Lethaia
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Exceptional preservation of Triassic-Jurassic fossil plants: integrating biosignatures and fossil diagenesis to understand microbial-related iron dynamics

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LETHAIA

Studying exceptionally well-preserved biotas can bring significant answers to the relationship between micro-organisms, biosignatures, and preservational processes. Among impressions of plants from Triassic and Jurassic beds of southernmost Brazil, there are branches and leaves coated by iron crusts, attributed to the precipitation of iron oxide-oxyhydroxides. Underneath the crusts, the leaves retained minute anatomical features of their epidermal cells and stomatal complexes, which are rare in other types of preservation. We evaluate the chemical nature and microstructure of these crusts to solve their genesis and the role of micro-organisms in the precipitation of iron minerals. For this purpose, we apply the following analytical geochemical techniques: Raman spectroscopy and Mössbauer spectrometry, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and energy dispersive spectrometry (EDS). The crusts are composed of α-goethite and traces of smectite. We identified potential biogenic microstructures such as ferrihydrite nodules, bacterial exudates morphologically compatible to extracellular polymeric substances (EPS), and structures like twisted stalks and sheaths that fit the biogenicity criteria established so far. These microstructures suggest that the iron crusts were produced by the activity of freshwater microaerophilic and neutrophilic organisms. The studied material allows us to reconstruct key diagenetic processes that facilitated authigenic preservation along with exceptionally well-preserved biosignatures. □ *Mesozoic, plant fossils, iron oxyhydroxides, microbial activity, biogenic structures*.

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Exceptionally well-preserved palaeobiotas (Fossil-*Lagerstätten*, Seilacher *et al.* 1985) are recorded in various sedimentary environments (e.g. lacustrine, marine), spanning millions of years of geological time. Some classical examples range from the Archaean microfossils of Australia, preserved in the Apex Chert (Schopf 1993) – that helped scientists to understand and establish biogenicity criteria – to the Devonian Flora of Rhynie, Scotland, attesting the earliest preserved stages of terrestrialization among plants (Anderson & Trewin 2003).

Lagerstätten provide geomicrobiological and other preservational information used to rescue key aspects of past environments (Martínez-Delclòs *et al.* 2004; Raff *et al.* 2008). Hence, detailed studies of these high-quality and high-fidelity preservations may clarify, for instance, essential evidence for understanding the history of biodiversity and the evolution of life on Earth, besides helping to delineate the role of micro-organisms in fossil preservation processes (Allison 1986; Laflamme *et al.* 2011).

Another aspect that can be addressed with exceptionally well-preserved fossils is the identification of biosignatures, which reveal indirect evidence of life on present and ancient Earth, and in other worlds from our Solar System (Conrad & Nealson 2001). Studies on fossil diagenesis and experimental taphonomy have revealed the importance of micro-organisms in replicating delicate structures and morphologies of organisms (Briggs 2003; Iniesto *et al.* 2018). Thus, the investigation, detection, and interpretation of fossil biosignatures, compared to modern experimental results, assist with defining and revising biogenicity criteria (Schopf *et al.* 2012; Bower *et al.* 2015; Gomes *et al.* 2019).

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Bacteria, and their biosignatures, play a role in the iron biogeochemical cycle, but they were so far observed only in recent environments or during experimental approaches (Suzuki *et al.* 2011; Fleming *et al.* 2014; Bryce *et al.* 2018). Here, we report potential biogenic microstructures in iron-bearing coatings that preserved plant remains with a unique degree of detail, within the Triassic–Jurassic interval of the Paraná Basin, southernmost Brazil. We also propose a reconstitution of the processes that enabled the preservation of fine anatomical details of this flora. Finally, we explore the biogenicity potential of structures and minerals, which can constrain the role played by micro-organisms in the fossilization process.

Material and methods

Origin and preservation of the fossils

The material analysed consists of gymnosperm leaf and stem remains, including pteridosperm fronds identified in situ in two lacustrine deposits (Fig. 1). The samples were dated as Carnian/Norian (Santa Maria Formation) and possibly early Jurassic (Caturrita Formation), both from the Paraná Basin, southernmost Brazil (Barboni & Dutra 2015; Barboni *et al.* 2016; Langer *et al.* 2018). The studied fragments are kept in the Paleontological Collection of the Museu de História Geológica do Rio Grande do Sul (MHGEO), at UNISINOS University, under the acronym ULVG followed by identification numbers (*Dicrodium:* ULVG – 09663; Conifer branches: ULVG – 10975; 7999; 7005a; 7976 and 10846). Additional information on the geological settings can be found in the online Supplementary Information.

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS)

Morphological and on-spot geochemical analyses were made by SEM and EDS using an EVO/MA15 Zeiss scanning electron microscope at the Technological Institute for Paleoceanography and Climate Change (itt OCEANEON), UNISINOS University. Tension ranged between 4–5 kV with a number of interactions = 5. We analysed transverse and horizontal polished sections of small branches (5 branches from São Luis (SL)) of the most resistant conifers. For the *Dicroidium* and related forms, a direct analysis, without any polishing of the iron coats, was performed over the leaves (5 leaves from Passo das Tropas (PT)). All samples were gold-coated during three minutes in a Quorum Q150TES.

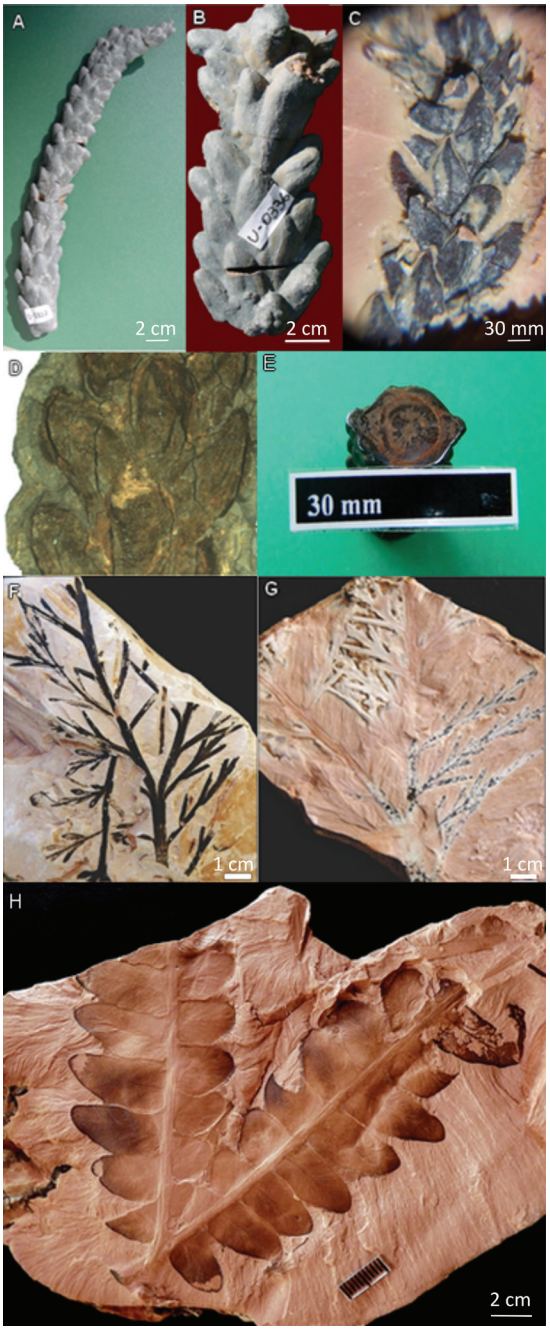

Fig. 1. Distinct modes of preservation of plant remains from the studied outcrops. A–E, fossil plants from the São Luis outcrop, Caturrita Formation). A–C, 3D-preserved branches of conifers (Crisafulli *et al.* 2018; Langer *et al.* 2018) showing their helical disposed leaves. D, a longitudinal section of the form in B. E, cross-section from a small branch of *Kaokoxylon zalesskyi* (Sahni) Maheshwari (Crisafulli *et al.* 2018), exposing the external crust, bark and sapwood, barely visible growth rings, as well as the pith and the admedial parts of two immature leaves. F–H, pinnae of Corystospermales from the Passo das Tropas outcrop (SM2 Sequence (Zerfass *et al.*, 2003), Santa Maria Formation). F, G, fronds of *Xylopteris spinifolia* (Tenison-Woods) Frenguelli, with and without iron coatings (Barboni *et al.* 2016). H, fine iron coating over a frond fragment and pinnule of a form related to *D. lancifolium* (Morris) Gothan, highlighting the venation pattern. Leaf coatings from SM2 are thinner and only partly cover the lamina.

X-ray fluorescence (XRF) and carbon/sulphur analyses

We performed XRF analyses to characterize the elemental composition of the samples in order to complement the EDS results (EDS detects elements with high and low atomic numbers, but XRF better detects higher atomic numbers of trace elements). We used the loose powder of the crusts surrounding the internal parts of coniferous branches and ran semi quantitative analyses in a Panalytical Epsilson 1 at itt OCEANEON. We also evaluated carbon and sulphur concentrations in the crusts with a LECO SC-144DR sulphur and carbon analyser at itt OCEANEON.

X-ray diffractometry (XRD)

Samples of iron oxide coatings from conifer branches (grain size fraction <4 μm) and aliquots of the fine fractions from the sedimentary matrix rocks (grain size fraction <2 μm) were analysed by X-ray diffraction (XRD). During the analysis of clay minerals, we used a Siemens D5000 Diffractometer, from the Laboratory of X-ray Diffraction of Geosciences Institute, Federal University of Rio Grande do Sul (UFRGS). The diffractometer operated in the following conditions: KαCu radiation, 40 kV, 30 mA filament current and interval from 2° to 28° (2θ). Fine fractions of the host rocks were first pulverized in an agate mortar and five grams of the resulting powder were dispersed in 50 ml of distilled water, later subjected to ultrasound in the presence of a solution of sodium pyrophosphate (a deflocculant). The fine fraction (FF) <2 μm was separated by centrifugation from the resulting solution. This fraction was deposited in two glass slides, so clay minerals were oriented according to the smear technique. The slides were then dried under natural conditions.

To identify clay minerals, one of the slides was initially analysed (denominated normal). For the interpretation of the diffractograms in the fine fraction aliquot (clay), we compared the main peaks with the PDF2 standards computer database, with the Diffrac Plus Siemens Bruker-Axs software that allows for the identification of minerals or phases present in the sample.

The other slide was treated in a desiccator containing ethylene glycol (CH_2OHOH_2OH). The desiccator was then taken to a heated oven at 60 °C for eight hours, to produce a glycolate slide, which enabled us to verify the existence of expansive clay minerals. After the analysis of this second slide in the diffractometer, calcination was carried out for two hours in an oven at 500 °C (calcinated slide). This technique assists in evaluating the collapse structures of specific clay minerals. From the joint analysis of the diffractograms (normal, glycolated and calcinated) and comparison with standards, we recognized the clay minerals present in the fine fraction.

For the analysis of pulverized aliquots of internal and external portions of the crusts of coniferous branches from the Caturrita Formation, we used an Empyrean Panalytical diffractometer at itt OCEANEON and compared the peaks to the reference database. The diffractometer operated in the following conditions: KαCu radiation, 40 kV, 40 mA filament current and interval of 5° to 80° (2θ).

Raman spectroscopy

Raman spectrometry was applied to the same pulverized samples of the crusts used for the XRD analyses, to characterize the iron oxide/hydroxide phases. The equipment used was a HeNe Laser Spectrometer 632.8, with a laser diode of 532 nm, located at the Laboratory of High Pressures and Advanced Materials (LAPMA), UFRGS.

Mössbauer Spectrometry

We used Mössbauer spectrometry to investigate the chemical phase of goethite. Measurements were performed at the Laboratory of the Physics Institute (IF), UFRGS. Room temperature ^{57}Fe Mössbauer spectra were recorded using a conventional spectrometer, operating in constant acceleration mode with a ^{57}Co (Rh) source. Isomer shift values are reported relative to α-iron at room temperature. The experimental spectra were treated using the least-squares method and, in the analysis, we used a method with the distribution of magnetic hyperfine fields corresponding to the different atomic environments of iron. These adjustments were considered as Lorentzian lines with fixed widths, and the Wivel and Morup, 1981.

Results

Preservation of anatomical structures

Two distinct and rich floras were analysed, preserved in different stratigraphical intervals, (see supplementary information). The occurring plant fossils, such as *Dicroidium*, *Xylopteris*, *Zuberia* and Bennettitales bear thin crusts of iron oxide-hydroxide minerals, mainly concentrated over the rachis, megaspores and veins of more coriaceous leaves (Fig. 1F–H).

Scanning electron micrographs reveal the fine preservational state of the anatomical macro- and microstructures of the Santa Maria Formation leaves (epidermal cells and stomatal complexes), and also from the wood branches (tracheids, pits and resin canals) from the Caturrita Formation. The coatings surrounding the fossil leaves have replicated the outer surface of the epidermal cells (Fig. 2A, C, D), and the woody materials are also preserved as replicas (Fig. 2B). In some micrographs, we observed stomatal complexes and their subsidiary cells associated with nanocrystals of iron oxide (compatible with ferrihydrite and goethite). Chemical analysis by EDS showed intensities of Fe, O, Al, and Si for the nanocrystals (Fig. 2E, F). We also detected structures compatible with extracellular polymeric substance (EPS) (Fig. 2D).

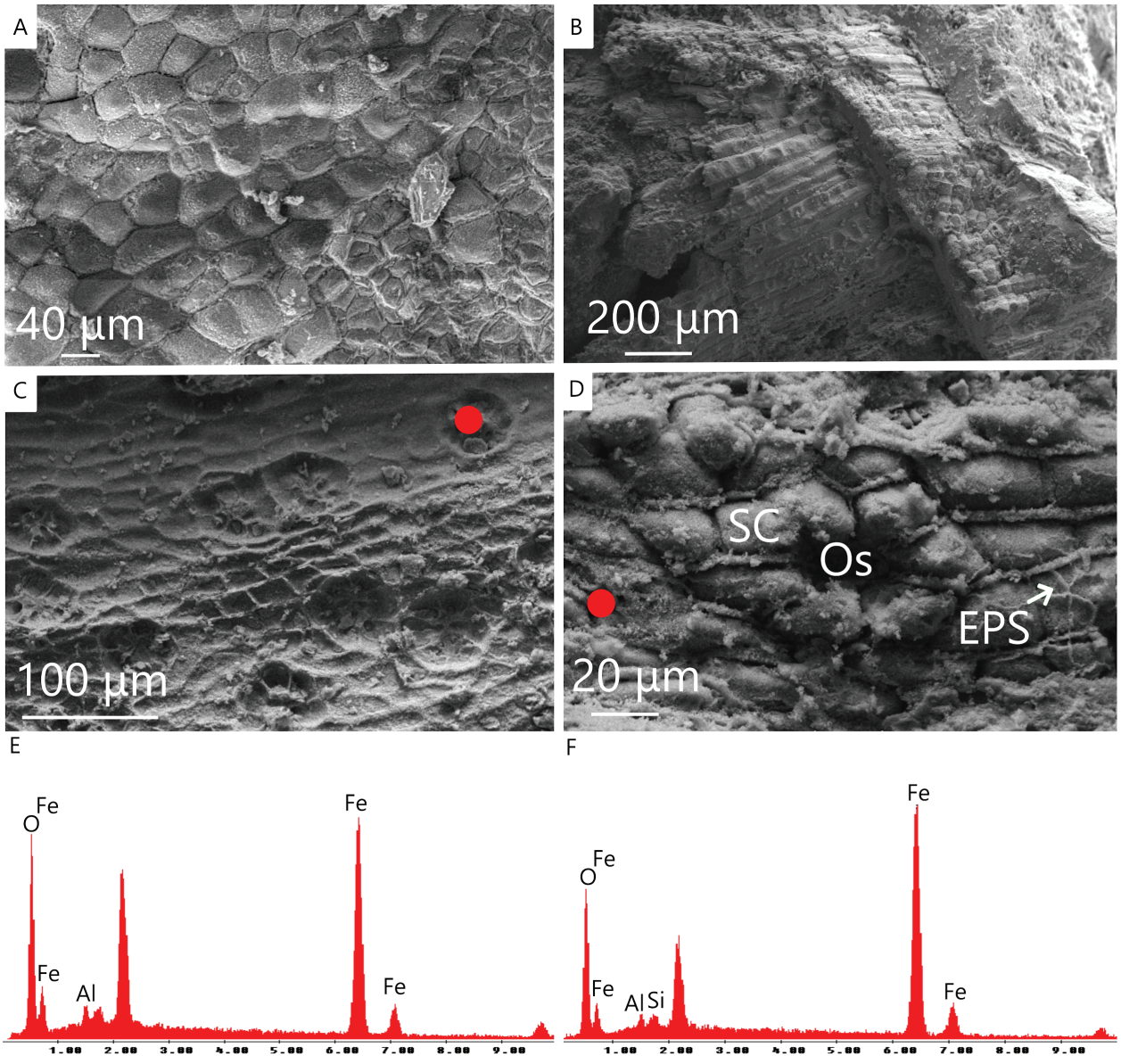

Fig. 2. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analyses of *Dicroidium* pinnule remains from the Santa Maria Formation. A, SEM micrograph of a counter slab (counterpart) exhibiting the anatomical structures and the quadrangular character of the mesophyll cells. B, part of a rachis or stem showing aligned and elongate tracheids. C, counterpart of a pinnule epiderm showing cells and stomatal complexes with a linear arrangement; D, detail of an actinocytic type of stomatal complex, with more than three subsidiary cells (SC) surrounding the ostiole (Os). Despite the guard cells being obscured, it is possible to see epidermal cells partially covered by EPS fragments (EPS). E, F, results of the EDS analysis highlighting the dominant presence of Fe and Al (analysed spots indicated by red dots in C and D). Scale bars represent: 40 µm (A); 200 µm (B); 100 µm (C); 20 µm (D).

Chemical and mineralogical analysis

The elementary intensities of mineral coatings are represented by more than 70% of iron, followed by silicon and aluminum (see Supplementary Information Table S2). No detectable intensities of carbon and sulphur were identified in the studied material. At the São Luís outcrop (Caturrita Formation), crystallographic and spectroscopic analysis (XRD and Raman) of the internal and external portions of crusts covering branches, and their connected leaves, revealed goethite as the only detectable mineral phase (Figs. 3, 4). The analyses of the fine-grained host rocks (siltstone/claystone) in the same succession showed a dominant composition of smectite, goethite and quartz (see in Supplementary Information Fig. S1).

In the conifer branches, iron oxyhydroxide spicules and spheres are common (Fig. 7F). We also observed goethite spicules associated with the filamentous structures compatible with EPS (Fig. 6A), together with spheres of ferrihydrite (potentially biogenic) (Fig. 6C, D). Nevertheless, the possibility that the spheres (Fig. 6C, D) represent bacteria-like arrangements or bacteriomorphs is not ruled out and is the subject of a forthcoming analysis. Ferrihydrite occurs in small crystalline sizes observed by SEM, but below the limit of detection by geochemical analysis. Other minerals, such as goethite, were locally identified with higher crystallinity (e.g. spicules) and in some cases with amorphous appearance (Fig. 6B, E). Mössbauer spectroscopy is sensitive to atomic nuclei capable of absorbing, without return, the emission of radiation γ (Thomasarrigo *et al.* 2018); i.e., any type of solid containing ^{57}Fe, structural or adsorbed. Given this, we applied Mössbauer spectroscopy to internal and external crusts of the fossil branches and we were able to identify the presence of α-goethite (Fig. 5).

Biogenic structures

To investigate preserved biogenic structures, we scanned sections of selected fossil remains using SEM. We observed curved rod-shaped structures, compatible with scaffolds of bacterial exopolymers (Suzuki *et al.* 2012) (Fig. 7A–C) and tubular iron oxide fibrils (Fig. 7D). Furthermore, filamentous web-like structures with irregular borders were interpreted as EPS covering the epidermis of plant remains (Fig. 7E, F).

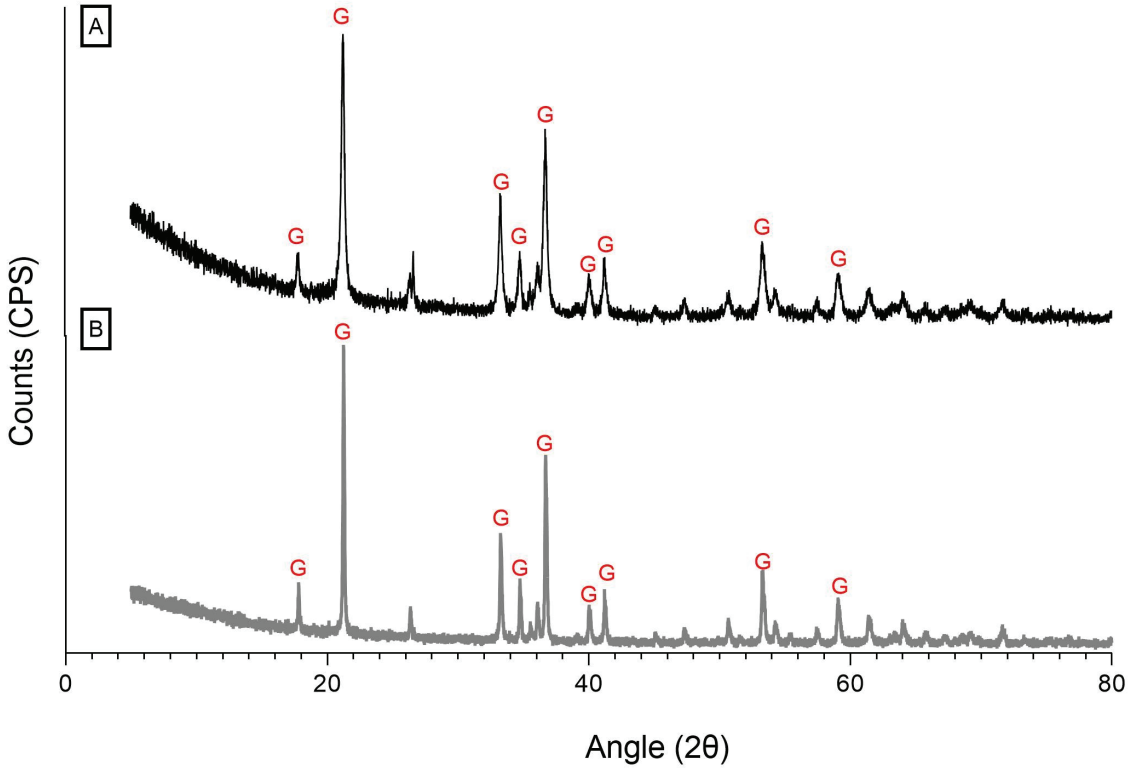

Fig. 3. X-ray diffractogram of a conifer branch from the São Luis outcrop. A, outer crust covering the branches. B, inner part of the crust, where the anatomical structures were replicated. G = goethite peaks.

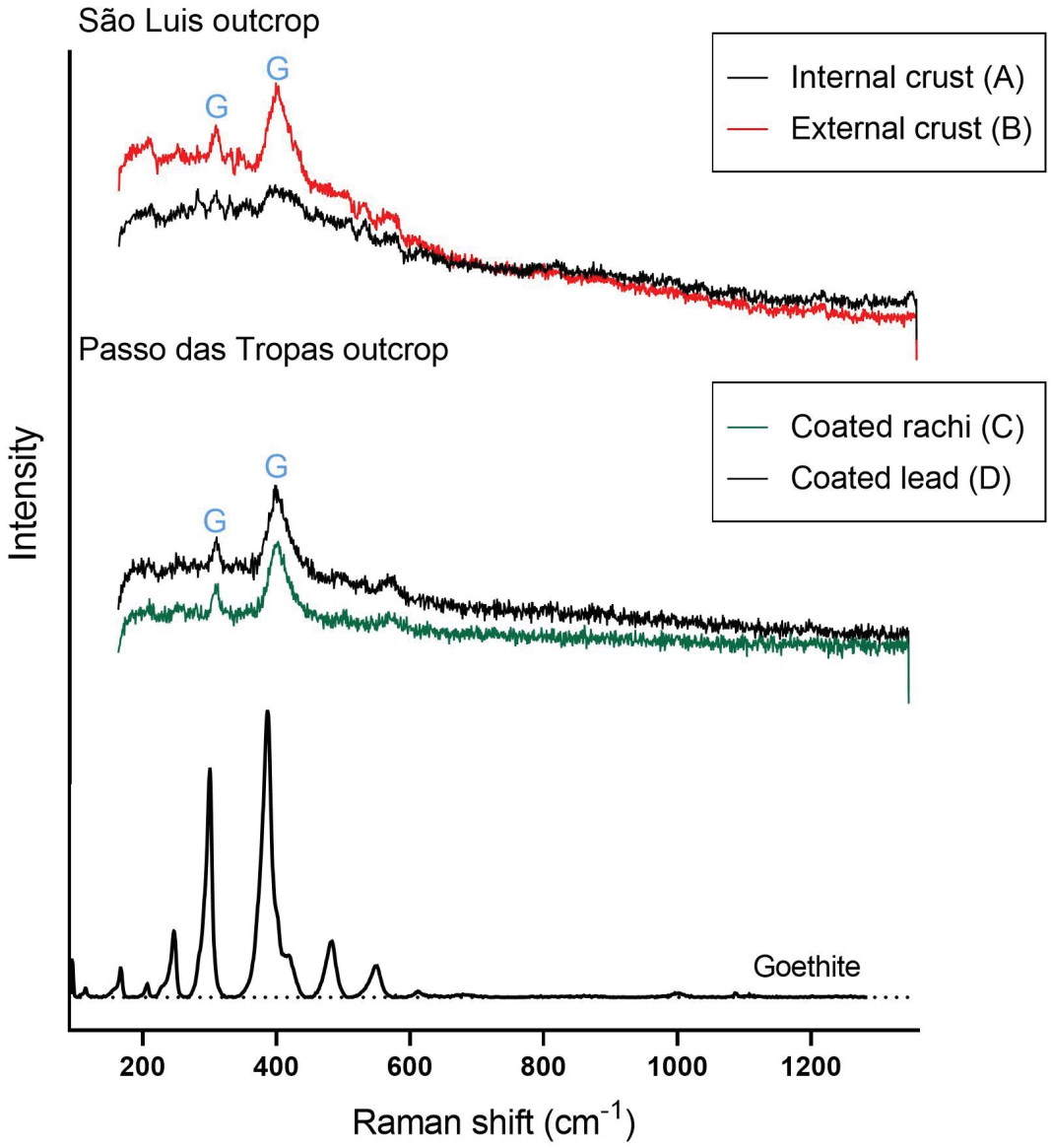

Fig. 4. Raman spectra from 200 to 1200 cm^{-1} of separate fossil plants from the two outcrops showing the common molecular presence of goethite bands. A, spectrum of the outer crust from conifer branches. B, spectrum of internal parts of coniferous branches. C, spectrum of the more coriaceous areas (e.g., rachis, coriaceous leaves) of the frond fragments assigned to the *Dicroidium* assemblages. D, spectra of crusts on the leaf blades of *Dicroidium* pinnules. G = goethite peaks. The black continuous line at the bottom refers to the theoretical model for goethite.

Discussion

Biogenic nature of minerals and other microstructures

We detected evidence that bacterial activity played a fundamental role in the preservation of the micro-anatomy of the studied plants. SEM imaging showed microstructures compatible with EPS in texture, morphology, and dimension (Fig. 7D–F). Other micro-organisms-related signatures were preserved as iron mineral precipitates (Fig. 6D–F). We interpreted those structures following biogenicity criteria (e.g. Schopf *et al.* 2005; Schopf *et al.* 2012).

Different biogenicity criteria are proposed to recognize the nature of different categories of structures (such as stromatolites, microbially induced sedimentary structures - MISS, microfossils). However, some aspects can be shared among all categories. According to Buick (1990); Schopf *et al.* (2005) and Schopf *et al.* (2012), some criteria for life recognition in the fossil record are: (1) age attributed to the rock; (2) insertion of the fossil within the rock, eliminating the possibility of the structure being a later contamination;

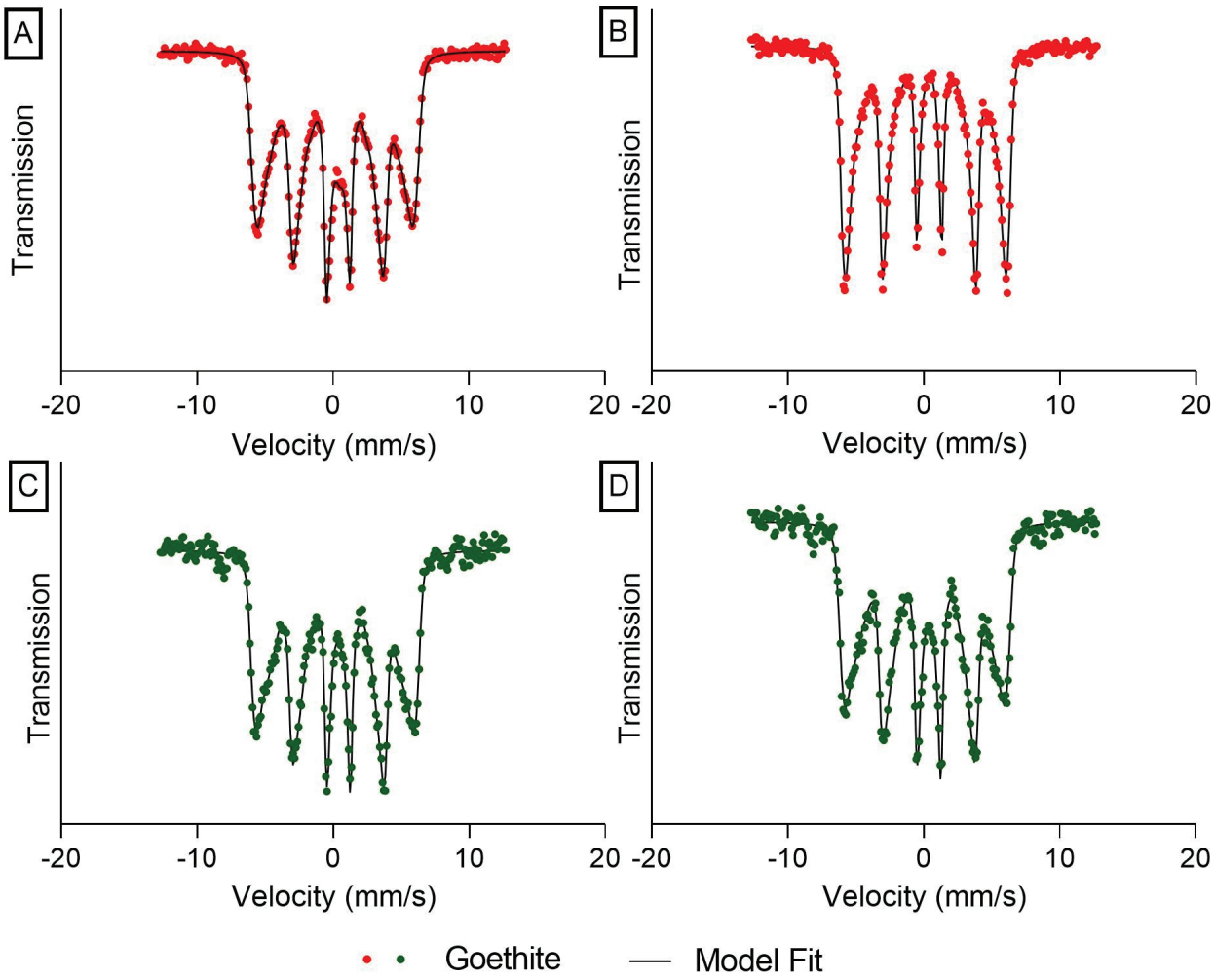

Fig. 5. 5K Mössbauer spectra obtained from fossil plants from the Caturrita Formation (red dots, A, B) and the Passo das Tropas outcrop (green dots, C, D), confirming the consistent presence of α-goethite nanoparticles A, external part of the crust covering wood branch fragments of a probable *Pagiophyllum* conifer. B, inner part of a conifer branch. C, spectrum obtained from the crust covering a *Dicroidium* pinnule. D, spectrum of the crust over a more coriaceous region (rachis) of a pteridosperm frond. The black continuous line refers to the modelled fit to the datapoints.

(3) time of deposition of the rock equivalent to the burial of the putative microfossil or biosignature; (4) inherent characteristics of organisms (remains or signatures) must be present, such as shape, biologically plausible size ranges, frequency, variable degree of preservation, three-dimensional preservation by permineralization composition; and (5) the presence of organic compounds (e.g. kerogen).

The structures associated with the preservation of our fossils meet several biogenicity criteria indicated above. All structures described here were identified inside the iron crusts, which present three-dimensional aspects of the fossil, thus ruling out the possibility of contamination by younger micro-organisms.

We have identified morphologies and textures (sheaths and twisted stalks) (Fig. 7A–C) recognized as produced exclusively by microaerophilic and neutrophilic iron-synthesizing bacteria. Modern experiments (Emerson & Ghiorse 1993; Chan *et al.* 2009; Vigliaturo *et al.* 2020) described the micrometre scale morphology (1 to 75 μm) for both sheaths and twisted stalks. We have identified well-preserved twisted stalks, with microscopic morphology and scale (~2 μm) consistent with observations of comparable structures produced by recent micro-organisms.

Our sheaths also match the expected morphology and size revealed by experiments with micro-organisms (Chan *et al.* 2009, 2016*a*; Fleming *et al.* 2014; Johannessen *et al.* 2020). The opening at the end of the tubes was not observed. However, we consider that this material underwent diagenesis. Hence, further silicification of tubes is expected (Johannessen *et al.* 2020),

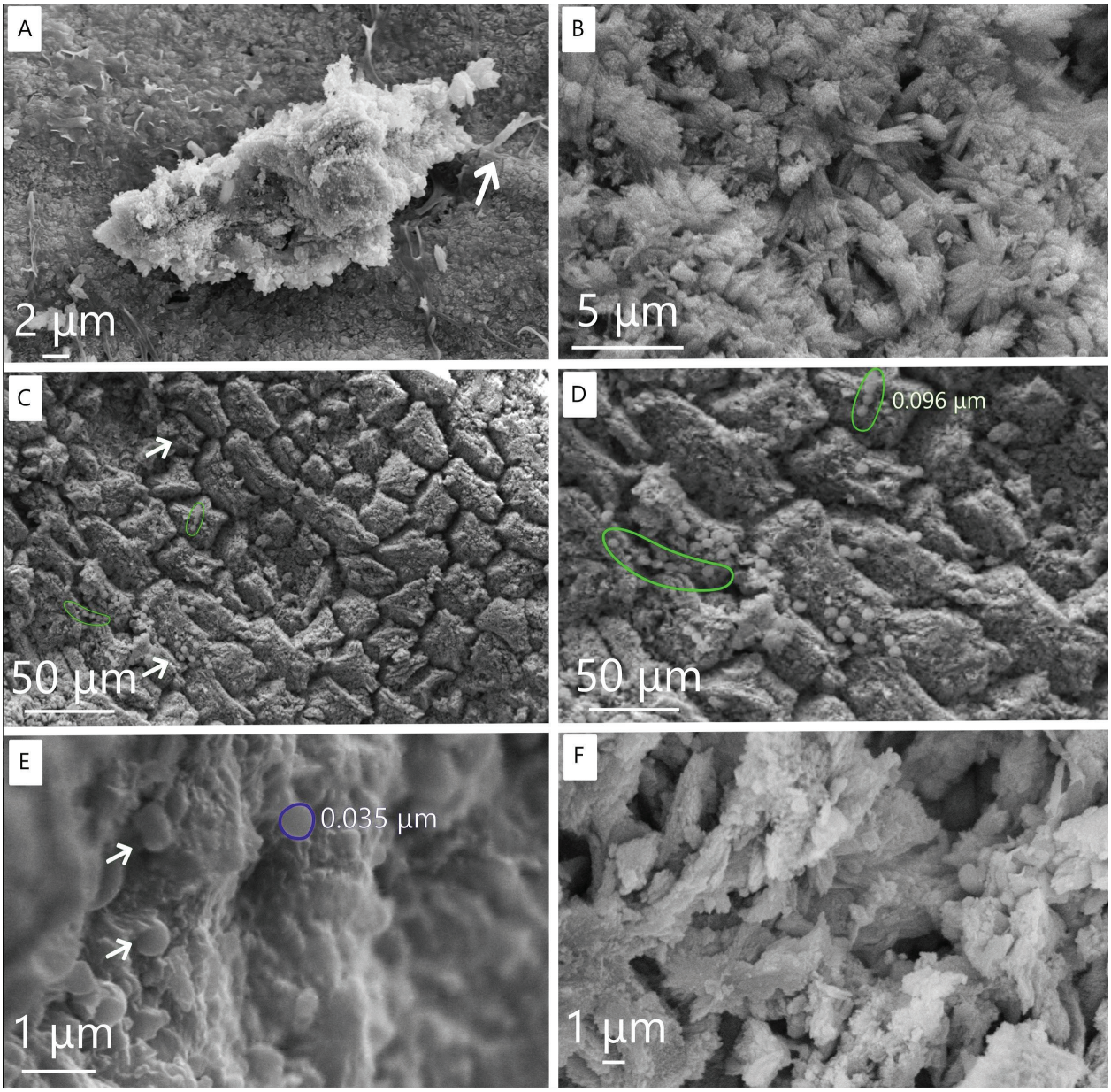

Fig. 6. Scanning electron microscope (SEM) micrographs of fossil plant fragments. A, iron oxyhydroxide spicules (goethite) with probable encrustation of EPS filaments (white arrow); B, crystals of goethite in the form of spicules. C, possible bacterial structures or small spheres of ferrihydrite (white arrow) over the epidermal cells of a *Dicroidium* sp. leaf from the Santa Maria Formation. D, image enlargement of C, demonstrating coccoid-like aligned structures (green circles). Measurement is related to a mean area from the four spheres in the upper. E, bacteria-like or ferrihydrite spheres over a conifer branch from the Santa Maria Formation. Measurements of a single sphere (purple circle) shown. F, amorphous crystals of goethite. Scale bars represent: 2 µm (A); 5 µm (B); 50 µm (C-D); 1 µm (E, F).

which can hamper the visualization of the openings at the tube extremities, contrary to modern experiments. Sheaths and stalks were reported in banded iron formations, in Jurassic stromatolites or in environments affected by hydrothermal fluids (Chan *et al.* 2016*a*; Grădinaru *et al.* 2020; Johannessen *et al.* 2020). In this sense, the age of our findings is also plausible.

Even though we did not find chemical signs of organic compounds, EPS were organized in the studied material as network morphologies over the substrate or covering grains (Fig. 6D-F). They are also in line with the expected morphologies and textures of recent and fossil biofilms (Emerson *et al.* 2010). Different groups of micro-organisms can produce this same kind of texture. However, the above discussed evidence (e.g. iron mineral precipitates, sheaths and twisted stalks, attributed exclusively to microaerophilic and neutrophilic iron-synthesizing bacteria),

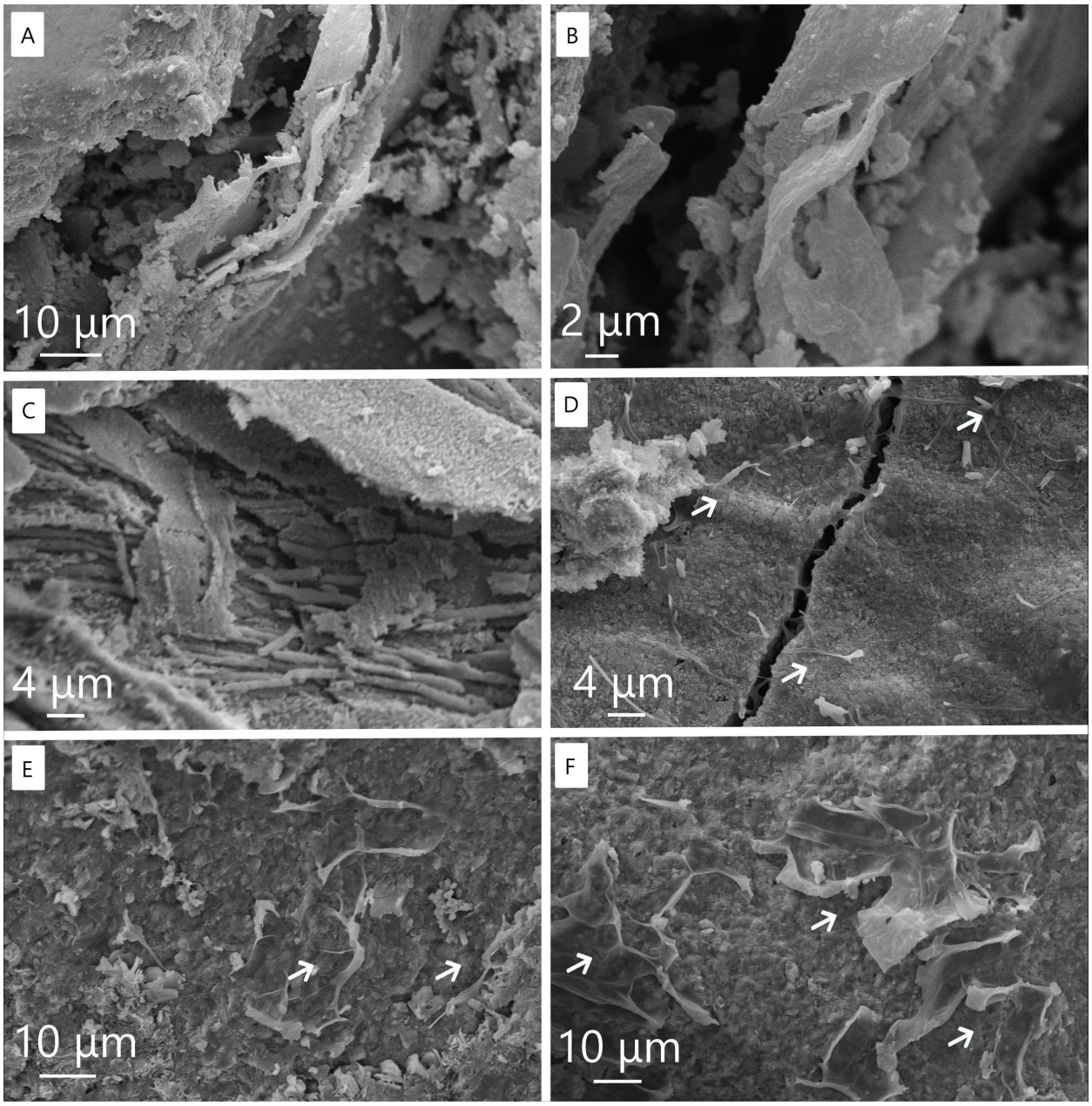

Fig. 7. Micrographs of biogenic microstructures from the Caturrita Formation. A, B, twisted stalks identified on conifers branches. C, tubular sheaths on conifers branches. D–F, filaments morphologically characteristic of mineralized EPS (marked by white arrow). Scale bars represent: 10 µm (A, E-F); 2 µm (B); 4 µm (C-D).

when taken as a whole, strengthens our hypothesis that those textures are consistent with biofilms produced by iron-synthesizing bacteria.

The textural aspect of goethite is evidence that also allows us to infer a biogenic origin for those structures. Abiotic goethite is characterized by more crystalline and prismatic shapes (Aeppli *et al.* 2019), but the textures of goethite in our material presents low crystallinity (Fig. 7A, B, F), lacking a defined arrangement and showing amorphous pattern, typical of biogenic minerals (Piepenbrock *et al.* 2014). The textural aspect of ferrihydrite (Fig. 7C–E) also brings the possibility of a biogenic origin due to the spherical and nanocrystalline aspect (e.g. Dunn *et al.* 1997). Ferrihydrite spherules, regardless of their origin, bear morphological similarity (size and shape) and organization with bacteria-produced structures (Westall *et al.* 2001). Their form and position near the aperture of stomata do not suggest casual distribution, as they resemble regular patterns usually displayed by

cocci, such as the 'necklace' *Streptococcus* arrangement (Westall *et al.* 2001). Therefore, we maintain the possibility that these structures represent bacteriomorphs or coccoid-like bacteria (Fig. 6C, E).

In light of this evidence, we propose that the exceptional preservation of micro-anatomical structures of plants and related biosignatures should be attributed to the activity of micro-organisms. We hypothesize that iron oxide-hydroxide minerals, precipitated by bacterial activity, allow for the preservation of those fossils with fine details. The patterns observed among the Santa Maria Formation and the Caturrita Formation floras are quite similar to what Schopf (1975) and Briggs (2003) considered typical of iron authigenic preservation, with in situ growth of minerals related to bacterial activity occurring during early diagenesis.

All fossils described here were preserved with reliable structures, but without the presence of the original organic carbon, which usually makes those kinds of preservation exceptional. The absence of organic compounds is likely related to the micro-oxic palaeoenvironments in which the studied continental red beds were probably deposited. In these palaeoenvironments, dissolved oxygen concentrations were likely high enough to oxidize/decompose organic matter.

Biosignatures related to microaerophilic and neutrophilic iron-synthesizing bacteria

The deposits of red beds are rich in Fe^{3+} and were likely the main source of Fe^{2+} at the time of deposition. These geological and depositional settings made iron ions available, which were probably used by ancient neutrophilic and microaerophilic micro-organisms in their metabolic activities, which, on its turn resulted in the production of exudates, such as the twisted stalks and sheaths found in the studied fossil material.

We propose that different parts of plants served as substrates for microaerophilic and neutrophilic bacteria that mediated the precipitation of biogenic iron-rich mineral phases (twisted stalks and sheaths) found in our fossil material. This is particularly the case for the modern bacteria *Gallionella ferruginea* (Suzuki *et al.* 2011, 2012; Chan *et al.* 2016b; Bryce *et al.* 2018) and *Leptothrix discophora* (Emerson & Ghiorse 1993; Suzuki *et al.* 2011; Chan *et al.* 2016*b*). This group of Fe^{2+} microaerophilic oxidizing micro-organisms oxidizes ferrous iron at pH 5-8 (slightly acid to neutral), using atmospheric oxygen as the terminal electron acceptor (Fleming *et al.* 2008, 2014). Owing to competition with spontaneous abiotic oxidation of ferrous iron at a near-neutral pH, these organisms are found more consistently in micro-oxic habitats that have moderate to high Fe^{2+} concentrations (Ehrlich *et al.* 2008; Vollrath *et al.* 2012, 2013).

Microbial oxidation of Fe^{2+} by microaerophilic organisms tends to occur in environments with reasonable concentrations of oxygen, possibly due to the ability of organic binders (e.g. EPS, organic matter) to stabilize Fe^{2+} and delay chemical reactions that lead to mineralization, providing an accurate replication of microstructures by iron minerals (Fleming *et al.* 2014). In this sense, the fragments of plants, when in contact with these bacteria, probably served as substrates, increasing the sites of organic binders and favouring the precipitation of biogenic iron minerals. The kinetics of abiotic and biotic oxidation of Fe^{2+} in the formation of ferric minerals and, therefore, the balance between these two processes, is governed by several factors, such as: the concentration of ferrous iron, oxygen partial pressure, abundance, and activity of microaerophilic oxidants of Fe^{2+}, surfaces availability for colonization (substrate), temperature and pH (Neubauer *et al.* 2002;

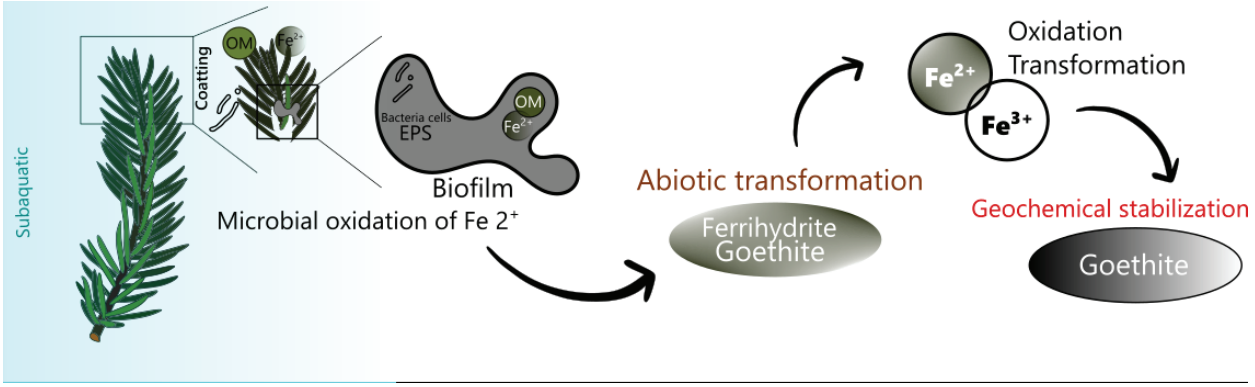

Fig. 8. Inferred biogeochemical cycle for the chemical stabilization of iron oxides into goethite in the studied material. The initial process was related to the activity of microaerophilic and freshwater neutrophilic micro-organisms, in a triple interaction between Fe^{2+} ions + organic matter, bacterial cells and EPS. This process led to oxidation of Fe^{2+} by biotic processes, which precipitated ferrihydrite and goethite. Finally, the iron oxides underwent an abiotic transformation when Fe^{2+} became Fe^{3+} through oxidation and ferrihydrite stabilized as goethite.

Druschel *et al.* 2008; Ehrlich *et al.* 2008; Vollrath *et al.* 2012, 2013) (Fig. 8).

In general, the process of biological oxidation of Fe is favoured over abiotic oxidation at relatively low concentrations of oxygen (micro-oxic environments) and Fe^{2+}. In modern environments, some microaerophilic micro-organisms produce extracellular biominerals, usually sheaths or stems (Fleming *et al.* 2008; Chan *et al.* 2016a, b), whereas others form particulate iron oxyhydroxides (Ehrlich *et al.* 2008). Experiments suggest that these structures (twisted stalks and sheaths) help bacterial cells to avoid incrustation by directing Fe^{3+} precipitation away from the cell surfaces (Chan *et al.* 2004, 2011).

The sedimentary succession in which our fossil floras were collected is composed of laminated claystones and siltstones of small lateral extent, and thicknesses of approximately two metres, suggesting lacustrine deposition or deposition within abandoned meanders (Zerfass *et al.* 2003; Barboni *et al.* 2016). Modern neutrophilic Fe^{2+} oxidant freshwater bacteria are mostly found in humid areas and stagnant water (marshes, mangroves) (Weiss *et al.* 2007). They are also present as iron plaques in root systems of plants living in humid environments, concomitantly with Fe^{2+} oxidizing or Fe^{3+} reducing bacteria (Weiss *et al.* 2003, 2007).

We identified sheaths and twisted stalks as diagnostic structures generated by Fe^{2+} oxidant bacteria (Ehrlich *et al.* 2008; Chan *et al.* 2016*a*, *b*), together with amorphous goethite and EPS. We conclude that: (1) those sheaths and twisted stalks are most-likely biosignatures of life; and (2) micro-organisms played an important role in the fossilization process of the studied Triassic-Jurassic fossil plants from southern Brazil.

Biotic and abiotic minerals

Iron minerals with a spherical shape were assigned to ferrihydrite, probably related to the precipitation of nanoparticles in biofilm rods (Dunn *et al.* 1997). The texture could be alternatively interpreted as framboidal pseudomorphs of pyrite, but: (1) we did not detect sulphur intensities in our samples; (2) even considering intense diagenesis and the limits of detection of the analytical techniques, sulphuric bacteria do not precipitated pyrite in the same conditions that microaerophilic and neutrophilic bacteria produce twisted stalks or sheaths; and (3) sulphuric bacteria live in more reducing environments, whereas microaerophilic and neutrophilic bacteria are adapted to micro-oxic environments.

The identification of iron oxides leads to the interpretation of the biogeochemical environment to which the plants were subjected during and after the coating process, which replicated micro-structures of the plants. Our chemical and mineralogical characterizations indicate that the crusts are composed of goethite, more precisely α-goethite (Fig. 5). The fact that we did not detect ferrihydrite in our other mineralogical analyses can be explained by diagenetic changes. Abiotic transformations of Fe^{3+} oxides to hydroxides from dissolved ferrihydrite occur via direct chemical precipitation by rapid hydrolysis of Fe^{3+}, followed by the crystallization and nucleation of secondary minerals (Cornell & Schwertmann 2003). Primary oxides and hydroxides of Fe^{3+} can be converted to other oxides and oxyhydroxides minerals by dissolution/reprecipitation, dehydration, partial reduction, and solid-state transformation (Cornell & Schwertmann 2003; Posth *et al.* 2014). Recrystallization rates, which may occur in minutes or months, are influenced by characteristics of the chemical solution, such as the concentration of ions in solutions that contain bicarbonate and phosphate, along with Fe^{2+} and Fe^{3+} (Cornell & Schwertmann 2003; Michel *et al.* 2007; Piepenbrock *et al.* 2014; Posth *et al.* 2014).

Another explanation for the impossibility to chemically characterize ferrihydrite in our samples may be related to the limitations of some techniques. The characteristic Raman bands of ferrihydrite are detectable at laser power than 1 mW (higher powers can degrade these minerals (Hanesch 2009). However, lower powers generate artefacts that can mask the mineralogical characterization of some compounds. In the case of elementary characterizations, small particles (e.g., nanominerals) can be chemically and texturally unrecognizable depending on the detection limits imposed by beam sizes and tensions of SEM/EDS, during the interaction of the electron beam with the samples.

Still, the occurrence of biogenic α-goethite (e.g. Konhauser, 1997) allowed us to deduce that the environment was aqueous, and to interpret that other iron oxides, such as ferrihydrite, may have stabilized to become goethite. Besides that, the amorphous structures of goethite strengthens the hypothesis that this mineral (Fig. 6F) precipitated via bacterial mediation when micro-organisms came into contact with the substrate (plants), thus an authigenic process (Konhauser 1997).

The presence of smectite (Fe, Al, Si) as the surrounding clay mineral also plays an essential role in the exceptional preservation. Some lineages of neutrophilic micro-organisms are able to oxidize Fe^{2+} on smectite ($Al_2Si_4O_{10}(OH)_2 nH_2O$), with nitrate as the electron acceptor (Schiffbauer *et al.* 2014). In addition to the importance of chemical exchange, the

presence of clay minerals has been considered one of the main factors contributing to a slower decomposition of carcasses, also due to their chemical properties (Butterfield 1995; Wilson & Butterfield 2014). For instance, clays can stimulate the formation of colloidal gels capable of inducing permineralization (We 2007) and can absorb enzymes despite the decomposition process (Butterfield 1995). Moreover, the tendency of adhesion of aluminosilicates to decomposing tissues can also favour the slow replication of minute anatomical detail (Butterfield 1995; Gabbott *et al.* 2008). Therefore, we hypothesize that the presence of smectite was a facilitator.

Fossil diagenesis

An additional factor contributing to the exceptional preservation of fossil remains is the occurrence of bacterial biofilms, which are essential for the preservation of soft tissues and for the geochemical balance between a triple interaction among iron ions, bacterial cells and EPS (Hao *et al.* 2016). Kryshtofovich (1944) was the first to suggest that a thin mineral layer, initially a fragile film, is produced around plants that remain in stagnant waters. In modern experiments, the formation of mineralized layers and the presence of ferrihydrite nanoparticles were detected in biofilm threads within days to weeks after plant remains were submerged in water (Dunn *et al.* 1997).

Bacteria and other micro-organisms invade leaves even while they are still attached to the plant (Melotto *et al.* 2008). This invasion process is particularly common. When plant parts enter a water body, they usually undergo colonization by microbes that live in the water column (Spicer 1989; Iniesto *et al.* 2018). Morphologies shown in figure 6C-D reinforce the interpretation that the studied Triassic-Jurassic plants were subjected to similar processes.

Micro-organisms produce EPS, whose fine structure and colloidal nature make it possible to replicate and create pseudomorphs of organic structures that serve as substrate, even in finer scales at the cellular level (Raff *et al.* 2008). As experimentally observed by Iniesto *et al.,* (2018) a thin layer of biofilm forms in a time span of 6-11 days after a leaf enters a water body. The mucilaginous elements present in the biofilm cover the substrate (leaf), creating a thin layer as a negative stamp of the outer layer of the leaf on the inner surface of the mat that is in contact with the epidermis. In our plant fossil material, inner surfaces of the crusts replicate, in a minute scale, the epidermis of the leaves in a way that it is possible to visualize and identify delicate features such as the guard cells of stomata and the plant cellular wall. In this way, and based on experimental data, we hypothesize that the precursor of the crusts was, at first, a plastic and moldable biofilm that got mineralized even before the final burial, preserving the tridimensional arrangement of the fossils.

For EPS/biofilm stabilization and mineralization to take place, it is necessary that the organic components undergo decomposition and that the soft tissues are later exposed to fluids rich in ions. The balance between decomposition and mineralization is crucial for the replication of anatomical structures in fine details (Briggs 2003; Iniesto *et al.* 2015; Osés 2016), which characterizes exceptional preservations. There are several characteristics of this biomineralization process that contribute to the exceptional preservation of plants, such as the formation of a barrier, avoiding abrasion, damage, and transportation, also preventing the action of decomposers (Spicer 1977; Osés 2016).

Precipitation of minerals on the labile parts of organisms (such as microstructures of surface of leaves) must occur within a decomposition window: it has to be fast enough to avoid the deterioration of delicate parts, and slow enough to ensure the preservation of fine anatomical details that are normally lost or obscured when decomposition starts together with the collapse and deterioration of the internal tissues (Spicer 1977; Dunn *et al.* 1997; Skawina 2010). Under natural conditions, tissues degrade so rapidly that they leave no evidence of their morphology (Spicer 1977). In addition to protecting against decomposition, the presence of EPS can prevent precipitation and transformation of existing minerals into more crystalline phases (Mikutta *et al.* 2012). EPS coatings, therefore, can alter the surface properties of minerals, in the same way as the presence of minerals can alter the EPS capacity for iron sorption (Mikutta *et al.,* 2012).

In modern experiments, results showed that EPS acts as a model for the precipitation of amorphous and (nano) crystalline Fe^{3+} minerals and allows microorganisms to adjust their geochemical microenvironments to increase colony growth (Chan *et al.* 2004; Elliott *et al.* 2014; Hao *et al.* 2016). The interaction process among microaerophilic micro-organisms, free iron ions, and EPS is complex. Nutrients, ions, and metals can be adsorbed to Fe^{2+} oxyhydroxides and sequestered until release due to changes in the geochemical configuration or microbial activity. The produced biogenic minerals have a cellular component consisting of cell dendrites, microbial exudates, organic metabolites, and EPS (Beveridge & Graham 1991; Chatellier *et al.* 2001; Cornell & Schwertmann 2003; Châtellier *et al.* 2004; Tadanier *et al.* 2005; Posth *et al.* 2010, 2014).

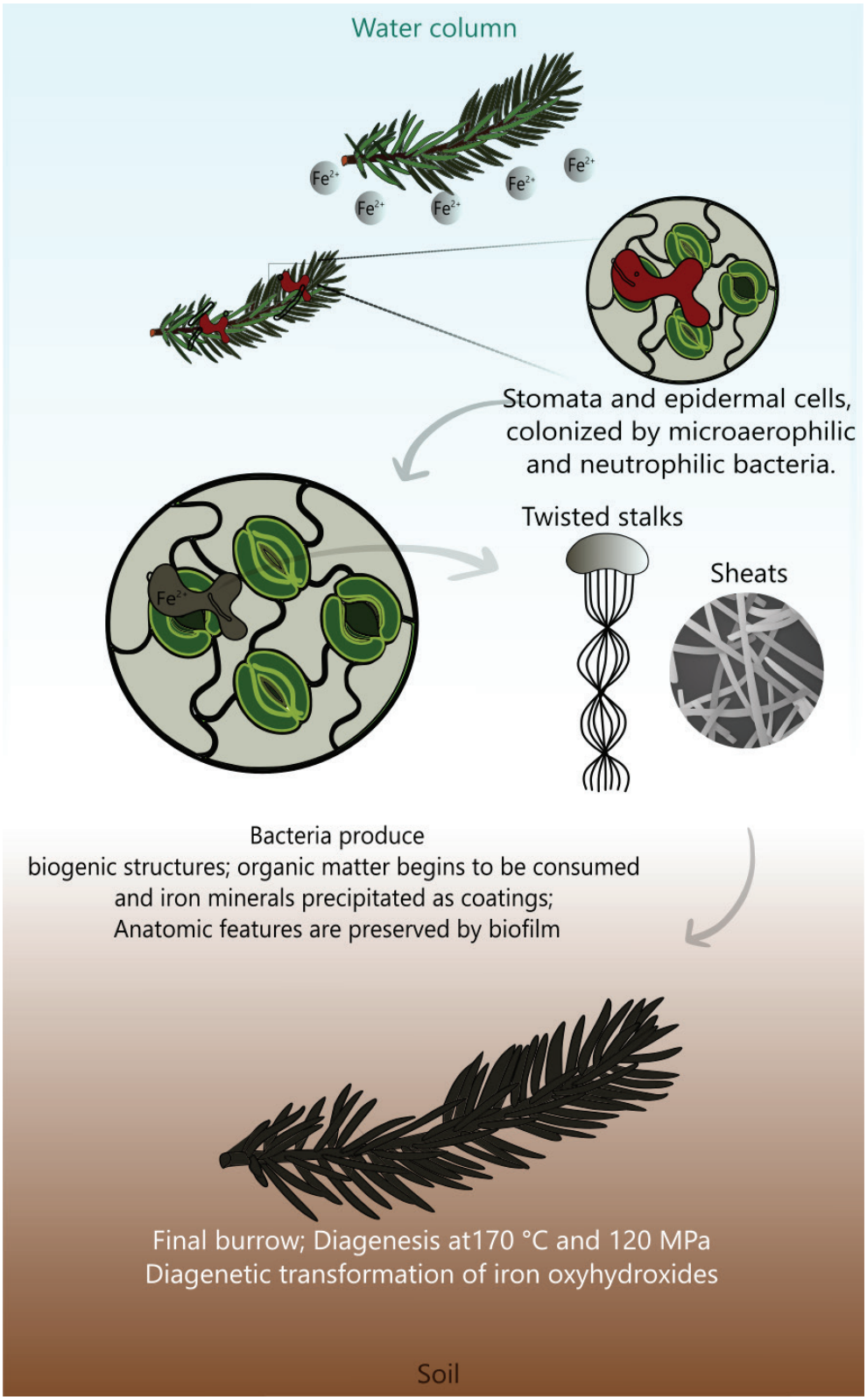

Fig. 9. Inferred fossil diagenetic history for the studied fossil plants. The conifer branches and other organic structures sunk into iron-rich lakes or small ponds of fresh water and were rapidly colonized by biofilms of microaerophilic and neutrophilic bacteria. Later, the triple interaction between Fe^{2+} oxides + organic matter, bacterial cells and EPS led to the precipitation of biogenic minerals containing iron. These mineral crusts contain biogenic structures, such as twisted stalks and sheaths, and protected the plant remains from decomposition. Finally, the coated plant remains were buried and underwent diagenesis at mild temperatures and pressures.

Finally, mild diagenesis seems to be equally important in guaranteeing the preservation of the fine anatomical structures and biosignatures observed in this study. Under controlled environmental conditions of a modern experiment (Picard *et al.* 2016), the presence of Si affected the precipitation/preservation of goethite around the cells. Fe-encrusted cells were morphologically well-preserved after one week at 250 °C and 140 MPa, and after 16 weeks at 170 °C and 120 MPa in the presence or absence of Si. At 250 °C and 140 MPa, some goethite crystals were transformed into hematite and magnetite; however, in the presence of Si, more goethite was preserved. The occurrence of EPS, twisted stalks and sheaths in our studied material leads us to infer that fossilization occurred under similar conditions of temperature, pressure and exposure to Si, mainly due to the presence of clay minerals. In addition, the geochemical stabilization of iron in goethite, not turning into hematite, also suggests similar conditions.

As a taphonomic scenario for the studied Triassic-Jurassic fossil remains from the Santa Maria and Caturrita formations (Fig. 9), we suggest that the recovered branches of conifers, rachis and fronds of *Dicroidium*, together with other associated plant fossils, fell into small water bodies that were rich in Fe^{2+} ions. In a timeframe of minutes to weeks, those plant remains served as substrate for colonization by microaerophilic and neutrophilic micro-organisms. Consequently, the fossils underwent the same coating process, due to biological precipitation of iron oxides and hydroxides in a Si-rich environment, thanks to the presence of clay sediments. The coating of the fossils was then followed by a rapid and mild diagenesis. A series of steps made it possible to preserve microstructures such as twisted stalks and sheaths, which had not yet been reported for the fossil record.

It has been hypothesized that the presence of biogenic iron, either available in the environment or in animal fossil tissue, during decomposition would facilitate the replication of anatomical structures, though not always preserving organic compounds (Saleh *et al.* 2020). With all the processes described here, we suggest that these plant fossils constitute an excellent material for the study of preservational processes associated with ancient micro-organisms and biogeochemical processes. Besides being a one-of-a-kind type of fossil preservation that lacks any evidence of organic molecules, the presence of biogenic structures is unprecedented for fossil plants biosignatures developed during exceptional preservation.

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Supplementary Information 1: Geological Settings
Supplementary Information 2: Data Set Mossbaüer
Supplementary Information 3: Data Set DRx
Supplementary Information 4: Data Set Raman

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