, p. 837-842, 2010.

UHL, D.; LAUSBERG, S.; NOLL, R.; STAPF, K. R. G. Wildfires in the Late Palaeozoic of Central Europe - an overview of the Rotliegend (Upper Carboniferous - Lower Permian) of the Saar -

Nahe Basin (SW-Germany). **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 207, n. 1-2, p. 23-35, 2004.

WERNER, K.; POMMER, L.; BROSTRÖM, M. Thermal decomposition of hemicelluloses. **Journal of Analytical and Applied Pyrolysis**, v. 110, p. 130-137, 2014.

WIEMANN, M. C.; WILLIAMSON, G. B. Geographic variation in wood specific gravity: effects of latitude, temperature, and precipitation. **Wood and Fiber Science**, v. 34, n. 1, p. 96-107, 2002.

WATSON, A.; LOVELOCK, J. E.; MARGULIS, L. Methanogenesis, fires and the regulation of atmospheric oxygen. **Biosystems**, v. 10, n. 4, p. 293-298, 1978.

YANG, H.; YAN, R.; CHEN, H.; LEE, D. H.; ZHENG, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. **Fuel**, v. 86, n. 12-13, p. 1781-1788, 2007.

ZODROW, E. L.; D'ANGELO, J. A.; HELLEUR, R.; SIMUNEK, Z. Functional groups and common pyrolysate products of Odontopteris cantabrica (index fossil for the Cantabrian Substage, Carboniferous). **International journal of coal geology**, v. 100, p. 40-50, 2012.

ATTACHMENTS

Table 1S - Detailing of the main peaks present in the spectra of Figure 2b

500ºC *Araucaria columnaris*	**700ºC *Araucaria columnaris***	**Charcoal Belvedere**	**Charcoal Faxinal**	**Vibrational group**	**Absorption range (cm^{-1})**
-	-	-	1892w		
-	-	-	1873w		
-	1871w	-	-		
-	1846w	-	1846w		
-	-	-	1830w		
-	-	-	1811sh		
-	-	-	1796w		
-	1775w	-	1775w		
-	1751w	-	1751sh		
-	1738m	-	1738w		
-	-	-	1719w	νC=O	1850-1610
1701s	1701s	1701vs	1701m		
1688sh	1688sh	1688sh	-		
-	-	-	1686w		
-	-	-	1674sh		
-	-	-	1666sh		
-	1672sh	-	-		
-	-	1653sh	1655sh		
-	1651sh	-	1651m		
-	-	-	1638sh		
-	-	1599vs	-		
-	-	-	1595m		
1591sh	-	-	-		
1580vs	-	-	1580w		
-	1576s	-	-	νC=C	
1562sh	-	-	1562m	νC=N	1650-1500
-	1560s	-	-	νN=O	
1545sh	1545sh	-	1545m		
-	1524sh	-	1524m		
1512sh	1512w	1512sh	-		
-	-	-	1510w		

Continues...

Table 1S - Detailing of the main peaks present in the spectra of Figure 2b

				Conclusion	
-	-	1497sh	-		
-	1493sh	1493w	1493w		
-	-	-	1477w		
1474w	1474sh	-	-		
-	1462w	-	-		
1458w	-	-	-		
-	-	-	1456w	δCH_2 δCH_3	1480-1440 1450-1375
-	1437w	-	1437w		
-	-	1425m	-		
	1422w	-	1422w		
1420m	-	-	-		
-	-	1410sh			
-	-	-	1400w		
-	-	1375w	1375w		
1360m	-	-	-		
-	1354m	-	-		
-	-	-	1341w		
-	-	1231vs	-		
1221m	-	-	-	*v*S=O vC=O	1350 – 1310
-	-	-	1167m		
-	1215m	-	-		
-	-	-	1096vs		
1092sh	-	-	-		
-	-	1036sh	-		
890w	-	890w	-		
-	878w	-	878w		
822w	822w	822w	-		
-	-	-	800m		
-	-	-	775sh	yCH	900-650
-	-	760m	-		
754w	754w	-	-		
-	-	-	698w		
675w	675w	675w	-		

Legend: vs: very strong; s: strong; m: medium; w: weak; sh: shoulder
Source: Authors' (2021)

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