Palynology and geochemistry of the Frasnian global transgression in the Parnaíba Basin, Brazil

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A B S T R A C T

An integrated palynological and geochemical approach has been initiated to date and to precise the geochemical events of the Pimenteiras Formation, in the late Devonian from the Parnaíba Basin, Brazil. Based on good biostratigraphic markers and presence of index species among miospores, acritarchs and chitinozoa, the investigated sequences are referred to the Middle to early Late Frasnian. Among miospores, Chelinospora concinna and Verrucosporites bulliferus are likely to be from the BPI Interval Zone defined in the Amazon Basin. Chitinozoans of the Early to early Late Frasnian Angochitina (Lagenochitina) avelinoi zone of the Parnaíba Basin are present, and acritarch assemblages are also consistent with a Middle to early Late Frasnian age, by comparison to assemblages previously described in other Brazilian basins. Some important accompanying species of palynomorphs are illustrated. In the studied outcrops, black shale intervals are referred to top of the Radioactive Sale B and Radioactive Shale C according to Rodrigues (1995) definitions. Top of Radioactive Shale B shows good concentration of terrestrial organic matter, but low potential source of gas. By comparison Radioactive Shale C of the upper part of the Pimenteiras Formation, with important concentration of marine organic matter have low to high potential as source of gas and condensate. This study shows that a progressive flooding took place during the Devonian period in the Parnaíba Basin with maximum marine transgression in the Frasnian. These global events of interest for hydrocarbon exploration, are regarded as markers for Gondwanan regional chronostratigraphic correlations.

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1. Introduction

The Brazilian Palaeozoic basins contain thick Devonian shaley sections. These sections often display interlaminated mudstones/siltstones/very fine sandstones deposited in offshore conditions. The chronology of Palaeozoic sea-level changes suggested by Haq and Schutter (2008) demonstrated that a new long-term sea-level rise began in the Middle Devonian and reached its peak in the early Late Devonian (Frasnian). In the Parnaíba Basin, black-shale intervals with relatively high Total Organic Carbon (TOC) values (>4.0%) are frequently detected in the Devonian section. These geochemical signatures are likely related to the Late Devonian worldwide transgression described in the literature (Lüning et al., 2004; Souza et al., 2013; Bond and Wignall, 2008; Trindade and Carvalho, 2018). Therefore, the present work intends to describe the TOC content excursions recorded in the Devonian section of the Parnaíba Basin and date these excursions by means of palynology, to fit the intervals to the global sea-level curve.

The complementary geochemical data used in this work detailed have made possible for a better understanding of the control of the anoxic/dysoxic conditions of the organic matter preservation, which would typically have taken place within the flooding surfaces associated with the transgression events. In the Devonian section of the Parnaíba Basin, these surfaces—which show the highest TOC content and the highest Hydrogen Index (HI)—represent the most important hydrocarbon generation intervals.

Rodrigues (1995) identified three potentially generating shale intervals within the Pimenteiras Formation, calling them Radioactive Shales A, B and C. According to Rodrigues (1995), the Radioactive Shale A is positioned approximately at the Eifelian/Givetian boundary; has a maximum thickness of 20 m and exhibits TOC contents ranging from 1.0 to 3.0% and contains type III organic matter. The Radioactive Shale B, Middle Givetian in age, has a maximum thickness of 20 m, TOC contents ranging from 1.0 to 3.5% and type II and III organic matter. According to Rodrigues (1995), the Radioactive Shale C, deposited during the Frasnian, is correlatable to the main source rock intervals in the Solimões (Jandiatuba Formation) and Amazonas (Barreirinha Formation) basins. It is the main interval of radioactive shale layer in the
basin, reaching a thickness of 40 m. It has TOC contents ranging from between 1.0 and 5.0% and type II organic matter.

The gas accumulations related to these intervals in the Parnaíba Basin normally display a dry composition. Dry composition is normally indicating a generation at high maturation stage. However, in Parnaíba Basin, this condition is not reached by burial, suggesting an atypical process of generation related to the heat effect of dolerite intrusions (Rodrigues, 1995; Rodrigues et al., 1995, 2012; Zambrano et al., 2017; Miranda et al., 2018; Cioccari and Mizusaki, 2019).

The palynological samples has revealed a rich assemblage of acritarchs, chitinozoans and miospores. Despite their relative abundance, they all agree with regard to dating the geochemical events of an equivalent Frasnian age. New observations in Brazil and new data from the Boulonnais Area, Northern France (Streel et al., 2021) have made it possible to correlate the Brazilian outcrops with the European conodont zones and therefore with the stratotypes of the Frasnian.

Finally, for the first time, a high precision palynological study has dated the most important source rock intervals of the Parnaíba Basin, the geochemical aspects of which have been described in detail. These integrated results are particularly important and will greatly contribute to more precise future basin modelling studies.

2. Geological background

2.1. Overview

The Parnaíba Basin is currently distributed over an approximately circular area, with about 600,000 km² of which is located in northeastern Brazil (Fig. 2), where it covers part of the states of Piauí, Maranhão, Tocantins, Pará, Ceará and Bahia (Pereira et al., 2012). Due to its great stratigraphic similarity with other basins (Gabon, Ghana, Northeast Brazil), some researchers (Milani and Thomaz Filho, 2000; Almeida and Carneiro, 2004; Pereira et al., 2012) suggest that the depositional basin scenario could have occupied an area two to three times greater than the basin’s current area during the Palaeozoic era. The thickness of the sedimentary column is about 3500 m in the depocenter, while the average thickness of the basin is about 2000 m.

2.2. Stratigraphic framework

Kegel (1953) was the first to suggest the Late Devonian age for sediments in the Parnaíba Basin. These sediments make up the upper part of the Pimenteiras, Cabeças, and lowermost Longá formations (Góes
The Pimenteiras Fm (than Member) was established by Small (1914) for a 20 m thick shale sequence near the town of Pimenteiras, in the State of Piauí. Plummer (1948) divided the Pimenteiras Formation into an upper sandy member and a lower shaly member. Andrade and Daemon (1974) assigned a Late Eifelian to Late Famennian age span to the Pimenteiras Formation, whereas Loboziak et al. (2000) do not consider the fully developed part of the top of the unit to be younger than Early or Middle Famennian. The upper part of the formation is partly developed into finely laminated and radioactive dark shales, which are best developed in the subsurface of the basin and only exposed in outcrops on its western margin (Loboziak et al., 2000). The maximum thickness of the formation is over 500 m in the central part of the basin. A gap corresponding to the Late Givetian and earliest Frasnian is present all over the basin, and the upper part of the Pimenteiras Formation is entirely of Late Devonian age (Rodrigues et al., 1995; Grahn et al., 2006). This younger interval of the formation is hitherto unknown in the eastern outcrop belt of the Parnaíba Basin (Melo, 1988). Similar ages for the upper levels of the

Fig. 2. Sedimentological compound section of sites 10, 12 and 11, and the correspondent TOC contents of the Pimenteiras Formation in the sites.
Pimenteiras Formation were also obtained recently by Andrade et al. (2020) on the western edge of the basin.

The overlying Cabeças Formation was established by Plummer (1948). Beurlen (1965) included its lowermost part in the Pimenteiras Formation, and Aguilar (1971) placed the upper part in the overlying Longá Formation. The Cabeças Formation is here treated in its original sense (Melo and Lobozoia, 2003; Grahn et al., 2006) as defined in its type area near Dom Expedito Lopes (formerly the town of Cabeças), State of Piauí. Daemon (1974) and Andrade and Daemon (1974) found evidence placing the formation in the western part of the Parnaíba Basin in the Late Famennian age. Throughout the basin an erosional hiatus separates the latest Famennian glaciogenic strata of the upper Cabeças from variably older sediments belonging to the Pimenteiras and lower Cabeças formations, and towards the western margin the former also overlap directly onto metamorphics of the Precambrian basement (Loboziak et al., 2000). The lithology in the lower Cabeças lacks diamicritics and differs from the Pimenteiras Formation in that it has a higher content of sandstone beds. In its upper part the Cabeças Formation features a regressive progradation and fast intergradation of alluvial fan, fan delta and fan delta front systems and glacial lobes at the top (Caputo and Crowell, 1985). The maximum thickness (on the eastern flank of the basin) is about 300 m. While no in-situ fossiliferous sediments older than the Famennian have been established in the Cabeças Fm, shelly faunas from the Middle Devonian occur in outcrops traditionally attributed to the lowest part of the formation along the eastern margin of the basin (Melo, 1988). These fossiliferous sandstones correspond to Kegel’s (1953) “Passagem Member”, now dated as late early or middle Givetian by Breuer and Grahn (2011), and consist of alternating tempestites, and sigmoidal lobes that are genetically related to the Pimenteiras Formation. The Longá Formation was introduced by Albuquerque and Dequech, 1950 for a section in the valley of the Longá River, and along the road between Campo Maior and Castelo in the State of Piauí. Kegel (1953) and Lange and Petri (1967) considered it Frasnian in age. Kegel (1953) reported a shelly fauna, including rare Malvinokaffric elements (Melo, 1988), and possible tentaculitids in basalt Longá Formation outcrops at the Barreiras Farm, on the eastern flank of the basin. Malvinokaffric faunas became extinct during the early Givetian (Bosetti et al., 2011), and tentaculitids are unknown later than the Frasnian. However, closer inspection of the latter (Melo in Grahn and Melo, 2005) revealed that the alleged “tentaculitids” are in fact serpulitid worm tubes characterized by annular structures. The lower (latest Famennian) part of the Longá Formation (lateral facies to the uppermost Cabeças Fm.) features rhythmites including micaceous, sideritic and well-laminated greenish-gray shale with bioturbated interbedded siltstone. The formation above (Tournaisian) contains argillaceous, cross-laminated sandstones with conglomeratic horizons, and silty shales and siltstones in the upper part. The total thickness of the formation is about 150 m (Caputo, 1984). Reworked palynomorphs were found in the lower Longá Formation, in the central and western parts of the basin. This corresponds to chitinozoans occurrences likely to have been reworked and which were reported by Cruz (in Lima and Leite, 1978) from the Valença do Piauí region, on the eastern flank of the Parnaíba Basin.

3. Material and methods

The samples that support the geochemical and palynological analysis of this study were collected from outcrops located on the western boundary of the Parnaíba Basin.

The samples were collected from outcrops along the roads in Tocantins State (Fig. 1). Three outcrops (sites 10, 11, 12) were described in detail at the edge of the road and were stratigraphically positioned (Fig. 2), producing a composite stratigraphic section of around 70 m. Fourteen samples were collected from these sections in the Pimenteiras Formation. In an additional 20 m thick section (Site 35) of the Pimenteiras Formation 31 samples were collected (Fig. 3). Twelve other samples were collected in site 37 (Fig. 4). They are distributed as follows in the sites: Site 10: samples 5–8; Site 11: samples 9–12; Site 12: samples 13–18; Site 35: samples 48–78; Site 37: samples 80–91. All the samples were processed for geochemical (Table 1) and palynological analysis.

Before sending the samples for TOC and Rock-Eval pyrolysis analyses, they were macerated and powdered at 80 mesh (0.177 mm), and then acidified with hydrochloric acid, for removal of carbonates.

The TOC of the samples was obtained via Leco SC-632 equipment and reported as a relative weight percentage of the original sample. The Rock-Eval pyrolysis analyses were made in a Vinci Technologies pyrolyzer, in accordance with the procedures of Espitalie et al. (1977). The S1 (free liquid hydrocarbons present in the rock, in mg HC/g rock); S2 (hydrocarbon generating potential of the organic matter present in the rock, in mg HC/g rock); S3 (CO2 generated by the organic
matter present in the rock, in mg CO2/g rock) and Tmax (maximum hydrocarbon generation temperature in °C, measured at the maximum height of the S2 peak) were then read. The hydrogen indices \[ HI = \frac{(S2/TOC) \times 100}{mg HC/g TOC} \] were also calculated.

The geochemical analyses were carried out in the Laboratory of Chemical Stratigraphy and Organic Geochemistry of the Faculty of Geology of the Rio de Janeiro State University.

All samples were also processed for palynological studies. This processing was performed by Palynological Laboratory Services, U.K. The samples were first scraped and washed before being crushed to <1 mm fragments. A weight of 35 g was then used for processing.

Samples were treated with 20% hydrochloric acid (HCl) until any reactions had ceased. The samples were then left in the HCl for approximately one hour, to ensure that carbonate digestion was complete. They were then topped up with water and allowed to settle for at least one hour, after which time they were decanted. This stage was repeated to bring the samples to a neutral pH.

Samples were then treated with 40% hydrofluoric acid (HF) and warmed on a hotplate at 50 °C for two hours. Next, they were removed from the hotplate and left in the HF for approximately 12 h to complete the silicate digestion, during which time they were stirred occasionally.

Samples were then topped up with water and sieved over a 10-μm sieve cloth; the collected fraction was brought to a neutral pH and placed in a Pyrex glass beaker. The samples were then simmered on a hotplate at 100 °C for approximately 1 h, before being topped up and re-sieved over the 10-μm sieve. The residue was collected and brought to a neutral pH.

The residues were then re-sieved to separate and provide a 10-53 μ and a >53 μ fraction. The >53 μ was then placed in a glass vial, as this would not require any oxidation. A representative sample of the 10-53 μ residue was placed in a glass vial to provide a kerogen (pre oxidation) slide.

Most of the samples required a short period of cold concentrated nitric acid, ranging in time from 5 to 10 min. One or two of the samples required a very short sonication of about 10 s, to reduce the amount of organic amorphous residue present.

Both the 10-53 μ and >53 μ fractions were mounted in Norland Optical adhesive No61.

The slides are housed at the University of Liège, Department of Geology, EDDy Lab/Palynology.

The different palynomorphs observed during this study have been photographed and are illustrated on Plates I to XV. They have been grouped by biological affinities: acirtarchs (Plates I–II), chitinozoans...
Table 1
Pyrolysis and Total Organic Carbon content (TOC) data from sites 10, 11, 12 and 35 using Rock-Eval Pyrolysis method.

<table>
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<th>S2 (mg HC/g rock)</th>
<th>S3 (mg CO2/g rock)</th>
<th>Tmax (°C)</th>
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4. Results and discussion

4.1. Geochemistry data

According to Rodrigues’ (1995) definitions, the geochemical characteristics (Table 1) of the lithological and sedimentological aspects of the outcrops studied (Figs. 2–4), allow for the recognition of the top of Radioactive Shale B in sites 10 and 37. The Radioactive Shale C—of the lower part of the upper Pimenteiras Formation—is recognized in site 12 and in the totality of the section recorded in site 35, as well as in the shales of the upper part of the Pimenteiras Formation in site 11. These radioactive shales were originally described by Rodrigues (1995) using geochemistry data and log profiles from wells located in the center of the Parnaíba Basin.

The top of Radioactive Shale B, recorded in site 10, and the lower part of site 37, is characterized by a TOC of around 1%, which implies a good concentration of organic matter. In most of the samples, the S2 values of between 0.69 and 3.00 mg HC/g rock, and the hydrogen index of between 70 and 200 mg HC/g COT, indicate low source potential for gas.

The data of the hydrogen index show that, in thermally immature samples (values of \( T_{\text{max}} < 430 ^\circ \text{C} \)), the organic matter ranges from type IV to type II. This suggests the predominance of degraded terrestrial organic matter according to Jones (1987). This interpretation concurs with the works of Rodrigues (1995) and Rodrigues et al. (1995), who concluded that the shales below Radioactive Shale C are characterized by a greater influence of higher plants in terms of organic matter composition.

The radioactive Shale C was recorded in sites 12 and 35 and the middle section of site 37. This interval is characterized by TOC contents of 1.0–6.95%, implying a moderate to high concentration of organic matter. The S2 values of between 1.17 and 11.28 mg HC/g rock, and the hydrogen index of between 100 and 336 mg HC/g COT, indicate a low to high potential source of gas and condensate.

Considering that the samples are thermally immature (values of \( T_{\text{max}} < 430 ^\circ \text{C} \)), the hydrogen index data suggests that the organic matter of this interval is heterogeneous, showing a mixture of type IV to type II. However, the literature (Rodrigues, 1995; Rodrigues et al., 1995) shows that the organic matter of Radioactive Shale C is predominantly composed of marine algae. As marine organic matter predominates, it is possible to infer that the lower values of the hydrogen content are causally related to the higher proportion of oxidized organic matter. As the radioactive shales C contains the highest proportion of marine organic matter and the highest total organic carbon contents (sites 12 and 35)—when compared to the Radioactive Shale B and to the upper shales of the Pimenteiras Formation—it can be concluded that they may represent deposits related to the maximum marine flood surface (Rodrigues, 1995) and may therefore represent deeper and more distal areas of terrestrial organic matter influx.

The shales of the upper part of the Pimenteiras Formation are recorded in site 11, where they come into contact with the Cabeças Formation. The total organic carbon contents range from 1 to 2%, representing a high concentration of organic matter. The S2 values of between 2 and 5 mg HC/g rock, and the hydrogen content of between 150 and 230 mg HC/g COT, characterize a moderate potential source of gas.

Since the samples analyzed are less thermally developed (values of \( T_{\text{max}} < 430 ^\circ \text{C} \)), the values of the hydrogen index—at around 150 mg HC/g COT—characterize a predominance of type III organic matter. This aligns with the findings of Rodrigues (1995) and Rodrigues et al. (1995), which describe a greater proportion of higher plants in the composition of the organic matter of the shales above the Radioactive Shale C.

The geochemistry results indicate that the Radioactive Shale B of the Pimenteiras Formation—recorded in the outcropping—exhibit a good concentration of terrestrial organic matter, with a low potential source of gas. The Radioactive Shale C of the Pimenteiras Formation, described in sites 12 and 35, has a good to excellent concentration of marine organic matter and is a low to high potential source of gas and condensate. Lastly, the shales of the upper part of the Pimenteiras Formation, recorded in site 11, show a moderate concentration of terrestrial organic matter with a moderate potential source of gas. However, the pyrolysis analysis shows that the organic matter contained in the Pimenteiras Formation is thermally immature in all outcrops studied in the southwestern area of the Parnaíba Basin.

4.2. Acritarchs and other microalgae (Fig. 5)

Müller’s (1962) palynozonal scheme, based on the combination of major palynomorph groups (acritarchs, miospores and chitinozoans) for the Silurian–Mississippian interval of the Parnaíba Basin in northeastern Brazil, represents the first attempt at dating the pre-Tertiary sedimentary sequence. Müller’s pioneering work was followed by other palynological investigations and the proposition of regional zonation by Brito (1967, 1971); Andrade and Daemen (1974); Daemen (1974, 1976); and Quadros (1982, 1988). Since that time, these studies have remained largely unrevised. However, the opportunity offered by a long collaboration with Petropolis in recent years, based mostly on the study of subsurface materials, has enabled us to systematically analyze acritarch assemblages from the Amazon, Parnaíba and Solimões basins, to define biostratigraphic subdivisions based on these marine and possibly freshwater planktonic microfloras, and to evaluate their stratigraphic value for the Palaeozoic succession in comparison with chitinozoans and miospores. This work is, for the most part confidential. Yet the experience acquired is used here to discuss the biostratigraphic dating of the outcrops analyzed, complementing the data with chitinozoans and miospores.

Acritarchs and other microalgae are well represented in the samples studied, even though miospores are dominant in some samples. A total

Plate I. Acritarchs: Specimens are located according the sample number and the England finders coordinates. The diameter size is provided in \( \mu \text{m} \). 1. Maranhites brasiliensis Brito, 1965 emend Burjack and Oliveira, 1985. Site 11, AM 12, 18K 224, D42 D, total diameter 125 \( \mu \text{m} \). 2. Maranhites lohubatus Burjack and Oliveira, 1985. Site 11, AM 12, 18K 224, Q26, total diameter 145 \( \mu \text{m} \). 3. Maranhites stockmansi (Martin) Martin, 1984, Site 11, AM 12, 18K 224, Q26, total diameter 145 \( \mu \text{m} \). 4. Maranhites mossesi (= M. imitulatus Burjack and Oliveira, 1985) (Sommer, 1956) Brito, 1967, Site 11, AM 12, 18K 224, E25/4, total diameter 120 \( \mu \text{m} \). 5. Petrovina comnato Oliveira and Burjack, 1996. Site 11, AM 17, 18K 220, K13/4, total diameter 145 \( \mu \text{m} \), cells 45 \( \mu \text{m} \). 6. Petrospermopsis crassimarginata Burjack and Oliveira apud Oliveira, 2007, nomen nudum. Site 11, AM 12, 18K 224, D19/2, total diameter 45–50 \( \mu \text{m} \). 7. Crucidia camirene (Lobo Boneta) Ottone, 1996, Site 10, AM 7, 18K 220, P16/3, total length of the processes 80–85 \( \mu \text{m} \). 8. Pseudolumulida multicornuta Brito and Quadros, 1984. Site 35, AM 68, 18L30, 77131, J44/2, central body width 41 \( \mu \text{m} \). 9. Neviusia batillae (Deunff) Playford, 1977 forma crescents. Site 10, AM 7, 18K 220, 742/4, width of central body 25 \( \mu \text{m} \). 10. Disparifusa urinamii Le Hérisse, 2013, nomen nudum. Site 11, AM 12, 18K 224, N13/2, length 52 \( \mu \text{m} \), width 22 \( \mu \text{m} \). 11. Urmellia soridium deflandrei (Moreau-Benoit) Jardiné et al., 1972, Site 11, AM 10, 18K 223, L31/2, total diameter 38 \( \mu \text{m} \). 12. Helogoniella quadrupina Jardiné et al., 1972. Site 11, AM 11, 18K 222, H17/4, central body 45 × 50 \( \mu \text{m} \), process length 6–10 \( \mu \text{m} \). 13. Site 35, AM 78, 18L33, 77146, G29, central body 42 × 24 \( \mu \text{m} \), process length 14.5 \( \mu \text{m} \). 14–16. Duvernoysphaera cruciformis Le Hérisse, 2001, nomen nudum sp. nov. sp. 14. Paratype, site 35, AM 58, 18L27, 77116, S16, central body 30 \( \mu \text{m} \), flange 5.6 \( \mu \text{m} \). 15. Paratype, site 35, AM 58, 18L27, 77116, P32, central body 36 \( \mu \text{m} \), flange 3 \( \mu \text{m} \). 16. Holotype, site 35, AM 76, 18L32, 77141, Q28, central body 36 \( \mu \text{m} \), flange 6.7 \( \mu \text{m} \). 17. Duvernoysphaera anghelae (= D. tessella) Deunff, 1964. Site 11, AM 12, 18K 224, Q38/3, total diameter 45 \( \mu \text{m} \).
of 70 species have been identified (see list in the appendix). Among those definitively identified, are some characteristic species of the Late Devonian. The data obtained enable the subdivision of that interval into two assemblages: the oldest from the Middle to earliest Frasnian age; the youngest from the early Late Frasnian age. The palynological results with acicracts are correlated and largely calibrated by available miospores and chitinozoans zonations (Melo and Lobozia, 2003; Grahn et al., 2006) in use in the same regions. As previously mentioned, we take account of the recent subdivision of the Early Frasnian, into Early and Middle Frasnian. This has affected the dating of the local Bpi miospore Zone of Melo and Lobozia (2003), with the upper part now being referred to as the Middle Frasinian instead of late Early Frasnian. These data makes it possible to correlate the assemblages, including acicracts and prasinophytes, with Late Devonian assemblages documented from the Amazonas Basin (Le Hérissé, 2001), and other regional studies providing information of the stratigraphical distribution of some species (Brito and Quadros, 1984; Oliveira and Burjack, 1996; Oliveira and Burjack, 1997). We also refer to the unpublished thesis by Oliveira (1997) and unpublished personal data. The difficulty lay in working with different outcrops, since we have observed variations in the suites of acicracts and other microalgae on a site by site basis—suggesting some variations in their bi stratigraphy, as previously suggested from the study of miospores. However, the first occurrence of some species, and the associations of species within the different sites, has allowed us to suggest quite an effective resolution in the bi stratigraphic analysis.

4.2.1. First assemblage

A first assemblage of the Middle to earliest Late Frasnian age is suggested, in the material studied. This is due to the association of the following species—Crucidia camirens (Plate I, fig. 7), Duvernoyshera cruciformis nov. sp. (Plate I, figs. 14–16), Leiofusa bisubulata (Plate II, fig. 6), Mediocorpore conspicus (Plate II, fig. 1), Petrovinna connata (Plate I, fig. 5), Pseudolunulidia micropunctata (Plate I, fig. 8) and Puteoscortum limai (Plate II, fig. 5)—in sites 10 and 12, and to the occurrence of Leiofusa bisubulata, Mediocorpore conspicus, Pseudolunulidia micropunctata and Puteoscortum limai in the lower two-thirds of site 35. Comparisons and correlations were made with coeval assemblages known to exist within subsurface successions in the Parnaíba and Amazonas Basins (Le Hérissé unpublished data).

Leiofusa bisubulata which we used in association with other species represented here to characterize the Middle Frasinian is an index species of interest in the eponymous zone. This zone existed prior to the Late Frasinian and overlaps with it and is marked by a consistent occurrence of Maranhites spp. with internal dots. The first specimens of this group appear sporadically in the upper part of the Leiofusa bisubulata zone.

The Leiofusa bisubulata Interval Zone encompasses the main part of the radioactive shale interval of the Parnaíba Basin (Frasnian anoxic event of Rodrigues, 2001; Rodrigues et al., 1995), with equivalents in the lower Frasinian of the Amazonas Basin (Barreireinha Formation). However, even though good components of the radioactive shales, such as the large Tasmanites and leiospheres are well represented in some samples, such as in site 12 but also higher, we never have an over-representation of these elements compared to the Amazonas basin. This fact along with some of the other biostatigraphical results detailed below, might suggest that we are above the interval with a maximum of radioactive shales.

The occurrence of Crucidia camirens and Petrovinna connata at the base of site 10 suggests that these samples are not of earliest Frasinian age. This is because the oldest records of the two species are in the upper part of the Leiofusa bisubulata bizone in other sections of the Parnaíba Basin (based on unpublished data), and this is also reflected in the reference core RSP-1 of the Paraná Basin, where Petrovinna connata was defined (Burjack and Oliveira, 1989).

Important additional species in the first interval, which were distinguished in this study include: Advenasphaeridium australis (Plate II, fig. 4), A. acerosum, ?Chomotrilites sp. (a new form, Plate II, figs. 7–9), Diaphororhocha gracile (Plate II, fig. 11), Duvernoyshera cruciforme nov. sp. (Plate I, figs. 14–16) associated with D. angulata/tessella (Plate I, figs. 17) and well represented, D. radiata (Plate II, fig. 2), D. tenuculigulata, Estiastra spinireticulata (Plate II, fig. 16), Exochodera arca, Geron elegans, Hemiruptia legaultii, Leiofusa fastidiana, common Maranhites (without dots) with Maranhites brasiliensis (Plate I, fig. 1), M. lobulatus, M. magnus, M. primus, M. stockmansi (Plate I, fig. 3), some Navjasca bacilla (Plate I, fig. 9) with the crescentic variants and the long and fine N. bacilla var. procera, Naevipsaferidium sprucegrovense (Plate II, fig. 12), Polyedryxium fragosulum, P. pharaone, Pterospornopsis permambucensis, Tinacula simplex (Plate II, fig. 19), Umbellaspheeridium defandrei (Plate I, fig. 11), U. saharicum, Unellum ampullium (Plate II, fig. 10), U. pirlorome and some tripasiadte Verruchiazia.

4.2.1.1. Correlation with previous regional zonation. In the Parnaíba Basin, the Leiofusa bisubulata zone encompasses the combined upper part of the Samarapisorites triangulatus (Trg), which is not represented here, the Verrucossiporites bullerus—Geminospora piliformis (Bpi) and the lower part of the Rugospora briceli—Diductes murraycon (BMu) miospore zones of Melo and Lobozia (2003). It corresponds to the L. avelinoi chitinozoan zone (Grahn et al., 2006). The higher part of the local Bpi miospore zone is now reassigned to the Middle Frasinian. The Early to early Late Frasinian strata of the Parnaíba Basin correspond to Müller’s (1962) palynozone Q, at least as well as the transition between interval V and VI, sensu Daemon and Contreiras (1971), Andrade and Daemon (1974) and Daemon (1974, 1976).

4.2.1.2. International correlations. Umbellaspheeridium saharicum also recently registered by Andrade et al. (2020) in the upper levels of the Pimenteiras Formation in the southwestern border of the Parnaíba Basin, while never abundant, is of interest in the zone—as a complement to the eponymous species and other key taxa—because of its stratigraphic value as an Upper Devonian index in the Brazilian Paleozoic basins (see also Melo, 2005). It is consistent with the Frasinian through Strunian (Zones L5–L7) range of the species in the Algerian Sahara (Jardín, 1972; Jardín et al., 1974). In Ghana, in some successions...
which are somewhat equivalent to the succession in the Parnaíba and Maranhão Basin, the species is recorded in the Frasnian (Bär and Riegel, 1974). It is also an important species present in the Frasnian assemblage SA3 of Argentina (Noetinger and Di Pasquo, 2011). The first record of the species was certainly by Regali (1964), in the Tucano-Jatobá Basin of northeastern Brazil. The said occurrence, first dated as Middle (?) Devonian by Regali (1964), was later reinterpreted as Frasnian by Brito (1976) and as Strunian by Quadros (1980) and Dino et al. (1996). Another historical record is in the Mac-Mahon Basin, in the upper Famennian-Strunian, as “acritarче à entonnois” N°441-33 by Lanzoni and Magloire (1969). The accurate stratigraphic distribution of Umbellaphaeridium saharicum in the U.S.A is more complex, since the material is associated with reworked elements in the Late Devonian (Wood, 1984).

There is a good correlation with the Late Devonian of Argentina, particularly the Los Monos Formation assemblages described in the Tarija Basin. Many of the species recorded by Ottone (1996) occur in the Leiofusa bisubulata biozone, such as: Leiofusa bisubulata (as Leiofusa sp. Plate VII, figs. 7, 8 in Ottone) (Plate II, 6), Maranhites mosesii (Plate I, 4) and Pseudolunulidia spp. The re-description of Crucidia camirense (Plate I, fig. 7) in Argentina is also noteworthy, after the species was first illustrated in Bolivia by Boneta, (1975). With the presence of Crucidia camirense in Argentina, among other elements in Argentina, we consider the age of these Argentinian assemblages as most likely early Late Frasnian, rather than Late Givetian to Early Frasnian as suggested by Ottone (1996).

As discussed earlier, direct comparisons are also possible with the Paraná Basin and the reference RSP-1 borehole, previously studied by Burjack et al. (1987), Loboziak et al. (1988), and Oliveira (1997). Many of the species found in the Leiofusa bisubulata biozone were described for the first time in the RSP-1 core-drill (Oliveira and Burjack, 1996; Oliveira and Burjack, 1997), yet many species are still nomen nudum. The equivalent of the Dc-Lb Zone is the interval between 60.50 and 200 m. Species in common include Advenasphaeridium acerosum (nomen nudum), A. australis (nomen nudum) (Plate II, fig. 4), Crucidia camirense (Plate I, 7), Diaphorochroa gracile (nomen nudum) (Plate II, fig. 11), Nuevissphaeridium hercyniana, Leiofusa bisubulata, Petrovina connata (Plate I, fig. 5), the netromorphs Navifusa bacilla crescentis (Plate I, fig. 9) and Pseudolunulidia micropunctata (Plate I, fig. 8).
4.2.2 Second assemblage

The stratigraphically higher assemblage is defined in the last three samples of site 35 the last four samples of site 11 and up to sample 86 in site 37. It contains significant species that are unrepresented in the lower assemblage, including Horologinella quadrispina (Plate I, figs. 12–13), Maranhites mosesii, Pseudomaranhites densus, Pterospermopsis crassimarginata (Plate I, fig. 6), Veryhachium capitata nov. sp. (Plate II, fig. 17), Veryhachium insanus nov. sp. (Plate II, fig. 18) and V. pannucecum.

In the Amazon Basin, the succession of Veryhachium insanus, Bipolarisvelata accreta and the introduction of Horologinella quadrispina is observed in the reference core Caima PH-2 (Le Hérisse, 2001), at the boundary between Middle and Late Frasnian. It corresponds also to an interval marked by the appearance of Maranhites mosesii.

The order of appearance of some of these species is also the same in the upper part of the RSP-1 core in the Paraná Basin (see Oliveira, 1997, fig. 18). But the material does not include the introduction of Horologinella quadrispina (Plate I, figs. 12–13).

Pterospermopsis crassimarginata is also a common component of the zone, but it can be mentioned as a precocious appearance of this species in the Paraná Basin, where it has been defined for the first time.

Putescortum williereae is the index species of Zone Pw (Vanguestaine et al., 1983) and is characteristic of the lower Famennian in Belgium. Our data point to an earlier introduction of the species in the Frasnian of Brazilian successions, whereas its regional exit is in the Middle Famennian.

In terms of correlation with previous regional zonation, the higher assemblage recognized here will be equivalent to the lower part of the Rugospora bricei–Diducites mucronatus (BMu) zone of the Late Frasnian age, according to Melo and Loboziak (2003) and Grahn and Melo (2005).

4.3 Chitinozoans

Devonian chitinozoans from the Parnaiba Basin were first discussed by Müller (1962). His Silurian through Lower Carboniferous Biozones were divided into seven zones, ranging from N (upper Visean) to T (upper Silurian), based on chitinozoans, spores and acritarchs. The Pimenteiras Formation corresponds to his Zone Q (upper Zone R–P by Brito, 1967, 1971 and Q–P by Quadros, 1982). These zones were, until recently, regarded as a reference palynomorph biozonation for the Parnaiba Basin (e.g. Brito, 1967, 1971; Daemon, 1974, 1976; Quadros, 1982; Molyneux et al., 1996). Daemon refined the Silurian–early Carboniferous sequence into 12 biozones based on miospores. In his scheme, the upper zones 5 and 6 correspond to the Pimenteiras Formation. Sommer and Boekel (1964) described Middle Devonian chitinozoans from outcrops of the lower Pimenteiras Formation on the western margin of the Parnaiba Basin. Concurrently, Daemon (1964) formulated a generalized chitinozoan biostratigraphy for the basin using Müller’s zonal scheme as a framework. Lange (1967) briefly mentioned chitinozoans from the Parnaiba Basin, and Cruz and Quadros (1985) described a new chitinozoan species from the latest Frasnian–early Famennian. More recently, chitinozoans have been discussed and correlated with miospores in papers by Grahn and Melo (2005), Grahn et al. (2001, 2006, 2008) and Breuer and Grahn (2011). The Pimenteiras Formation consists of a lower Middle Devonian section, separated by a hiatus from the upper Late Devonian section.

The chitinozoans encountered in the present study constitute a characteristic Frasnian assemblage, although not earliest or latest Frasnian. They are typical for the early to early Late Frasnian Angochitina (Lagenochitina) avelinoi (Lage, 1952) are recorded in the Late Devonian of the major intracratonic basins of Brazil. The latter species has a more restricted range in the Paraná (early Late Frasnian) and Amazonas Basins (early Frasnian). In the Parnaiba Basin, there is a variety of Angochitina mouri with a long neck, common in the early Late Frasnian. Lagenochitina sp. A in Grahn and Melo (2005) (Plate IV, figs. 15–16), along with similar specimens, are recorded from the early Frasnian but are also common in the early Late Frasnian. Fungochitina pilosa (Collinson and Scott, 1958) (Plate IV, figs. 11, 12) is something of a vast basket, and specimens like Fungochitina pilosa have been recorded from the late early Eifelian to the Frasnian. Lagenochitina sommeri (Lange, 1952) (Plate IV, figs. 13–14) was first described from the early Frasnian in the Amazonas Basin, but also occurs in the early Late Frasnian of the Parnaiba Basin. Both Angochitina sp. C and Fungochitina microspinosa (Grahn and Melo, 2005) (Plate III, figs. 9–10) are common Frasnian species in the Parnaiba Basin. Although an early Frasnian age cannot be excluded, the chitinozoans present are altogether more similar to an early late Frasnian age.

4.4 Miospores

4.4.1 Results

Several studies on miospores are available for the Frasnian of the Parnaiba Basin. Most have been carried out by Loboziak and his co-authors (e.g., Burjack et al., 1987; Dino et al., 1996; Grahn et al., 2006, 2008; Loboziak et al., 2000; Loboziak et al., 1994; Loboziak et al., 1992b). Few papers describing the whole Frasnian assemblage of outcrops or cores from the western Gondwana are available.

The miospores observed here are well preserved, and yellow to pale brown in color. The assemblages are rich and diverse. The most prolific samples in miospores are the N” AM7, AM8, AM9, AM89 and AM95. Samples AM50, AM53, AM55, AM60, AM65, AM70, AM80, AM85 and AM88 contain rare miospores. In all the samples, miospores are more abundant than marine palynomorphs, especially in the upper part of the section where acritarchs are rarer. This decrease in the quantity of acritarch input has also been noted in the upper part of the Pimenteiras Formation of the Well 2-PM-1-MA (Loboziak et al., 1992b), probably corresponding to a regression.

Weak variations in the composition of the assemblages have been observed throughout the sequence, except for very minor differences. Moreover, as the different sections are being separated by outcrop
gaps, their lateral geometrical relationship is somewhat difficult to achieve.

The richest levels in miospores contain more or less the same assemblage in which the most helpful species for biostratigraphy are known from the classical Boulonnais area from Northern France (Streel et al., 1987; Loboziak et al., 1988). Among them, the following species have been observed: *Samarisporites triangulatus* (Plate XV, figs. 1–3), *Chelinospora concinna* (Plate VII, figs. 6–9), *Verrucosisporites bulliferus* (Plate XV, figs. 4–6), *Lophozonotriletes media* (Plate XIII, figs. 9–10), etc. These suggest the Frasnian age. The oldest sample from
the site 10 (AM7) already contains, among others, Verrucosisporites bulliferus (Plate XV, figs. 4–6) and Lophozonotriletes media (Plate XIII, figs. 9–10).

In the Boulonnais area of northern France (Streel et al., 2000a), miospores occur in the same sections as conodonts. The chrono-stratigraphic limits of the Frasnian stage, fixed on conodonts in the Montagne Noire area, can thus be transferred to the Boulonnais area.

In this area, Chelinospora concinna and Samarisporites triangulatus—which characterize the TCo Zone—first occur in the upper Givetian but are still present in the Early and Middle Frasnian. Verrucosisporites bulliferus first occurs in the early Frasnian and Lophozonotriletes media in the Middle Frasnian (BJ and BM Zones), but both are still present in the upper Frasnian and the Famennian. Rugospora bricei, Grandispora gracilis and Diducites plicabilis (BA Zone or Regional “IV” Zone) first occur successively in the upper Frasnian but are still present in the Famennian (Streel, 2009).

A Middle to Late Frasnian (but not latest) age is therefore suggested for all the studied samples.

4.4.2. Discussion

4.4.2.1. Correlations with Brazilian biostratigraphic scale (Fig. 6). Miospores from the Givetian to the Tournaisian have been studied by Loboziak et al. (2000) in the Tocantins Valley of the Parnaíba Basin located some 120 km away from the sections studied here. The biozones from the Boulonnais area (Streel et al., 1987), ranging from TCo to
BM-“IV” (or BA Zone), were used in this paper as well as in Loboziak and Melo (2002). New biozone names (BPI–BMu-TP) were introduced later by Melo and Loboziak (2003) in the Amazon Basin. Among the Tocantins Valley samples from the Pimenteiras Formation, 12 are shown to belong to the Frasnian. A total of 32 taxa have been identified in these 12 samples including 9 taxa which are restricted to the Frasnian. From our samples there are only 15 taxa in common with these 32 taxa recorded in the Tocantins Valley. 7 of the 32 taxa are also known in the Cabeças Formation belonging to the Latest Famennian where they are “ascribed to reworking on the basis of differential preservation or color” (Loboziak et al., 2000, p. 308). However, it is possible to correlate the two areas, thanks to the species Lophozonotriletes media, Grandispora tabulata (Plate XIII, figs. 1-2), Verrucosisporites bulliferus and Samarispores C (synonym of S. sp. E in Melo and Loboziak, 2003) (Plate XIV, figs. 10-12).

In the samples studied herein, Verrucosisporites bulliferus is one of the eponymous species of the BPI Interval Zone—along with Geminospora piliformis—according to the biozonation established in Brazil by Melo and Loboziak (2003). This biozone is marked by the FOB of Verrucosisporites bulliferus. The analyzed samples should thus belong to the BPI Interval Zone in Brazil, despite the absence of observation of Geminospora piliformis—a species that is poorly scattered and controlled. However, Melo and Loboziak (2003) note that in the Paraná Basin’s Ponta Grossa Formation, Geminospora piliformis appears with Lophozonotriletes media in the upper part of the zone, allowing the zone to be subdivided into two parts, and demonstrates a correlation of this higher interval with the BM Oppel zone of Western Europe. The
BPi Zone has also been observed in the Amazon Basin, and probably also in the Solimões Basin within the Jandiatuba and Uerê Formations.

*Rugospora bricei* is a species appearing in Biozone BA (ex “IV” Refional Zone) in Western Europe (Streel et al., 1987). This species is also known in Brazil and appears close to the base of the BMu Biozone (Melo and Loboziak, 2003). Two specimens like *Rugospora bricei* have been observed in site 10, samples 7 and 8. However, the nature of the convolute proximal muri is different to those of the original species; they are too coarse. Thus, the two specimens are here considered as *Rugospora cf. Rugospora bricei* (Plate XIV, figs. 7–8). *Rugospora bricei* is also close to *Rugospora radiata*. The main differences are in the size and arrangement of the rugulae in *Rugospora flexuosa* are much coarser (Higgs et al., 2013). These last two species are known in the Famennian.

Among other important species for the biostratigraphy, *Camarozonotriletes concavus* (Plate VII, figs. 4–5) first appears in the Eifelian and is supposed to have disappeared close to the Bj–BM boundary (Loboziak and Melo, 2002). *Grandispora tabulata* first appears just below *V. bulliferus* and is known up to the Famennian (Loboziak et al., 1988). *Auroraspora macra* (Plate VII, figs. 1–3), which has been known
since sample 7, first appears at the boundary between Biozones BM and BA (ex “IV” Regional Zone) (Loboziak et al., 1988) and is known up to the Tournaisian (Zwan, 1980).

Most of the spores are geographically cosmopolitan, except for some species that are restricted to the Gondwana like *Geminospora piliformis, Grandispora gabiesensis, Grandispora libyensis* (Plate X, figs. 6–7) and *Grandispora tabulata*.

4.4.2.2. Correlation with the European biostratigraphic scales (Fig. 6). Givetian to Lower Famennian deposits, containing miospores, are widespread on the territory of the Pripyat Depression in SE Belarus and the Timan–Pechora Province in Russia. The biostratigraphy of these deposits is based also on conodonts in the Timan–Pechora Streel et al., 2021.

Correlations during the Late Givetian to Middle Frasnian between Boulonnais and Eastern Europe are shown to be obvious from varcus to punctata conodont Zones. They are less obvious from the Middle Frasnian to the Early Famennian (Obukhovskaya, 2000; Streel et al., 2000b; Telnova, 2008; Telnova et al., 2019).

*Geminospora lemurata* (Plate IX, figs. 5–6) is well known and distributed worldwide, appearing just above the Eifelian/Givetian boundary.
This species characterizes the Lem Interval Biozone (Streel et al., 1987). *Samarisporites triangulatus* first appears in the late Givetian and is the eponymous species of the TA and TCo Biozones (Streel et al., 1987) in Europe. The species may reach the Tournaisian in both Brazil and Tunisia (Loboziak et al., 1992a; Loboziak et al., 1988; Melo and Loboziak, 2003). *Chelinospora concinna*, the second eponymous species of the TCo Biozone, appears below the Givetian/Frasnian boundary. *Verrucosisporites bulliferus* appears above the base of the Frasnian and characterizes Biozones BJ and BM (Streel et al., 1987), which are both included in the lower part of the Frasnian. Finally, *Lophozonotriletes media* is characteristic of the BM Biozone (Streel et al., 1987), around the Middle Frasnian.

The synthesis of miospore based on Givetian to Famennian biostratigraphy in the Boulonnais (Loboziak et al., 1988) did not provide detailed analysis of the data accumulated by Loboziak et al. (1983) in the Upper Frasnian. Restudy of this data and new samples collected in boreholes from neighboring Flanders (Belgium) allow for better characterization of the transition from Middle to Lowermost Famennian and a comparison with contemporary Eastern Europe miospores based zonations. (Streel et al., 2021). The correlation at the BM/BA transition dated...
Upper Frasnian by the *rhenana* conodont Zone in Eastern Europe points to the inaccuracy of the Ferques succession and Hydrequent Formations with regard to tracing the base of the Upper Frasnian in the Boulonnais. A first look at the many recorded ranges of taxa immediately suggests, in the first instance, a sampling gap between these formations. Obviously, it also suggests a deep change in the vegetation cover occurring at that level corresponding more or less to the Lower Kellwasser Event (LKW) starting in the lower *rhenana* conodont Zone (Becker et al., 2016).

If the Melo and Loboziak’s (2003) correlation of the Brazilian BPI Zone with the West European BJ and BM Zones makes sense, alignment of the base of the Brazilian BMu Zone with the base of the West European BA (ex “IV”) Zone is not secure. Nevertheless the FOB in the Pimenteiras Formation of *Auroraspora macra, Samarisporites* sp. C in Loboziak et al., 1983) (synonym of S. sp. E in Melo and Loboziak, 2003) and possible *Rugospora bricei* occurring within the lowermost part of BA Zone (ex IV a-b or BA pre-gracilis subzone in Stree, 2009) confirm the presence of an early part of the Upper Frasnian.

### 5. Geochemistry and maximum flooding surface

Some authors (Myers, 2004; Sutton et al., 2004; Lüning et al., 2004; Rodrigues, 2005; and references therein) have described the relationship between TOC content and the stratigraphy of sequences. Organic matter preservation in the sedimentary record depends on many factors. Myers (2004) pointed out that the most important factors are the physiography of the basin, climate, terrestrial organic productivity, marine aquatic organic productivity, oceanic circulation, sedimentation rate and water depth. With the exception of climate and oceanic circulation, the other factors described by Myers (2004) are influenced by relative sea level change.

Under lowstand conditions, the high sediment influx product, the dilution of the organic marine matter content and the organic terrestrial
matter are highly oxidized. In this context, the amount of organic matter preserved in the sediments is low and the consequent TOC values are inexpressive.

In the transgressive system tract, the rapid increase in relative sea level caused the shoreline to retreat landward. It resulted in a progressive extension of the shallow marine shelf deposition, and in a reduction of the clastic sediment supply. According to Lüning et al. (2004), the transgression has likely led to sediment starvation because the detritus became trapped in river mouths, thus preventing the dilution of the organic matter on the shelf. These conditions led to the progressive expansion of the deep distal area of the basin until it reached the maximum flooding surface (MFS). In this basin, therefore, there was an extension of the anoxic conditions, which permitted an increase in the preservation of organic matter. The retreat of sediments at the shoreline decreased the dilution of organic matter in the depositional setting. In contrast with the lowstand conditions, the TOC values increased, reaching a maximum at MFS.

As also observed in the section studied in this work, Creaney and Passey (1993) noted that many marine source rocks are characterized by an initial abrupt upward increase in organic content, which, in contrast with background values, and a subsequent gradual decrease in organic content (Myers, 2004). The authors attributed this pattern to the control of the organic carbon contents by the clastic sedimentation rate, under anoxic bottom water conditions. The rapid increment of TOC results from the retreat of the sediments in the source, during the transgression. The subsequent gradual decrease in TOC reflects the increase in the clastic sediment supply and the dilution of organic carbon during highstand progradation. In this context, the MFS is positioned at the turning point of the TOC curve. Most authors consider it to be partly contained in the lower highstand, and partly in the upper transgressive systems tracts (Sutton et al., 2004; Posamentier and Allen, 1999).

This succession is well defined in the section studied, where the TOC ranges from low to moderate in site 10 (Fig. 3). In the subsequent interval (site 12), associated with Radioactive Shale C, the TOC shows an
abrupt increase, defining the improved conditions for organic matter preservation. These conditions mark the maximum flooding surface. This interval is also observed at the base of site 35. In the interval above (site 11), the TOC decreases towards the Cabeças Formation, which indicates the start of the regression system and the consequent increased inflow of sediment toward the basin.

6. Conclusions

The palynological results—based on acritarchs, chitinozoans and miospores—are relatively well concordant, and correlatable with Devonian palynozones in use in northern Brazilian basins.

The occurrence of several species of acritarchs—such as Leiofusa bisubulata, Mediocorpore conspicuus and Pseudolunulidia micropunctata—in sites 10 and 12, and in the lower 2/3 of site 35, have made it possible to distinguish a first assemblage of Middle to earliest Late Frasnian age. In the last three samples of site 35 and the last four samples of site 11, and from site 37 up to sample 86, we observe the occurrence of Horologinella quadrispina, Maranhites mosesii, Pseudomaranhites densus, Pterospermopsis crassimarginata, Veryhachium capitata nov. sp., Veryhachium insanum nov. sp. and V. pannuceum. This points to a late Frasnian age, quite equivalent to that of the miospore Biozone Rugospora bricei–Diducites mucronatus (BMu).

The chitinozoans that were identified in the different slides belong to a common assemblage characteristic of the Frasnian and, more
Plate XV. Miospores: Specimens are located according the sample number and the England finders coordinates. The scale bar is annotated in μm. 1–3. Samarisporites triangulatus Allen, 1965. 1: Site 10, Am8 6, X21/2; 2: Site 11, Site 11, Am8 10, Q22/1; 3: Site 10, Am7 2; G21/0. 4–6. Verrucosisporites bulliferus Richardson et McGregor, 1986. 4: Site 10, Am7 2, V16/4; 5: Site 37, Am89 96, V17/1; 6: Site 7, Am 8 6, G27/4. 7–8. Verrucosisporites premnus-scurrus Morphon Breuer and Steemans, 2013. 7: Site 10, Am7 2, B17/1–3; 8: Site 11, Am9 10, N18/3; Site 10, Am7 2, S18/3.

Fig. 5. Miospore biostratigraphic scale from the Old Red Sandstone Continent (A), correlated with Brazil (B). Most probable age of the analyzed samples (C). Extension of the most diagnostic species of Acritarchs and other microalgal remains recognized in the material studied, age and correlation of the interval represented.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We would like to thank the two anonymous reviewers who have made valuable improvements to the realization of this manuscript. We thank M. Jones for the processing of the samples and Enda Breen for the reviewing of the English. PS is FSR-FNRS Senior Research Associate. EP, MB, SB, and RR are grateful to CNPq, FAPERJ, Finep and FUSP for the research fellowship (MB) and for financial support in the scope of the Project “Rede GASBRAS”.

Appendix A. Appendix

List of species encountered in the material and/or cited in the text

Acritarchs

*Advenasphaeridium acerosum* Burjack and Oliveira *apud* Oliveira, 1997, *nomen nudum*

*Advenasphaeridium australis* Burjack and Oliveira, 1997, *nomen nudum*

*Arkonites bilixus* Legault 1973

*Bimerga bensonii* Wood, 1995

*Bipolarisvelata accreta* Burjack and Oliveira *apud* Oliveira, 1997, *nomen nudum*

*Chomotriletes* sp.

*Cruclidia camirense* (Lobo Boneta) Ottone, 1996

*Diaphorochroa gracile* Burjack and Oliveira *apud* Oliveira, 1997, *nomen nudum*

*Disparifusa urariaensis* Le Hérissé, 2013, *nomen nudum*

*Duvernaysphaera angulata (=D. tesselata)* Deuff, 1964

*Duvernaysphaera capitana* (Wicander) Le Hérissé nov.comb.

*Duvernaysphaera cruciformis* Le Hérissé, 2001, *nomen nudum*

*Duvernaysphaera heliocentrica* Burjack and Oliveira *apud* Oliveira, 1997

*Duvernaysphaera radiata* Brito, 1967a

*Duvernaysphaera stellata* Deuff, 1964b

*Duvernaysphaera tenuicingulata* Staplin, 1961


*Estiastria spinivinculata* Oliveira and Burjack, 1997

*Exochoderma arca* Wicander and Wood, 1981

*Exochoderma irregulariae* Wicander, 1974

*Geront elegans* Oliveira and Burjack, 1997

*Gorgonisphaeridium winslowiae* Staplin et al., 1965

*Hemiruptia legaultii* Ottone, 1996

*Horologinella horologia* (Staplin) Jardiné, Combaz, Peniguel and Vachey, 1972

*Horologinella quadrispina* Jardiné, Combaz, Magloire, Peniguel and Vachey, 1972

*Leiofusa bisubulata* Brito and Quadros, 1984

*Leiofusa fastidiosa* (Cramer and Diez) nov. comb.

*Maranhites brasiliensis* Brito, 1965 emend *Burjack and Oliveira, 1989*

*Maranhites britoi* Stockmans and Willière, 1969 *R5 + R6 + R7 + R8

*Maranhites lobulatus* Burjack and Oliveira, 1989

*Maranhites magnus* Burjack and Oliveira, 1989

*Maranhites mosesii* (Sommer, 1956) Brito,1967

*Maranhites stockmannsi* (Martin) Martin, 1984

*Mediocorpore conspicuosus* Burjack and Oliveira *apud* Oliveira, 1997, *nomen nudum*

*Multiplicisphaeridium ramosculosum* (Deflandre) Lister, 1970

*Naevisphaeridium desideratum* (Burjack and Oliveira *apud* Oliveira, 1997) *nomen nudum* nov.comb

*Naevisphaeridium sprucegrovense* (Staplin, 1961) nov.comb.

*Nanofusa bacillar* (Deuff) Playford, 1977

*Nanofusa bacillar* (Deuff) Playford, 1977 *forma crescentis*

*Nanofusa bacillar* var. *procera* (Deuff, 1966) nov.comb.

*Palacanthus ledanoisii* Deuff, 1957, emend Playford, 1977

*Petrovina connata* (Deunff, 1966) nov.comb.

*Polyedryxium embudum* Crémant, 1964

*Polyedryxium fragosulum* Playford, 1977

*Polyedryxium pharaone* Deuff, 1961
Polypeditygium sp. or Muraticavia multinucifera Wicander and Wood, 1981
Pseudolunulidul sp. mucropunctata Brito and Quadros, 1984
Pseudomaristites densus Quadros, 1996
Pterospermopsis crassimarginata Burjack and Oliveira apud Oliveira, 2007, nomen nudum
Pterospermopsis pernambucensis (Brito) Eisenack
Umbellasphaeridium saharicum
Pseudolunulidia micropunctata
Umbellasphaeridium de Tasmanites
Pterospermopsis crassimarginata
Tinacula simplex
Rugospora
Lophozonotriletes media
Grandispora tabulata
Grandispora libyensis
Grandispora gabesensis
Geminospora piliformis
Diducites plicabilis
Cyrtospora tumida
Chelinospora concinna
Rugospora radiata (Kedo) Byvscheva, 1985
Samarisporites sp. C in Lobzoi ib et al., 1983
Samarisporites amplus (I.M.) de Quech, 1986
Verruciterissuspora magnifica (McGregor) Owens, 1971
Verrucosiporites bulliferus Richardson and Mc Gregor, 1986


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P. Steemans, E. Pereira, A. Le Hérissé et al. Review of Palaeobotany and Palynology 284 (2021) 104345


