Chemical and elementary characterization of *Spongiophyton nanum*: Understanding the phylogeny, paleoenvironment, and fossilization processes of an enigmatic flora

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ABSTRACT

The record of thalloid macrofossils in the North-Northwest region of the Paraná Basin is less studied compared to that of invertebrate paleofauna in the same area. Consequently, the lack of important information regarding the niches occupied by thalloid embryophytes during early land colonization in this coastal paleoenvironment is evident. This study presents the first chemical and elemental data on *Spongiophyton* for this region of the basin, offering insights into its paleoenvironment and fossilization processes and providing considerations about the phylogeny of this enigmatic assemblage *Spongiophyton nanum* Krausel emend. Chaloner et al. (1974) collected fragments from an outcropping rock in Jaciara, Mato Grosso, Brazil, and studied them using scanning electron microscope/energy X-ray dispersive spectrometer (EDS) and Fourier transform infrared (FTIR) spectroscopy techniques. The EDS analysis showed the highest elemental concentration of carbon, oxygen, and calcium as the main elements of the cuticle composition. Silicon and aluminum were better represented inside the pores than in other areas of the cuticle. The high carbon concentration in the cuticle suggested an anoxic condition prevalent during the deposition of the fine-grained sediments, which prevented its oxidation before and during diagenesis. The carbon present in the EDS spectra was restricted to the cuticle area, and the FTIR spectra indicated the presence of some functional groups, both related to the original organic matter, possibly cutin. Based on elemental characterization, the fossilization of *S. nanum* may involve more than one process, such as carbonification and mineralization, and *S. nanum* has more affinities with lichen groups.

1. Introduction

The records of adaptations and taxa that appear in the fossil record associated with plants before the emergence of the first embryophytes in the early Devonian are always intriguing and challenging to interpret. In this sense, there are several genera, such as *Spongiophyton*, *Haplostigma*, *Palaeostigma*, *Cooksonia*, *Sporogonites*, *Hostinella*, *Aberlemnia*, *Tarrantia*, among others (Gerrienne et al., 2001, 2006, 2019; Mussa et al., 2002; Gómez and Gerrienne, 2010; Milagres et al., 2018). The genus *Spongiophyton* has four described species (*S. lenticularis*, *S. nanum*, *S. minutissimum*, and *S. articulatum*) and an astonishingly large distribution (South America, Africa, North America, Central Europe, and Western Asia; Fig. 1), although it does not have transport-resistant structures or even organs (Krausel, 1954; Krausel and Venkatachala, 1966; Andrade Ramos, 1967; Boureau and Pons, 1973; Chaloner et al., 1974; Zdebska, 1978; Gensel et al., 1991; Guerra-Sommer, 1993; Gerrienne, 1999; Griffing et al., 2000; Bosetti et al., 2011; Ponciano et al., 2012; Matsumura et al., 2013, 2016, 2023). In South America, *Spongiophyton* can be found in Brazil (Krausel, 1954; Andrade Ramos, 1967; Guerra-Sommer, 1993; Bosetti et al., 2011; Ponciano et al., 2012; Matsumura et al., 2013, 2016, 2023), Bolivia (Boureau and Pons, 1973; Di Pasquo and Noetinger, 2008; Di Pasquo et al., 2015), and Colombia (Moreno-Sánchez et al., 2020). (See Table 1.)
Studies on the Devonian of Paraná Basin have concentrated on the knowledge of its invertebrate paleofauna (e.g., Rodrigues et al., 2003; Soares et al., 2008a, 2008b; Bosetti et al., 2010, 2011, 2012; Ghilardi et al., 2013; Comniskey and Ghilardi, 2013; Zabini et al., 2013; Carbone and Ghilardi, 2016; Scheffler et al., 2019; Ribeiro et al., 2019) and palynomorphs (Burjack and Paris, 1989; Loboziak et al., 1988; Oliveira, 1991, 1997; Oliveira et al., 1995; Grahn et al., 2000, 2002, 2010; Mauller et al., 2007, 2009; Muro et al., 2020; Matsumura et al., 2023). Few papers exist on the topic of the Devonian paleoflora of the Paraná Basin, especially on its North-Northwest (NNW) part, which encompasses parts of the Brazilian states of Mato Grosso (MT), Mato Grosso do Sul (MS), and Goiás (GO) (Fig. 2).

The fossil plant taxa found in NNW were documented by Barbosa (1949), Kräusel (1954), Schubert and Borghi (1991), Pereira (2000), Carbonaro and Ghilardi (2016), Vieira et al. (2018), and Ribeiro et al. (2019). The taxa include Cooksonia, Spongiophyton, Haplostigma, and Palaeostigma.

Data regarding the elemental composition of Spongiophyton were obtained from samples collected in other locations of the Paraná Basin and Gondwana. The first cuticles of S. nanum studied using an energy X-ray dispersive spectrometer (EDS) coupled to a scanning electron microscope (SEM) were collected in Ghana (Chaloner et al., 1974). They identified the elementary percentages that make up the cuticles of this species. S. nanum was also studied using Fourier transform infrared (FTIR) spectroscopy by Matsumura et al. (2016) from the phytofossils collected in the Devonian layers of the Paraná Basin within the state of Paraná, Brazil. In addition to this taxon, they also studied the cuticles of S. lenticalis and S. minutissimum from the same locality. Through this chemical study, Matsumura et al. (2016) supported the taxonomic separation of the three species of Spongiophyton, inferring the portion of the body plant that each taxon represents (distal or proximal), and their kerogen analysis reinforced the hypothesis that approximates the genus Spongiophyton to lichens.

However, so far, no further studies have applied EDS and FTIR analysis in S. nanum cuticles from other locations. None of these studies approached fossil diagenesis using EDS or other microscopic analytical techniques in order to characterize them chemically. However, this information has been very relevant in taphonomic studies, as the joint application of EDS can reveal data about diagenesis and paleoenvironment and even determine biofacies (Callefo, 2014, 2018; Ricardi-Branco et al., 2018; Callefo et al., 2019; Marchetti et al., 2019). Along this line, fossil plants are examined using SEM/EDS and FTIR techniques to determine the elemental composition of plant tissues preserved in outcropping rocks in the NNW portion of the Paraná Basin and point out relevant aspects about their habitat, sedimentation environments, and phylogenetic affinity with groups of lichens and bryophytes.

Table 1

<table>
<thead>
<tr>
<th>Genus/Species</th>
<th>Location</th>
<th>Age</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooksonia sp.</td>
<td>Cachoeira das Andorinhas (MT)</td>
<td>Lochkovian-Pragian</td>
<td>Schubert and Borghi (1991)</td>
</tr>
<tr>
<td></td>
<td>Amorinopolis (GO)</td>
<td>Early Devonian</td>
<td>Quadros and de Melo (1986)</td>
</tr>
<tr>
<td></td>
<td>Cachoeira das Andorinhas (MT)</td>
<td>Lochkovian-Pragian</td>
<td>Pereira (2000)</td>
</tr>
<tr>
<td>Spongiophyton nanum</td>
<td>Jaciara (MT)</td>
<td>Emsian-Eifelian</td>
<td>Ribeiro et al. (2019)</td>
</tr>
<tr>
<td>(Barbonia) Krausel, 1974</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spongiophyton lenticulare</td>
<td>Rio São Lourenço (MT)</td>
<td>Early Devonian</td>
<td>Krausel (1954)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haplostigma sp.</td>
<td>Caiapónia (GO)</td>
<td>Givetian-Frasnian</td>
<td>Carbonaro and Ghilardi (2016)</td>
</tr>
</tbody>
</table>

Fig. 1. Map of the cosmopolitan distribution of the genus Spongiophyton (Red blocks: Gondwana records; Blue block: Laurentia records; Green block: Central Europe records; Yellow block: China records). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
2. A brief scenario of the Paraná Basin geology

The Paraná Basin is a huge basin located in South America (Fig. 2); it covers a total area of 1,100,000 km² only in Brazil, including the MT, GO, Minas Gerais, São Paulo, Paraná, Santa Catarina, and Rio Grande do Sul states, besides extending to other countries like Argentina, Paraguay, and Uruguay (Petri and Fúlfaro, 1988; Melo, 1988; Milani et al., 2007).

The Devonian rocks that occur in NNW of the Paraná Basin (with outcrops in the states of GO, MT, and MS) are stratigraphically assembled in the Chapada Group from bottom to top: Units 1, 2, 3, and 4, with ages ranging from Lochkovian to Frasnian (Melo, 1988; Grahn et al., 2010).

In Unit 1 (Late Lochkovian), chronocorrelated to the Furnas Formation, there are records of small fossils of psilophytes and ichnofossils (Andrade and Camarço, 1980; Quadros and de Melo, 1986; Petri and Fúlfaro, 1988; Grahn et al., 2010; Sedorko et al., 2018). Unit 2 (Neo-pragian-Eoemsian to Neoemsian-Eifelian) has a considerable increase in invertebrate fossils, such as polychaetes, brachiopods, tentaculites, bivalves, gastropods, trilobites, crinoids (Andrade and Camarço, 1978, 1980; Grahn et al., 2010; Sedorko et al., 2018). Unit 3, Neoemsian-Eifelian (Andrade and Camarço, 1980; Grahn et al., 2010), few fossil records were found by Ribeiro et al. (2019), and they identified specimens of fossil plants in the deltaic facies of the Jaciara region, MT. Finally, Unit 4 was associated with the maximum marine transgression of the early Givetian (Assine, 2001; Grahn et al., 2010); the presence of trilobites, brachiopods, and Lycopsids (e.g., Haplostigma sp. and Palaeostigma sp.) has been recorded (Carvalho et al., 1987; Carbonaro and Ghilardi, 2016).

2.1. Devonian macroflora on the NNW flank of the Paraná Basin

Few studies have dealt with fossil plants found on the NNW flank of the Paraná Basin. Barbosa (1949) described specimens of Haplostigma lenticularis in greenish-gray shales found near the upper São Lourenço River in MT. Later, Krause (1954) synonymized this taxon with Spongiophyton lenticulare (Barbosa, 1949) emend. Chaloner et al., 1974 due to the presence of thalloid structures and the spongy surface morphology of this species.

In the Devonian outcrop located in the Chapada dos Guimarães National Park (near the Degrau and Andorinhas waterfalls), Pereira (2000) documented the occurrence of early vascular plants identified as Cooksonia Lang, 1937. Specimens of this same genus were found by Schubert and Borghi (1991) in coastal sediments from the upper portion of the Furnas Formation (Chapada Group, Paraná Basin), close to the Cachoeira das Andorinhas locality. They described the occurrence of scattered triangular and fusiform sporangia, as well as disconnected and smooth axes, in some cases, with dichotomous ramifications, which are characteristics of the Cooksonia genus. In addition, they accept an early
Devonian age for the bedrock associated with these outcrops.

Recent publications (Vieira et al., 2018; Ribeiro et al., 2019) have documented the occurrence of plant remains preliminarily identified as *S. nanum* in an outcrop located in the southeastern part of MT. Compression with cuticles was collected in a heterolytic sequence of medium- and light-gray sandstones of sequences characterized as delta plains. The present manuscript will provide more data on this material.

Near the city of Amorinópolis, Southwest of GO, on the northern flank closest to the northwestern edge of the Paraná Basin, Quadros and Melo (1986, p. 611) reported the occurrence of fragmentary *Cooksonia* cauloid impressions, characterized by dichotomized caulinar axes and possible apical sporangia. The fossils were found in a grayish-white layer, soft, well-laminated, and fissile micaceous siltstone, interbedded with medium to conglomeratic, whitish feldspar sandstones, with planar and concave cross-stratification, correlated with the Furnas Formation.

Moreover, in the North/Northeast portion of the Paraná Basin, in the outcrop located in the municipality of Caiapônia (GO), belonging to Unit 4 of the Chapada Group, Alto Garças Sub-basin (Paraná Basin), Carbonaro and Ghilardi (2016) recorded the occurrence of *Haplostigma* sp. and *Palaeostigma* sp.

3. Material and methods

3.1. Location and geology of the study area

The collection area (Fig. 2) of *S. nanum* is located near the city of Jaciara, MT, on the outcrop at the edge of BR-364 (15°56'31.68" S, 55°0'56.78" W) and was named “AJ-03” by Ribeiro et al. (2019).

Fragments of *S. nanum* occur in two packs of medium-light gray sandstone interspersed with reddish siltstones, with plane-parallel stratification and trace fossils, forming a heterolithic bedding. In the smaller sandstone pack (50 cm thick), there are grooved cross-bedding and wavy marks, whereas, in the larger bedding (80 cm thick), the stratifications are flat-parallel. Ribeiro et al. (2019) classified the section of the *S. nanum* cuticles as a deltaic plain with the rupture of marginal dikes. Although Ribeiro et al. (2019) have described the packages as medium sandstone, we propose sandy silt as a more accurate description due to the pronounced presence of silt and fine grain size.

The studied cuticles of *S. nanum* belong to sample PJ-187 housed in the scientific collection of the Laboratório de Paleontologia e Palinologia (PALMA) of the Federal University of MT (UFMT). The plant remains...
were preserved as compressed cuticles (Fig. 3) and detached from the matrix rock using the Dégagement technique (LECLERCQ, 1960). For FTIR analysis, the fragments were detached from the matrix and, subsequently, macerated. After 24 h in an oven at 50 °C, the samples were examined by FTIR.

All sample preparations were conducted in the Macroinvertebrate Paleontology Laboratory (LAPALMA) at São Paulo State University (UNESP).

3.2. Elemental characterization

3.2.1. Energy dispersive spectrometry coupled to a scanning electron microscope

Two fragments of *S. nanum* were studied using an EDS detector coupled to a SEM of the Carl Zeiss brand EVO LS 15, located in the Anelasticity and Biomaterials Laboratory at UNESP. SEM/EDS allows a qualitative and semi-quantitative chemical evaluation of the compositional elements of the cuticle surfaces. The fragments of external tissue were fixed to the equipment’s sample holder using gold adhesive tape to increase electron conductivity. The SEM/EDS studies were performed at a magnification of 250 ×, with a maximum of EHT 15.00 Kv, and were

![Elemental analysis by SEM/EDS in *Spongiophyton nanum* Specimen 1. A. Hit areas; Hit 1 in the cuticle (Spectrum 1) and Hit 2 inside the pore (Spectrum 2); B and C. Histograms; B. Histogram of the point located in the cuticle of Specimen 1; C. Histogram of the area located in one of the pores of Specimen 1.](image-url)
not operated under vacuum.

Points on each fragment were randomly selected within a pre-defined area to define the elemental composition of different parts of the cuticle. The Raman technique was applied in this study, but it did not yield additional results because of the background fluorescence that prevented the visualization and identification of elementary peaks.

3.2.2. Fourier transform infrared spectroscopy

FTIR spectra of the cuticle fragments were obtained with a Bruker FTIR spectrometer located at the Faculty of Science, UNESP, model Vertex 70, at a resolution of 4 cm⁻¹, in the 4000–400 cm⁻¹ spectral range. To interpret the spectra obtained in FTIR, an “identification key” was used, elaborated by Lopes and Fascio (2004), to identify functional groups according to spectra obtained in the infrared and also the attributions of the functional groups for each region of the number of waves established by Workman and Workman and Weyer (2012). Both identification methods are often used in similar studies.

4. Results

4.1. Systematic paleontology

Order: Spongiphytales Sommer 1959
Family: Spongiphytaceae Krausei, 1954

Fig. 5. Elemental analysis by SEM/EDS in Spongiphyton nanum Specimen 2. A. Hit areas; Hit 1 in the cuticle (Spectrum 1) and Hit 2 inside the pore (Spectrum 2); B and C. Histograms; B. Histogram of the point located in the cuticle of Specimen 2; C. Histogram of the area located in one of the pores of Specimen 2.
4.2. Elemental characterization

Spectrograms were obtained by SEM/EDS (Figs. 4A–C and 5A–C). Carbon (C), oxygen (O), and calcium (Ca) were the main elements found in the cuticles of *S. nanum* (Figs. 4 and 5). Iron (Fe), copper (Cu), aluminum (Al), and silicon (Si) were also present in the cuticle of Specimen 1, and barium (Ba) and magnesium (Mg) were present in the cuticle of Specimen 2 (Fig. 5B). The main mineral elements that fill the pores of Specimen 1 consist of O, Si, Ca, and zircon (Zr) (Fig. 4C). In the interior of the pore not filled by the rock matrix (Fig. 5A), the main elements identified were Al, Si, C, and O (Fig. 5C).

Analysis of the cuticles of Specimens 1 and 2 revealed the presence of Ca weight (1.38% and 2.87%) and atomic percentages (0.52 and 1.40) much lower than those of O (22.43% and 28.95% weight, 21.14 and 35.29 atomic percentage) (Table 2). However, the intensity of the Ca peaks in the EDS spectra obtained for both cuticles was higher than that of the O peaks (Figs. 4B and 5B). The same occurs with Al and Si present in addition to the presence of pores on only one of the two faces, because they did not present a direct semi-quantitative analysis of these elements, as the measurement of their percentage was based on the subtraction of 100% (total percentage of all elements present) from the percentage of other elements identified. The highest elementary concentration in the matrix was O, followed by Ca. The elements Zr, Si, Fe, and Al also showed considerable concentrations (above 1% both in weight and in atomic percentage).

The main elements of the cuticular pores were different (Figs. 4C and 5C). This difference was due to pores being filled by the rock matrix in the case of Specimen 1 (seen in Fig. 4A). O was the only element present in both cuticles of *S. nanum*, while it was absent in the pores filled by the rock matrix; therefore, it confirms the preservation of organic C (compression). The most volatile elements of the original organic matter in the plant cuticle were dissipated into the atmosphere, increasing the C concentration and resulting in fossilization by carbonification. The presence of C in the pores of Specimen 2 was possibly due to the absence of a rock matrix in its interior. Thus, the X-ray beam probably reached the other side of the cuticle through the examined pore.

The element O is present in both the cuticles and the matrix because it is an atmospheric component (Zabini, 2007). The high percentages of O in the matrix (present in the pore of Specimen 1) in relation to the percentages of this same element in the cuticles reinforce the incorporation of these elements during fossil diagenesis.

The FTIR spectrum of *S. nanum* (Fig. 6) revealed a broad band between 3200 cm$^{-1}$ and 3600 cm$^{-1}$, low-intensity peaks at 2920 cm$^{-1}$ and 2855 cm$^{-1}$ and in the interval between 1830$^{-1}$–630 cm$^{-1}$, and slightly higher intensity peaks near 1450 cm$^{-1}$.

5. Discussion

According to the information obtained and shown in Table 2, the highest elementary concentrations in the studied cuticles were C and O, similar to those found by Chaloner et al. (1974), with a larger difference between the percentages found for O. This discrepancy might have occurred because they did not present a direct semi-quantitative analysis of these elements, as the measurement of their percentage was based on the subtraction of 100% (total percentage of all elements present) from the percentage of other elements identified. The highest elementary concentration in the matrix was O, followed by Ca. The elements Zr, Si, Fe, and Al also showed considerable concentrations (above 1% both in weight and in atomic percentage).

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The preservation of organic C in the fossils can be attributed to the anoxic conditions prevalent during the deposition of the fine-grained sediments, which prevented their oxidation before and during diagenesis. Notably, the fossilization process may involve more than just C. The data in Table 2 also show that the element Si is concentrated inside the pores and has expressive values (above 1% in both weight and atomic), while its concentration in the region of the cuticle further from the pore was irrelevant. The higher Si levels observed in the pores, even without filling by the rock matrix (Specimen 2), compared to the cuticle regions, suggest that Si may also play a role in preserving the cuticle pore region. Therefore, multiple fossilization processes may occur within the same sample.

The presence of Si in both the rock matrix and fossils provides valuable insights into the deposition environment. Al was better represented inside the pores in relation to the other cuticle areas. Al and Si are possibly linked to O atoms, also identified in these analyses, constituting clay-mineral phyllosilicates (aluminosilicates) of a group of kaolinites (Al$_2$Si$_2$O$_5$(OH)$_4$), an authigenic mineral.

The element Ca also had a good representation in the analysis of the pore of Specimen 1 but not in Specimen 2. Considering that the pore of Specimen 1 was filled by the mineral matrix, while that of Specimen 2

**Table 2**

<table>
<thead>
<tr>
<th>Element</th>
<th>Cuticle 1 Weight</th>
<th>Cuticle 1 Atomic</th>
<th>Pore 1 Weight</th>
<th>Pore 1 Atomic</th>
<th>Cuticle 2 Weight</th>
<th>Cuticle 2 Atomic</th>
<th>Pore 2 Weight</th>
<th>Pore 2 Atomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>60.09</td>
<td>75.45</td>
<td>–</td>
<td>–</td>
<td>34.54</td>
<td>56.08</td>
<td>23.83</td>
<td>44.29</td>
</tr>
<tr>
<td>O</td>
<td>22.43</td>
<td>21.14</td>
<td>51.08</td>
<td>75.98</td>
<td>28.95</td>
<td>35.29</td>
<td>21.12</td>
<td>29.46</td>
</tr>
<tr>
<td>Al</td>
<td>1.01</td>
<td>0.56</td>
<td>2.83</td>
<td>2.50</td>
<td>1.06</td>
<td>0.77</td>
<td>14.36</td>
<td>11.87</td>
</tr>
<tr>
<td>Si</td>
<td>1.19</td>
<td>0.64</td>
<td>6.41</td>
<td>5.43</td>
<td>0.77</td>
<td>0.53</td>
<td>8.94</td>
<td>7.10</td>
</tr>
<tr>
<td>Ca</td>
<td>1.38</td>
<td>0.52</td>
<td>13.78</td>
<td>8.18</td>
<td>2.87</td>
<td>1.40</td>
<td>0.85</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe</td>
<td>3.12</td>
<td>0.84</td>
<td>7.15</td>
<td>3.05</td>
<td>9.34</td>
<td>3.26</td>
<td>11.17</td>
<td>4.47</td>
</tr>
<tr>
<td>Cu</td>
<td>0.08</td>
<td>0.02</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg</td>
<td>–</td>
<td>–</td>
<td>0.86</td>
<td>0.84</td>
<td>0.57</td>
<td>0.46</td>
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</tr>
<tr>
<td>Zn</td>
<td>–</td>
<td>–</td>
<td>0.77</td>
<td>0.28</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
<td>–</td>
<td>11.92</td>
<td>3.11</td>
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<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ba</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.06</td>
<td>0.15</td>
<td>2.14</td>
<td>0.35</td>
</tr>
</tbody>
</table>

**Stratigraphic Horizon:** Lower–Middle Devonian (Late Emsian–Early Eifelian).
was unfilled, we interpreted that Ca was also part of the mineral composition of the minerals that constitute the rock matrix; however, it was not concentrated in the pore region, unlike C, Si, and O. Ca may have originated from the sediment provenance or the dissolution of invertebrate shells that were not preserved in the fossil assemblage. This could justify the monospecific record of *S. nanum* that these organisms were not living alone in the environment. Possibly, there was selective pressure from organic residues in the environment that promoted the preservation of cuticles but not of other organic structures.

The element Fe presented relevant values in all samples and probably originated from sediment provenance. Possibly, its incorporation occurred during early diagenesis through the sulfur reduction process in an anaerobic environment, as the preservation of these plants requires an anoxic environment.

We obtained well-defined and accurately positioned spectral peaks in the FTIR analysis (Fig. 6). Comparing the obtained spectra with the spectral patterns of *S. nanum* reported by Matsumura et al. (2016, 2018), the results indicated similarities in the positioning of peaks (Fig. 6) but with differences in intensity levels.

Our materials belong to Unit 3 of the Chapada Group, with Neoemian-Eifelian ages (Grahn et al., 2010). In contrast, Matsumura et al. (2016) collected samples of *S. nanum* from an outcrop belonging to the upper portion of the São Domingos Formation, Middle Devonian. Such similarities may indicate the preservation of the original organic matter as the specimens of *S. nanum* used in this study belong to Chapada Group Unit 3 (Late Emsian), which corresponds to the Tibagi Member, the lower portion of the São Domingos Formation (Grahn et al., 2013, 2016; Matsumura et al., 2023). More precise dating of our materials can reinforce the preservation of the original organic matter.

The sample containing fragments of *S. nanum* exhibited peaks at 2920 cm\(^{-1}\) and 2855 cm\(^{-1}\), as shown in Fig. 6. The absence of a strong peak within the 1830 cm\(^{-1}\) and 630 cm\(^{-1}\) intervals, combined with these
peaks, suggests the possible presence of aliphatic stretching between C and hydrogen (H). Additionally, the peaks close to 1450 cm⁻¹ support the indicating of asymmetric deformation of CH₃. Peaks were also observed in the long band region between 3200 cm⁻¹ and 3600 cm⁻¹, indicating possible stretching of O bound to H (hydroxyl). According to Beisson et al. (2012), the cutin that makes up the cuticle, together with cuticular waxes, is characterized by the abundant presence of hydroxy and hydroxy-epoxy fatty acids. Furthermore, a sequence of peaks was positioned between 900 and 700 cm⁻¹, indicating possible out-of-plane aromatic CH vibrations.

Upon comparing the FTIR spectra of S. nanum with those of lichens and bryophytes (Hu et al., 2011; Maksimova et al., 2013; Sriviboon et al., 2014), similarities were observed in both groups. Various living lichen species have shown a long band peak between 3000 and 3500 cm⁻¹, as well as a less intense peak near 3000 cm⁻¹ (Sriviboon et al., 2014). Similar features were identified in a study conducted on current bryophyte species (Hu et al., 2011; Maksimova et al., 2013). In general, all peaks presented in the analysis of S. nanum were also present in the spectra obtained for both lichen and bryophyte species. However, a greater similarity could be noticed between the S. nanum spectra and the Relicina abstrusa and Cladonia submutiformis spectra obtained by Sriviboon et al. (2014). Therefore, our results agree with those obtained by Matsumura et al. (2016). Notably, in S. nanum, only one peak exists between 1000 and 1500 cm⁻¹, similar to what occurs in these two species, mainly in the spectrum of C. submutiformis. Although this analysis can bring about taxonomic discussions, more studies should be conducted on the chemical characteristics of lichen and bryophyte organisms (fossil and current) using this technique to help establish more accurate botanical affinities.

6. Conclusion

Based on the analysis of the elemental composition of the plant cuticle and its rock matrix, as well as the results obtained from the FTIR analysis, we arrived at the following conclusions.

The fossilization of S. nanum may involve more than one process, such as carbonification and mineralization, in the presence of elements such as C, Si, O, Al, and Ca. The high C concentration in the cuticle suggested an anoxic condition prevalent during the deposition of the fine-grained sediments, which prevented its oxidation before and during diagenesis. Si and Al were better represented inside the pores compared to the other areas of the cuticle, even without being filled by the rock matrix, revealing a tendency for these elements to be concentrated in the pore area during diagenesis and contributing to the preservation of the cuticle pores.

The high percentage of O in the matrix compared to that in the cuticles suggests that the elements were incorporated during fossilization. The presence of Fe and Ca may come from sediment provenance of the origin of the deposited sediments. The sulfur reduction process in an anaerobic environment may have facilitated the incorporation of Fe during early diagenesis. The existing Ca is probably the remains of invertebrate shells that were not preserved in the fossil assemblage because it was selective pressure from organic residues in the environment that promoted the preservation of cuticles but not of other organic structures.

The C presence in the EDS spectra was restricted to the cuticle area, and the FTIR spectra indicated the presence of hydroxyl groups, both with cuticular waxes, is characterized by the abundant presence of hydroxy and hydroxy-epoxy fatty acids. Furthermore, a sequence of peaks was positioned between 900 and 700 cm⁻¹, indicating possible out-of-plane aromatic CH vibrations.

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Data availability

We have shared our data at Attach File step.

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