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Crostas de ferro geradas pela ação microbiana: um importante marcador de superfícies de descontinuidade para correlações estratigráficas de alta resolução

São Leopoldo
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Crostas de ferro geradas pela ação microbiana: um importante marcador de superfícies de descontinuidade para correlações estratigráficas de alta resolução

Dissertação de mestrado apresentada como requisito parcial para obtenção do título de Mestre em Geologia, pelo Programa de Pós-Graduação em Geologia da Universidade do Vale do Rio dos Sinos (UNISINOS).

Orientadora: Prof.ª Dra. Renata Guimarães Netto

São Leopoldo

2023

1. **APRESENTAÇÃO DA DISSERTAÇÃO**

O objetivo desta dissertação foi testar a hipótese de que a atividade microbiana exerce influência na gênese das crostas ferruginosas associadas a arenitos da porção média da Formação Rio Bonito (Grupo Guatá, Bacia do Paraná). Essa hipótese foi concebida a partir da interpretação de uma mediação microbiana na formação de uma dessas crostas exposta no paleovale do Cambaí (Vila Nova do Sul, Rio Grande do Sul), durante meu trabalho de conclusão de curso. Para testar essa hipótese, analisamos crostas semelhantes provenientes de outros paleovales do estado do Rio Grande do Sul.

As crostas ferruginosas são observadas no topo de arenitos pós-glaciais da Formação Rio Bonito. Estas rochas são produto da deposição de sedimentos arenosos em eventos de alta energia (tempestades) na porção interna de estuários, os quais se desenvolveram em paleovales. Esses depósitos apresentam *hummocky cross stratification* e *swalley stratification.* É possível verificar estruturas de enrugamento (*wrinkle structures*) induzidas pela ação microbiana nestas crostas ferruginosas, permitindo aventar a hipótese de uma origem autigênica para o ferro como resultado da mediação microbiana. As bactérias constituem importante papel na ciclagem do ferro na crosta. Todos os organismos, à exceção de um pequeno grupo de bactérias homoláticas, necessitam do ferro para realizar suas atividades metabólicas (e.g., Pandey et al., 1994). Diversas enzimas metabólicas e proteínas regulatórias utilizam o Fe como um cofator em alguns processos enzimáticos que envolvem a transferência de elétrons (Kappler et al., 2016). O Fe pode ainda ser precipitado indiretamente, a partir da excreção de substâncias poliméricas extracelulares (EPS) produzidos por bactérias que podem atuar na adesão e nucleação de óxido de ferro (Fortin e Langley, 2005).

Partindo destas observações e tendo em vista que bactérias podem mediar a precipitação de minerais de ferro de forma direta ou indireta, buscamos avaliar a gênese destes depósitos no intuito de caracterizá-los quanto a sua origem biogênica ou abiogênica. Entender qual a relação da potencial atividade microbiana com as concentrações de ferro encontradas no topo de camadas de arenitos da Formação Rio Bonito, determinando a natureza destas crostas, contribuiu no aprimoramento dos modelos deposicionais já estabelecidos para a área estudada.

Para a caracterização das crostas ferruginosas coletamos amostras em cinco afloramentos distintos, todos estratigraficamente situados na porção média da Formação Rio Bonito no Rio Grande do Sul. As coletas ocorreram nos afloramentos Cambaí Grande (Vila Nova do Sul), Arroio Jaguarão (Hulha Negra), Cascatinha (Cachoeira do Sul), Forninho e Barrocada (Caçapava do Sul), orientadas no sentido base→topo. Analisamos as amostras macroscopicamente sob o estereomicroscópio e as preparamos para análises petrográficas e geoquímicas no Laboratório de Laminação Petrográfica e no Instituto Tecnológico de Paleoceanografia e Mudanças Climáticas (ittOCEANEON), respectivamente, ambos da UNISINOS. Realizamos análises de Espectroscopia Raman na Unidade de Pesquisa em Astrobiologia da Universidade de São Paulo (NAPAstrobio, PRP-USP). O tratamento das amostras obedeceu aos padrões praticados pelos laboratórios e os procedimentos encontram-se descritos no capítulo sobre materiais e métodos do artigo que compõe a dissertação.

Usamos as seções delgadas polidas geradas para observações no microscópio óptico e microscópio eletrônico de varredura (MEV). Cada amostra coletada possui dois pares de lâminas, sendo um conjunto perpendicular e outro paralelo ao plano de acamadamento das crostas de ferro. Analisamos as lâminas delgadas no microscópio óptico ZEISS AXIO na UNISINOS. Algumas seções delgadas foram metalizadas com ouro por um tempo de 3 min no aparelho Quorum Q150TES para análise das características morfológicas presentes nas amostras na Microscopia Eletrônica de

Varredura (MEV). No intuito de obter a composição elementar dos materiais analisados utilizamos as técnicas de Espectroscopia de Raios-X de Energia Dispersiva (EDS) e Fluorescência de Raios-X (FR-X).. Já nas análises de Difração de Raios-X (DR-X) e Espectroscopia Raman reconhecemos as fases minerais presentes nas crostas de Fe, sendo a última responsável também pela identificação dos compostos orgânicos presentes no material.

Os resultados obtidos e sua discussão compõem o manuscrito que conforma essa dissertação, o qual foi submetido à publicação no periódico *Sedimentary Geology* em 20 de março de 2023. O periódico escolhido atende aos pré-requisitos do Programa de Pós-Graduação da Universidade, possuindo classificação A1 segundo o indexador Qualis da CAPES na área de Geociências e foi escolhido por já ter publicado um trabalho sobre crostas ferruginosas arenosas que foi uma importante referência para o estudo aqui realizado (Garcia-Hidalgo et al., 2018).

As referências citadas no texto introdutório e síntese integradora foram também utilizadas para a composição do artigo.

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MICROBIALLY-GENERATED FERRUGINOUS CRUSTS: A VALUABLE MARKER OF DISCONTINUITY SURFACES FOR HIGH-RESOLUTION STRATIGRAPHIC CORRELATIONS

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Abstract

Thin ferruginous sandy crusts are common on top of sandstone beds in the Lower Permian post-glacial deposits of the Paraná Basin in southern Brazil. These crusts usually preserve wrinkle structures, suggesting that they might be a product of microbial mediation. Iron-synthezing bacteria use iron to realize essential metabolic activities and precipitate iron minerals as a byproduct. Bacteria could also indirectly mediate iron minerals precipitation through the excretion of extracellular polymeric substances, which act as a glue, favoring iron adhesion and nucleation, and create an ideal environment due to the pH and Eh changes they cause. Samples of ferruginous sandy crusts from different sandstone beds of the Rio Bonito Formation were analyzed by microtextural high-resolution, mineralogical, and geochemical methods to evaluate this hypothesis. Lumpy and filamentous morphologies and globular goethite minerals are abundant in these samples and were herein interpreted as bacterial products. The presence of kerogen reinforces the evidence of bacteria-substrate interaction and suggests the development of biofilms/microbial mats on the top of these beds. Quiescence is needed to develop and preserve microbial mats, and low sedimentation rates are required to form ironstones. The ferruginous sandy crusts thickness of only a few centimeters implies a short time for its development. All these aspects allowed interpreting the analyzed ferruginous sandy crusts as representing a depositional hiatus, possibly controlled by high-order eustatic fluctuations. The analysis of these features in sedimentary successions can provide a useful tool for identifying discontinuity surfaces.

Keywords: ferruginous crusts, microbial activity, iron bacteria, Early Permian, Paraná Basin.

1. Introduction

The presence of ferruginous crusts (FSCs) in the post-glacial deposits that characterize the middle and upper portions of the Rio Bonito Formation (Lower Permian of the Paraná Basin, S Brazil) is relatively common. These crusts are frequently observed in outcrops in Rio Grande do Sul State (RS; Fig. 1) but also occur in subsurface deposits (e.g., Aboarrage and Lopes, 1986; Netto, 1994; Silveira, 2000; Tybusch et al., 2016; Schmidt-Neto et al., 2018). Some authors interpreted these Fe-rich crusts as the result of a supergenic alteration process, more specifically as lateritization (Silveira, 2000; Tybusch et al., 2016). According to Schellmann (1981), laterites result from the intense chemical weathering of exposed rocks richer in Fe and/or Al and poorer in Si than the parent rock. However, these ferruginous crusts occur at the top of weak weathered sandstones, not resulting from supergenic alteration since a lateritic profile with soil formation was not established. Hence, another genesis for these crusts should be postulated.

According to García-Hidalgo et al. (2018), FSCs represent iron-rich sedimentary rocks formed under low sedimentation rates and limited iron supply. The occurrence of wrinkle structures induced by microbe action in some well-exposed ferruginous crusts in the Rio Bonito Formation sedimentary succession (e.g., Schmidt-Neto et al., 2018) allowed us to raise the hypothesis of synsedimentary iron precipitation by microbial activity. Except for a small group, bacteria use iron to perform key metabolic activities or indirectly favor its precipitation (e.g., Pandey et al., 1994). In many enzymatic processes involving electron transfer, iron is used by metabolic enzymes and regulatory proteins as a cofactor (Kappler et al., 2016). Bacteria can also indirectly mediate mineral precipitation through the production of extracellular polymeric substances (EPS) that can help iron sorption and iron oxide nucleation (Fortin and Langley, 2005).

Thus, this work seeks to understand the relationship between potential microbial activity and iron deposits found at the top of the sandstone beds from the Rio Bonito Formation, evaluating the nature of these crusts, and discuss their value as a marker of discontinuity surfaces on a high-resolution stratigraphic scale.

2. Geological setting

The ferruginous sandy crusts studied in this paper occur in the Rio Bonito Formation, which is part of the 2nd-order transgressive systems tract of the Gondwana I Supersequence in the Paraná Basin. The Paraná Basin is a huge intracratonic basin (~1,700,000 km^2) that occupies the southern portion of Brazil and its surroundings (Fig.

1), filled by mostly siliciclastic sediments accumulated from the Upper Silurian until the Cretaceous (Milani, 1997). According to Milani et al. (2007), the southwestern Gondwana occupied high latitudes during the Mississippian and was impacted by the extensive continental glaciation that inhibited sediment accumulation. With the progressive migration of the paleocontinent to the north, sedimentation was resumed in the area, marking the beginning of the deposition of Supersequence Gondwana I. This supersequence comprises the basin infill during the Late Paleozoic Ice Age in Gondwana, represented by the glacial deposits of the Itararé Group and the overlying post-glacial deposits of the Rio Bonito Formation (Guatá Group; Milani et al., 2007; Holz et al., 2010) (Fig. 1).

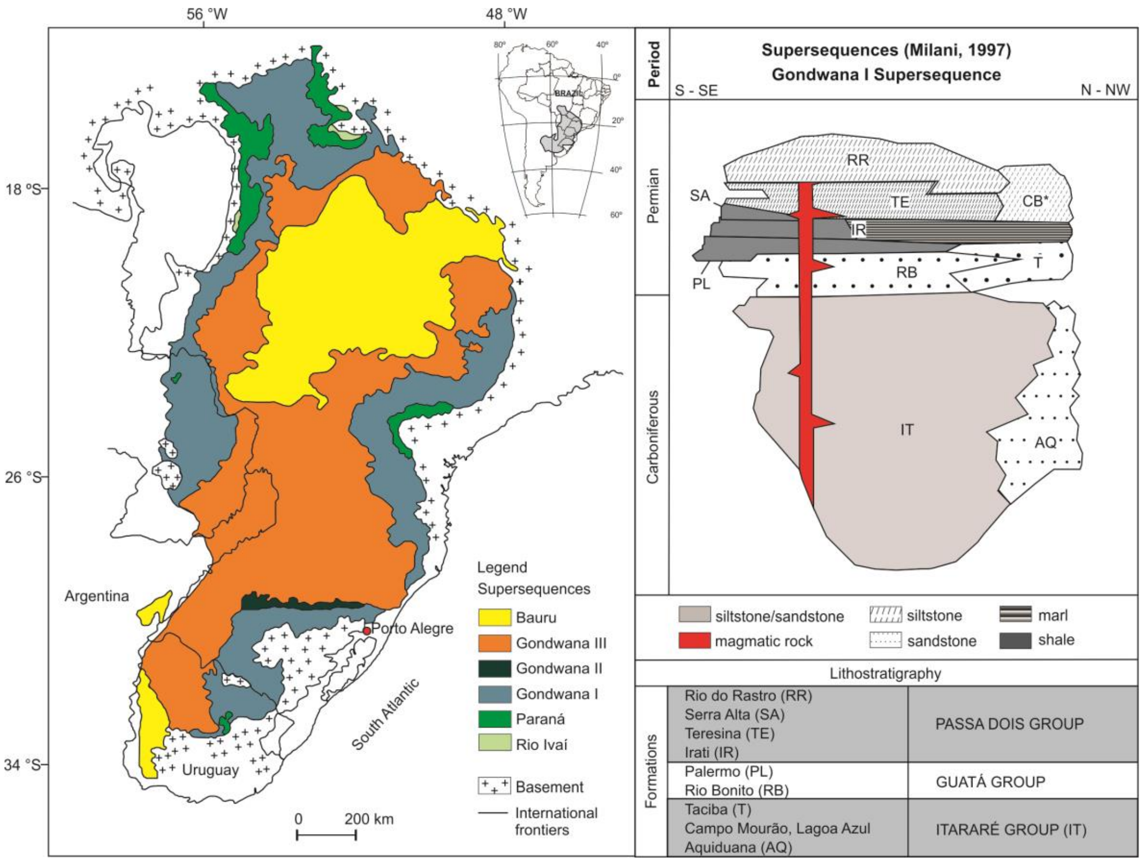

Figure 1. Map of the Paraná Basin showing the chrono- and lithostratigraphic scheme of Supersequence Gondwana I that comprises the Rio Bonito (RB) Formation (adapted from Milani, 1977).

The Rio Bonito Formation shows remarkable sedimentary cycles representative of glacial paleovalleys infill triggered by the sea-level rise caused by deglaciation (e.g., Lavina and Lopes, 1987; Holz et al., 2010; Cagliari et al., 2014, 2016; Tedesco et al., 2016; Schmidt-Neto et al., 2018; Mello et al., 2021). Its deposits were accumulated during the Asselian–Sakmarian (Cagliari et al., 2014, 2016; Griffis et al., 2018, 2023) and comprise conglomerates, sandstones, mudstones, and coal layers formed in fluvial-deltaic or fluvial-estuarine settings that evolved into tide-dominated estuaries and, later, estuaries and shoreface settings dominated by waves (Lavina et al., 1985; Lopes et al., 1986, 2003a,b,c; Elias et al., 2000; Buatois et al., 2007; Gandini et al., 2010; Netto et al., 2012; Villegas-Martín et al., 2020; Mello et al., 2021). The jagged relief in these paleovalleys led to the development of swamps and mangroves in supratidal settings. These conditions allowed the formation of peat bogs that generated beds and layers of coal interspersed with carbonaceous siltstones and quartz sandstones. Coal and siltstone deposits, widely distributed in the NE-SW direction, represent these protected marshy environments.

The samples analyzed in this paper came from surface deposits exposed in four different paleovalleys located on the southern border of Paraná Basin, at the Rio Grande do Sul State: Cambaí, Iruí, Candiota, and Capané (Fig. 2). The FSCs occur preferentially on the top of quartzous, fine-grained sandstone beds showing wavy bedding, swaley and hummocky cross stratification, and erosive base. Coal beds or lenses occur interspersed with the storm deposits in all outcrops except for the Cambaí paleovalley, where they are represented only by local thin (< 5 cm-thick) coal drapes, many carbonaceous intraclasts, fossil plant fragments, and phytodebris (Schmidt-Neto et al., 2018).

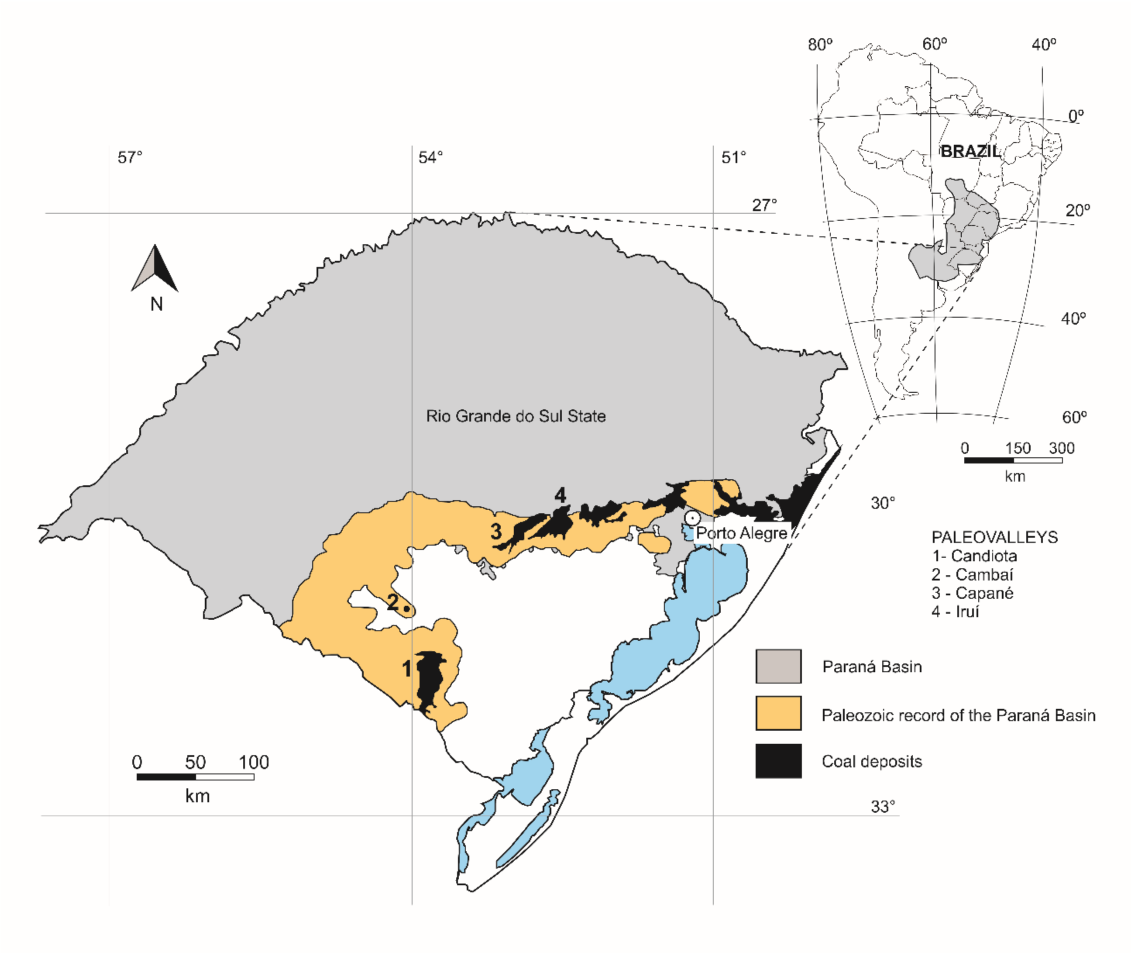

Figure 2. Location map of the studied deposits from the Rio Bonito Formation (Rio Grande do Sul State, southernmost Brazil).

The storm-related beds are preserved preferentially in the tide-dominated inner estuary zone in each paleovalley (Mori et al., 2012; Schmidt-Neto et al., 2018; Cagliari et al., 2019; Fritzen et al., 2019; Villegas-Martín et al., 2020; Mello et al., 2021; Fig. 3). These settings were episodically impacted by storm events during transgressive pulses, returning to their normal dynamics after these events ceased (e.g., Dalrymple et al., 2011). According to Cagliari et al. (2019), the high ash and sulfur contents (Saraiva and Marques, 1983) and the presence of framboidal pyritic nodules in these deposits are suggestive of marine incursions in these inner portions of the estuary during storm surges. The presence of pectinid mollusk-dominated shell beds and the crowded

Rosselia ichnofabric (CRI) in Cambaí paleovalley (Schmidt-Neto et al., 2018; Fig. 5b, d) and of CRI with large *Rosselia* specimens showing coal concentric linings in Capané paleovalley (Mello et al. 2021; Fig 5c) are also signatures of storm events. The mollusk shell beds show taphonomic signatures of reworking and burial by storm processes (Schmidt-Neto et al., 2018) the CRI is a product of high-energy, high-frequency storm events (Nara, 2002; Netto et al., 2014; Mello et al., 2021).

Despite the similarity in the facies architecture of these deposits, it is not possible to assume a stratigraphic correlation between them due to the lenticular geometry of the sandstone beds, their occurrence in distinct paleovalleys, and their potential recurrence in time and space.

3. Material and methods

The analyzed FSCs were sampled at bed tops bearing microbially induced sedimentary structures (MISS), mostly wrinkle structures, at five different outcrops in the Rio Grande do Sul State, southern Brazil (Figs. 2-5; Table 1). After extraction, the samples were oriented from the top toward the base and prepared for petrographic and geochemical analyses of the ferruginous crust.

Thin sections perpendicular and parallel to the bedding plane were used for petrographic descriptions using a ZEISS AXIO optical microscope. Samples UVLG-14278b, UVLG-14279c, UVLG-14280b, UVLG-14282a, UVLG-14283, UVLG-14285a, UVLG-14286b, UVLG-14287d, and UVLG-14290b (Table 1) were metalized with gold (3 min in Quorum Q150TES) to analyze MISS features and the elementary chemistry of the rock with an EVO/MA15 ZEISS system scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). Thin sections were prepared and analyzed at Unisinos University Polytechnical School lab facilities and are stored at the Museu da História Geológica do Rio Grande do Sul (MHGEO/UNISINOS) repository under the numbers ULVG-14282 and ULVG-14290 (Table 1).

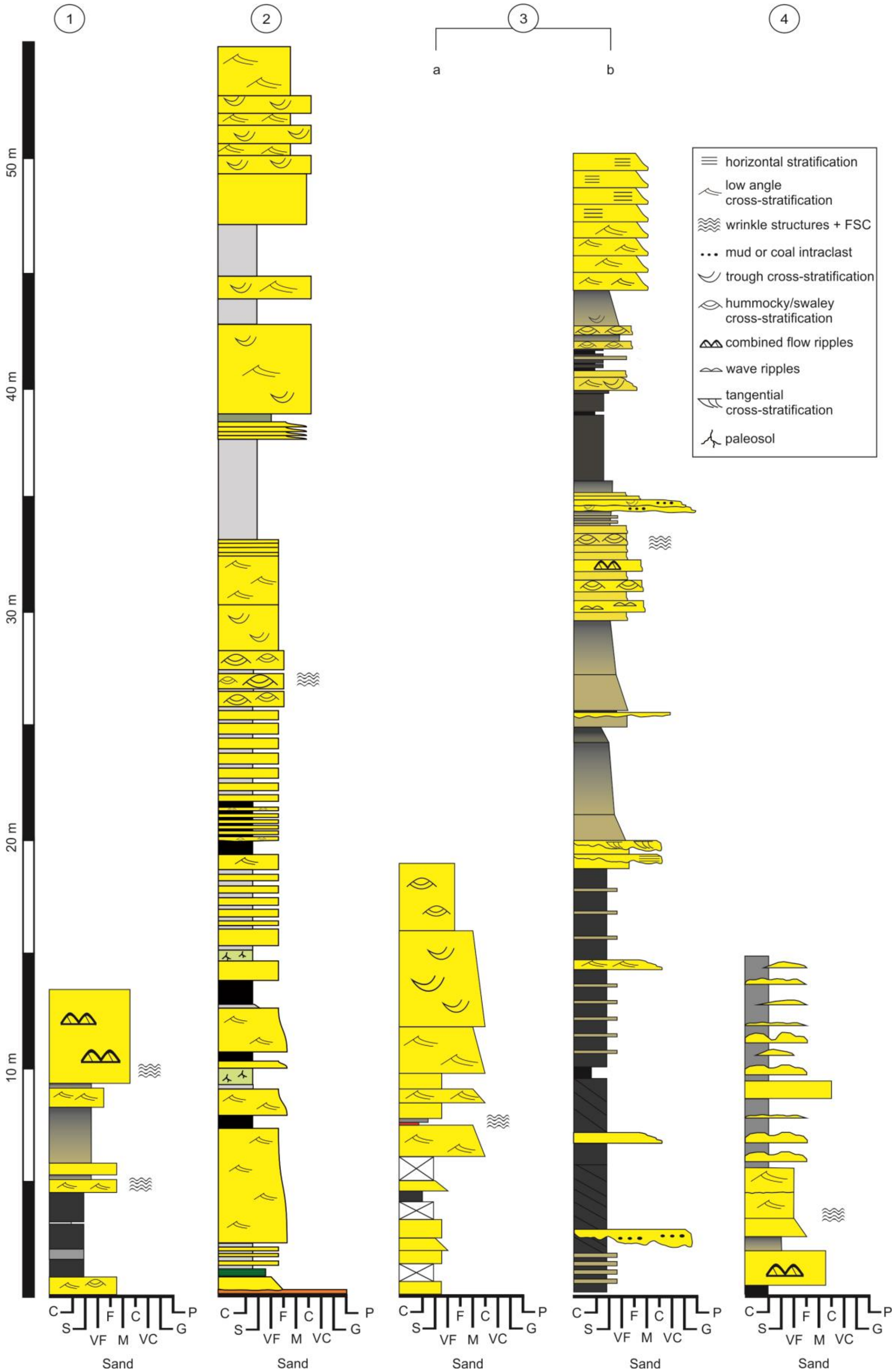
1
2
3
a
b
4
50 m
40 m
30 m
20 m
10 m
horizontal stratification
low angle cross-stratification
wrinkle structures + FSC
mud or coal intraclast
trough cross-stratification
hummocky/swaley cross-stratification
combined flow ripples
wave ripples
tangential cross-stratification
paleosol
C
S
VF
F
M
C
VC
G
P
Sand

Figure 3. Sedimentary succession of the Rio Bonito Formation in main studied outcrops highlighting the stratigraphic levels bearing the ferruginous sandy crusts cropping out at Arroio Jaguarão (Candiota paleovalley), Cambaí Grande (Cambaí paleovalley; adapted from Schmidt-Neto et al., 2018), Forninho (Capané paleovalley; adapted from Mello et al., 2021), Barrocada (Capané paleovalley), and Cascatinha (Iruí paleovalley; adapted from Netto, 1994). For outcrop location, see Table 1.

The mineral phases of the FSCs were obtained by X-ray diffraction (XRD) analysis performed exclusively in the Fe-rich top layer with an Emppyrean PanAlitycal device with radiation KαCu, 40 kV, 40 mA of filament current and range from 5º to 80° (2θ). The resulting data were processed by HighScore software, with the peaks being compared according to the database (PDF) referring to the used device, and graphics were edited using the software OriginPro 8.5. The chemical composition of the FSC were obtained by micro-Raman spectroscopy performed directly on the Fe-rich top layers with a inVia Renishaw microscope, using lasers of 633 nm and 785 nm with 17 mW and 300 mW total power (attenuated to 0.1 - 10%, respectively), and with variables exposure time and accumulation. The spectra were collected in microscopic mode using an objective 20x long-distance work and corrected for cosmic rays. The spectra was processed using the software OriginPro 8.5, in which a polynomial baseline was subtracted to highlight spectral features from the samples. No additional processing work was done on the data.

The SEM, EDS, and XRD analyses were performed at Instituto Tecnológico de Paleoceanografia e Mudanças Climáticas (itt OCEANEON, Unisinos University). Micro-Raman analysis was carried out at the Astrobiology Research Unit of the University of São Paulo (NAPAstrobio, PRP-USP). Treatment of the samples obeyed the standards practiced by these laboratories.

4. Results

4.1. Macroscopic and microscopic sedimentary features

The studied ferruginous crusts characterize the top of elongated lenticular sandy bodies, sometimes amalgamated. These sandy bodies show, in general, low-angle cross-stratification, hummocky cross-stratification, and swaley cross-stratification. The bed tops in which these crusts occur are laterally continuous (≥ 100 m) and show MISS macroscopic features, like wrinkle structures (Fig. 5f), remnant pockets (Fig. 5g), and trapping and binding (Fig. 5h) structures. Contacts with the overlying deposits are abrupt. The overlying deposits are heteroliths composed of intercalations of siltstone and very fine-grained sandstone (Fig.3-5).

Figure 4. The Rio Bonito Formation sandstone beds from where the ferruginous sandy crusts were sampled. (a-b) east of Arroio Jaguarão bridge at BR-293 road (Candiota paleovalley) from sandstone beds interspersed with the coal beds (a) and those that capped it (b); (c) Cambaí Grande Outcrop (Cambaí paleovalley); (d) Forninho Outcrop (Capané paleovalley; € Barrocada Outcrop (Capané paleovalley); (f) Cascatinha Outcrop (Iruí paleovalley). The arrows indicate the stratigraphic level from where de samples were collected. Average human scale = 1.70 m.

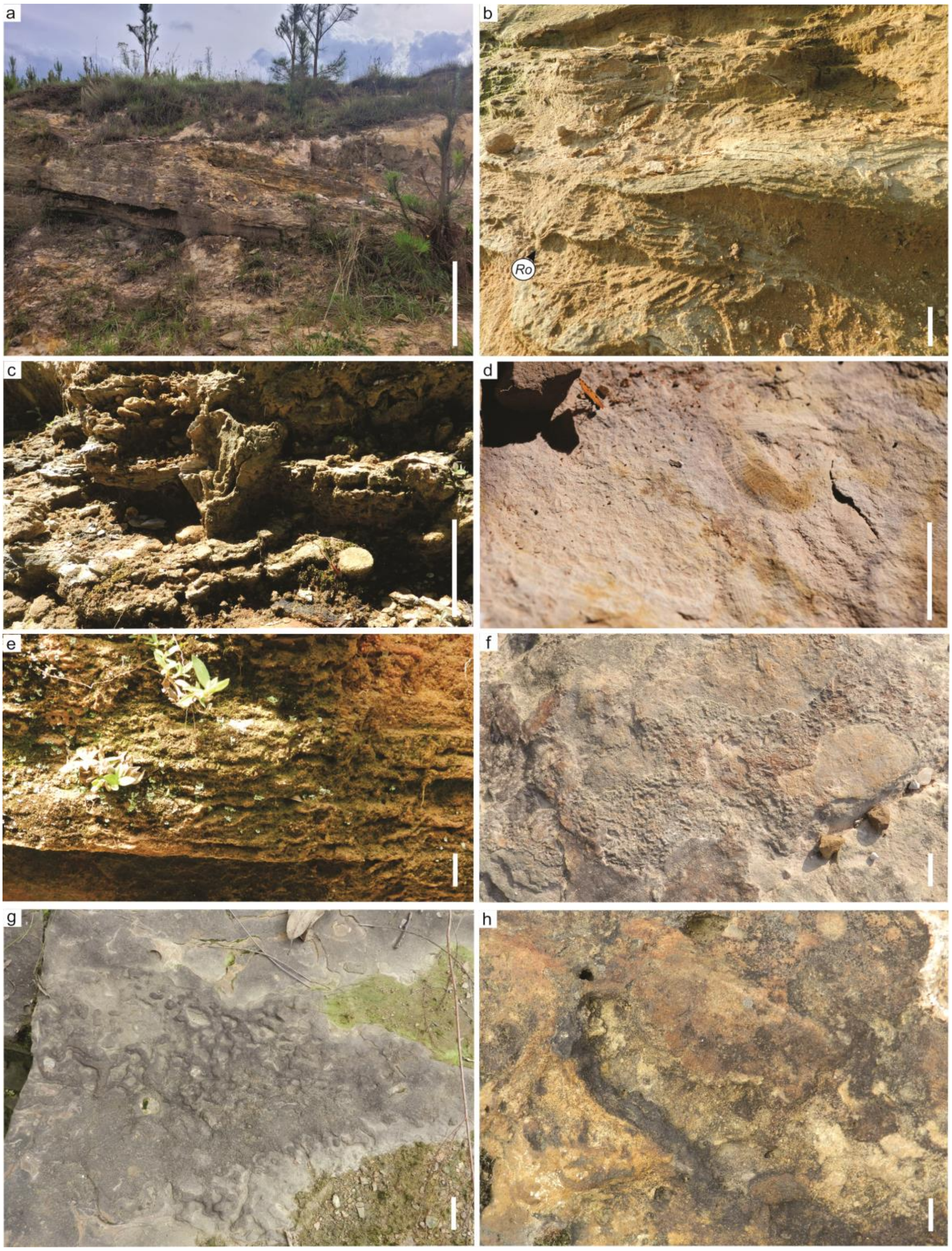

Figure 5. Sedimentary features associated with the storm-generated fine-grained sandstone beds bearing the ferruginous sandy crusts (FCSs). (a) Truncate, low-angle cross stratification, hummocky cross stratification, wavy bedding, and lenticular geometry; (b) Swaley cross stratification and funnel-shaped *Rosselia* isp. (*Ro*); (c) Close-up of *Rosselia* isp.; (d) Pectinid-dominated mollusk shell pavements. Microbially-induced sedimentary features observed in the FSCs: crenulated lamination (e) in FCS, wrinkle structures (f), remnant pockets (g), and trapping and biding (h). Scale bars: a = 1 m; b-d = 10 cm; e-h = 10 mm.

The iron-rich sandstone is composed predominantly of fine to medium quartz grains and subordinate rounded to subrounded grains of feldspars. In some samples, feldspar crystals are replaced by clay minerals, like kaolinite. These rocks are enriched in iron oxi-hydroxides (goethite and hematite). Muscovite, zircon, and epidot are minor components. The Fe oxi-hydroxides present globular, filamentous and amorphous morphologies and are immersed in an organic matrix (Fig. 6a-b, e). The ferruginous sandy crusts are particularly well-indurated iron-cemented beds. Chalcedony cement fills the pores of the rock in some samples UVLG-14282, UVLG-14284, and UVLG-14285, which are composed of grains with a ferruginous coating (Fig. 6f). In general, an organic-rich clay matrix with Fe oxi-hydroxides cementation occurs between the grains at the top of the sandstone beds. Microlamination and sinoidal structures (e.g., Nofke, 2010) are observed in some thin sections perpendicular to the bedding plane (Fig. 6d). In sample UVLG-14281 a (perpendicular cut), it was possible to verify a crenulate lamination on the top in association with organic matter and Fe oxi-hydroxides (Fig. 6c). Such crenulate laminations are a characteristic feature of microbial mat grow (e.g., Noffke, 2010; Noll and Netto, 2018). Microscopic filamentous and lumpy structures are also observed, reinforcing microbially induced features (Fig. 6e).

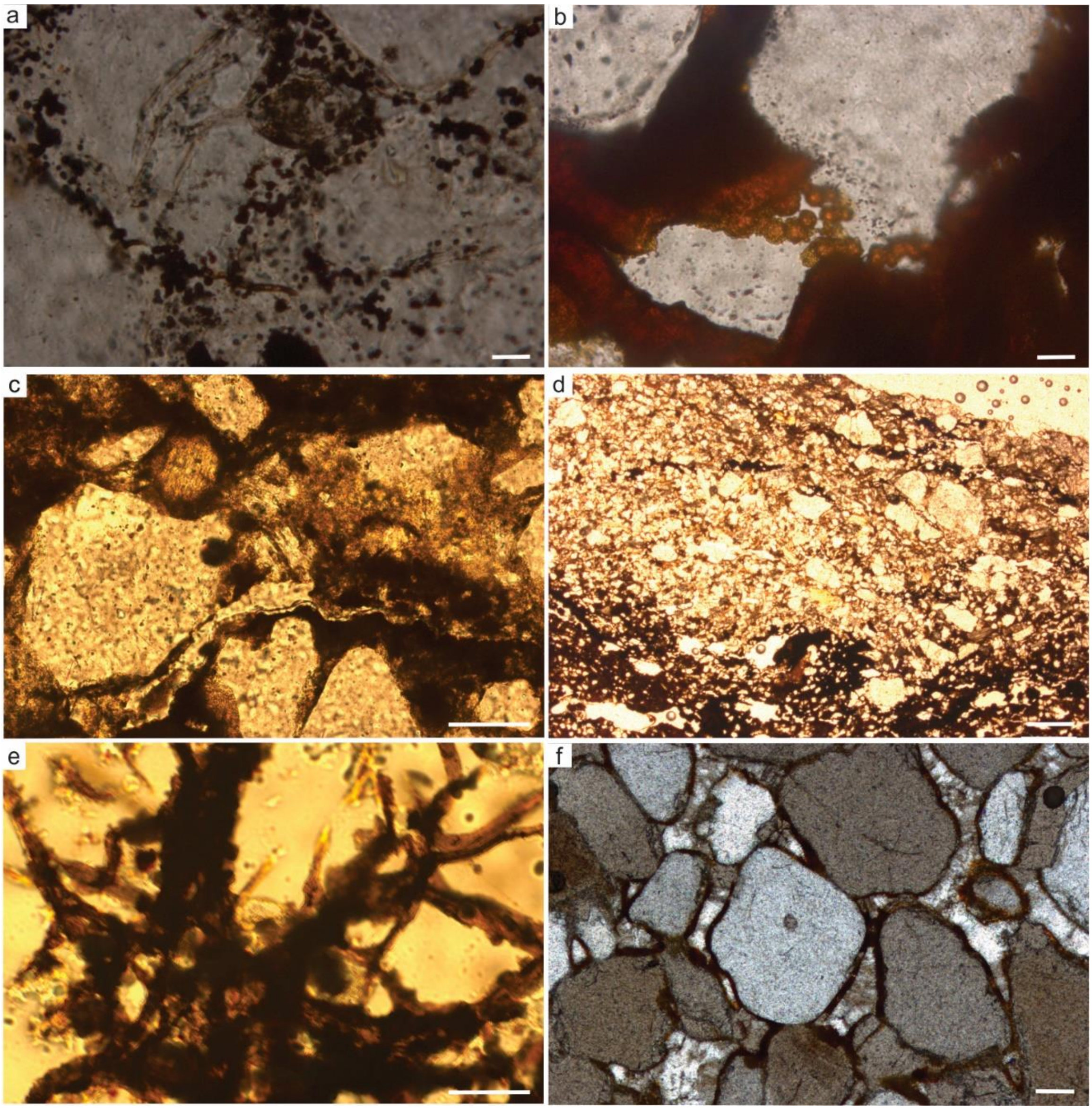

Figure 6. Organic-like features verified in thin sections, under natural light. (a) General view of the thin section, in which there are botryoidal forms dispersed in the matrix (ULVG 14285); (b) Botryoidal Fe oxides around the quartz grains (ULVG 14286); (c) Crenulate lamination on the top, in association with organic matter and Fe oxi-hydroxides (ULVG 14281a, perpendicular cut); (d) Microlamination (dark zone at the bottom of the image) and sinoidal structures (dark films in the lighter zone at the top of the image) observed in sample ULVG 14287; (e) Occurrence of filamentous structures (ULVG 14280b); (f) Grains that compose the rock with a ferruginous coating and chalcedony cement (ULVG 14284). Scale bars: a, b = 20 µm; c, e = 50 µm; d = 500 µm; f = 100 µm.

Outcrop	Paleogeographic location	Geographical coordinates (22J zone)	Samples	Description	
				Macroscopic features	Microscopic features
Cascatinha	Iruí Paleovalley	323598 E 6645951 N	ULVG 14282, ULVG 14283	Fine- to medium-grained sandstone. Well indurated/cemented sandstone with symmetric ripples preserved on the top.	Monocrystalline quartz and feldspar, partially dissolved, and replaced by clay minerals (kaolinite). Overgrowth quartz, microcrystalline silica, and Fe oxide are observed. Precipitation of globular goethite.
Forninho	Capané Paleovalley	268034.7 E 6643449.5 N	ULVG 14284	Fine- to medium-grained sandstone with medium-to low-angle planar stratification, symmetrical ripples preserved on the top, and wrinkle structures.	Monocrystalline quartz (dominant), polycrystalline quartz, feldspar, and mica. Zircon and epidote occur as accessory grains. Some grains are coated by Fe oxide cuticle. Microcrystalline silica (chalcedony) occurs filling the intergranular pores. Botryoidal goethite.
Arroio Jaguarão	Candiota Paleovalley	234914 E 6523299 N	ULVG 14285	Fine- to medium-grained quartz and felspars sandstone with low-angle cross-stratification.	Monocrystalline quartz and feldspar, partially dissolved and replaced by clay minerals (kaolinite). Overgrowth quartz, microcrystalline silica, and Fe oxide. Globular goethite. Volcanic fragments occur in thin sections ULVG 14285b and ULVG 14285c.
			ULVG 14286 to ULVG 14288	Medium to coarse-grained, locally very coarse-grained, sandstone with wave bedding, bi-directional cross-stratification, double mud drapes, reactivation surfaces.	Same of ULVG 14285. Abundant globular goethite; filaments. Volcanic fragments not observed.

			ULVG 14289	Fine to medium-grained sandstone amalgamated on top with symmetrical (locally interference) ripples, and wrinkle, remnant pocket and trapping and binding structures.	Monocrystalline and polycrystalline quartz, feldspars, and epidote (accessory). Clay silty matrix. Quartz overgrowth, little Fe oxide, chlorite nodules, and kaolinite.
Cambaí	Cambaí Paleovalley	212378 E 6645006 N	ULVG 14278 to ULVG 14281	Fine to medium-grained sandstone with hummocky cross-stratification and wrinkle structures.	Quartz, feldspars, and micas. Globular morphology; filaments. A crenulated surface is observed in thin section (ULVG 14281a).
Barrocada	Capané Paleovalley	278450 E 6640781	ULVG 14290	Fine- to medium-grained sandstone. Well-indurated/ cemented sandstone. Low-angle cross-stratification.	Quartz, feldspar, and muscovite (accessory). Microlaminated Fe bands (hematite and goethite). Fe oxides with globular morphologies.

Table 1. Macroscopic and microscopic description of the analyzed samples.

Long, thin filaments involving the sediment grains are observed in SEM analysis, arranged in the same way as bacterial filaments in an exopolysaccharide (EPS) matrix typical of biofilms and microbial mats (e.g., Noffke, 2010) (Fig. 7a, c-d and f). These filaments are similar in shape to those illustrated by Noll and Netto (2018) for fossil and modern records of microbial mats. SEM images also revealed the presence of twisted stalks (Fig. 7b) and tubular sheaths (Fig. 7e).

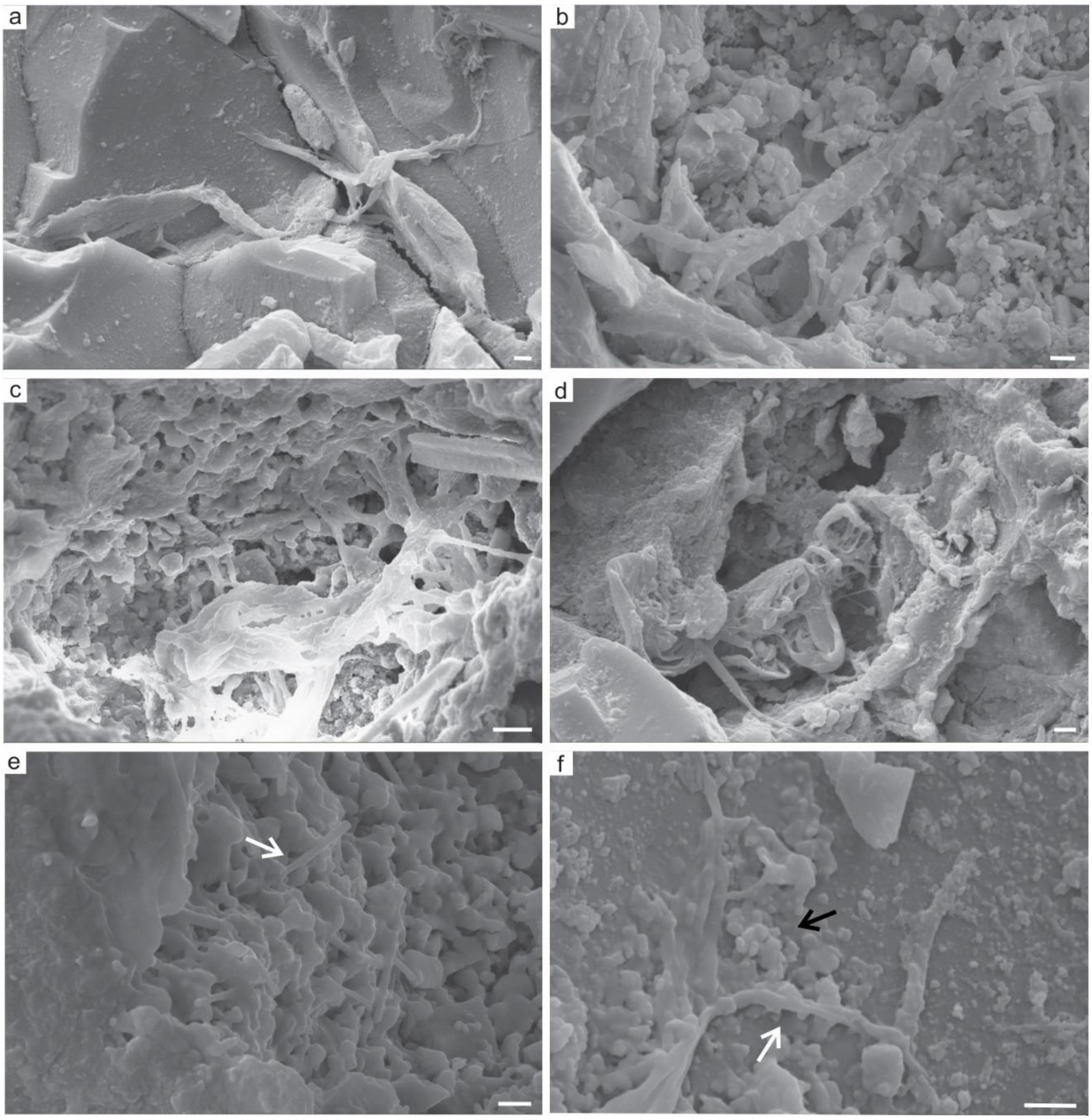

Figure 7. Scanning electron microscope (SEM) photomicrographs showing the presence of different organic-like forms. (a) Filamentous structures adhered to quartz grains; (b) Twisted stalk identified in the samples; (c-d) Filaments characteristic of mineralized EPS; (e) Presence of tubular sheaths; (f) Filamentous and lumpy structures. Scale bars: a-b, d-f = 2 µm; c = 10 µm.

4.2. Geochemical analyses

EDS analysis indicated Si, Fe, C, and O as the main chemical elements in the ferruginous crust. C and Fe are predominant in the composition of filaments and lumpy structures (Fig. 8). XRD and micro-Raman analyses allowed recognition of the mineral phases of quartz, microcline, kaolinite, goethite, hematite, graphite, and calcite (Fig. 9).

Kerogen occurs in samples UVLG-14280 and UVLG-14286 and graphite in sample UVLG-14280 (Fig. 10). The kerogen spectrum is composed by two principal peaks, so-called bands D and G.

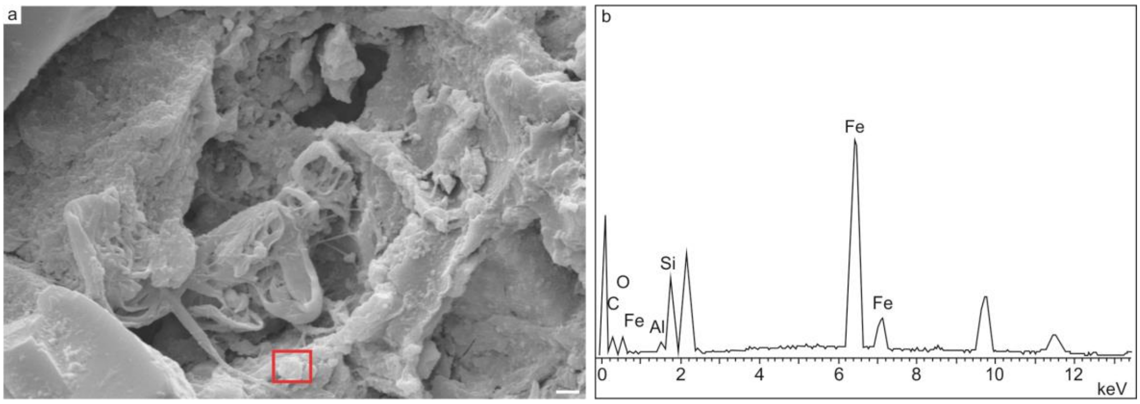

Figure 8. Results of the EDS analysis (sample UVLG-14278-b) highlighting the dominant presence of Fe and C in the analyzed spot (indicated by the red rectangle). Scale bar = 2 μm.

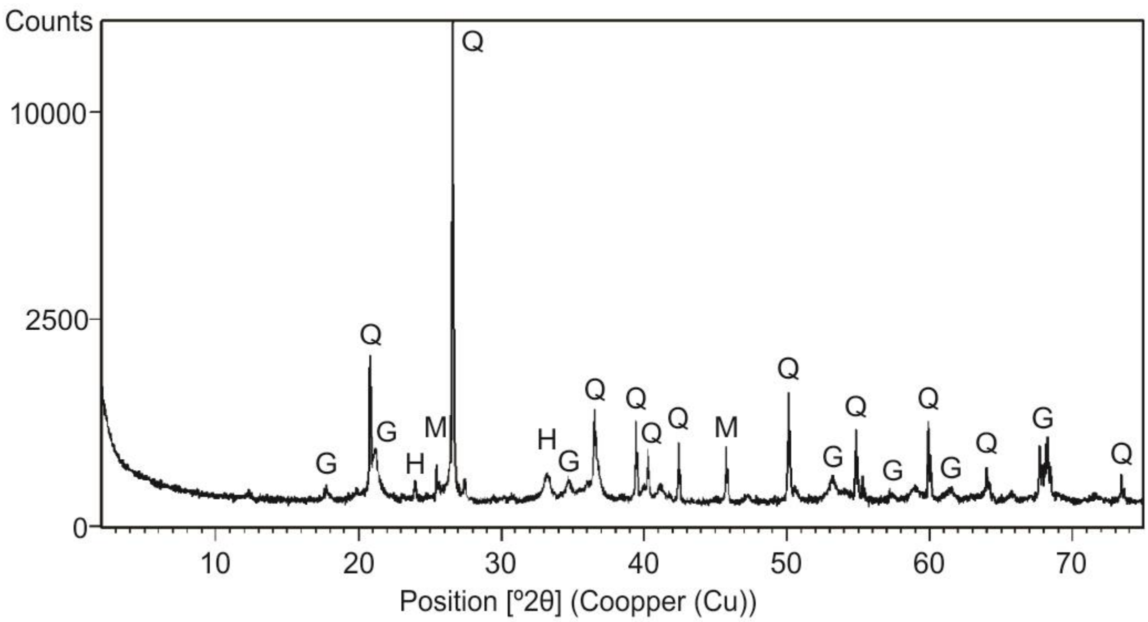

Figure 9. X-ray diffractogram of the ferruginous sandy crusts showing the mineral phase present in these samples (sample UVLG-14286). G= goethite; H= hematite; M= microcline; Q= quartz.

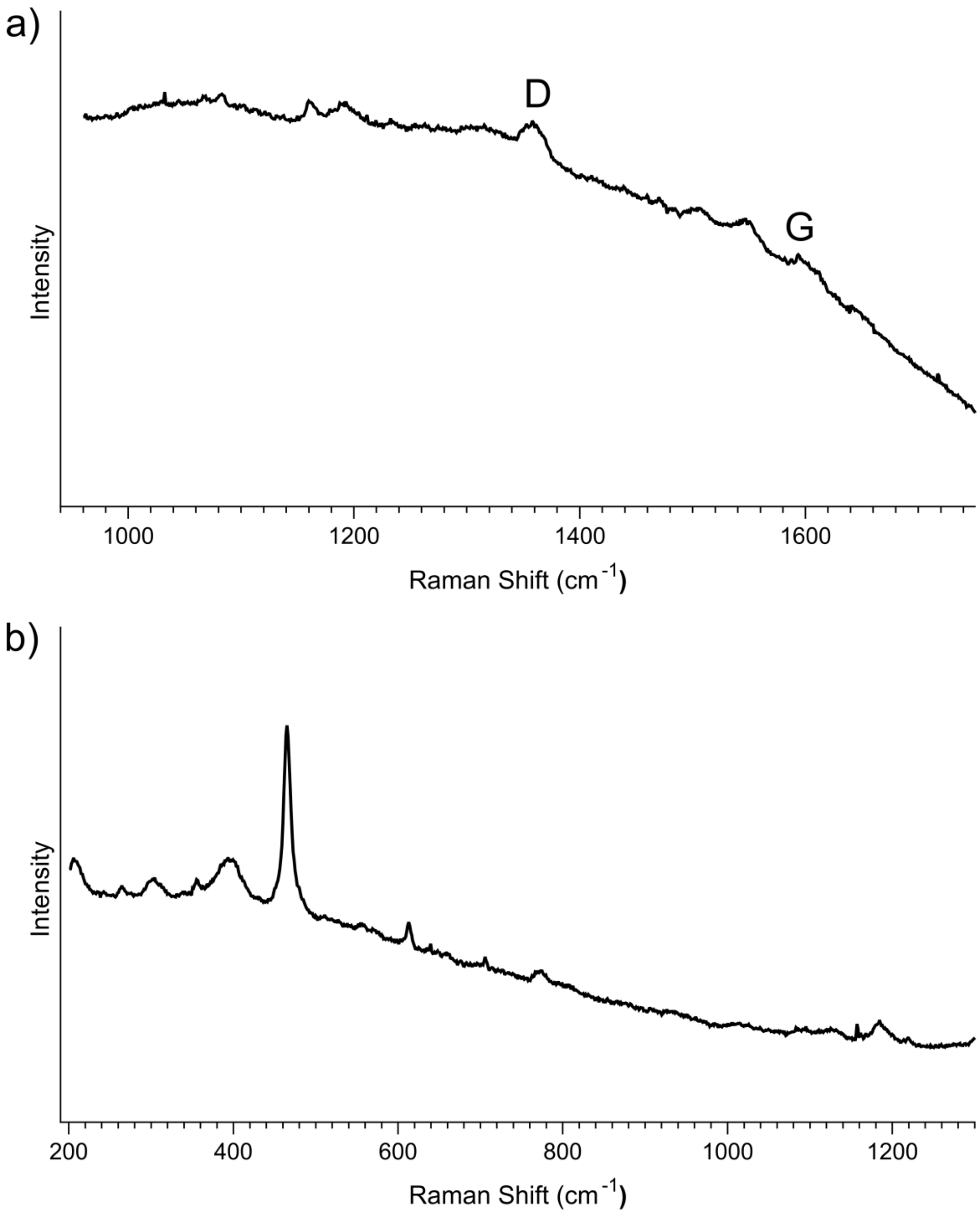

Figure 10. Raman spectra from sample UVLG-14287. (a) Raman spectra from 900 to 1720 cm^{-1} showing kerogen spectrum, with its two principal peaks, so-called D and G, and (b) Raman spectra from 200 to 1300 cm^{-1} showing the goethite peak.

5. Discussion

5.1 The nature of ferruginous crusts

Organic and mineral matrices interact and help determine minerals' stability in a substrate (Kappler et al., 2016). The interactions between organisms and substrate results in the production of biosignatures with information about the organism's physical structure, chemical composition (e.g., DNA, membrane lipids), metabolism, and life habits (e.g., Heim, 2010; Westall et al., 2006; Westall, 2008). These biosignatures also comprise the small-scale physical sedimentary structures resulting from the microbial-substrate interactions that can be preserved as microscopic MISS (e.g., Noffke, 2010; Davies et al., 2016; Noll and Netto, 2018). During the metabolic process, the environment may undergo physical and chemical changes, leaving some traces like biomorphs, organic molecules, stable isotopes and fractionated elements, biomineral deposits, and corrosion marks (Tucker, 2001; Heim, 2010).

The FSCs from the Rio Bonito Formation fulfill the criteria established by Jones (2010) to determine biosignatures, which are: the presence of mineralized microbes and remnants of microbial activity, the presence of sedimentary fabrics that can be attributed to microbial activity and the presence of geochemical proxies considered indicative of microbe activity.

We observed in the FSCs samples the occurrence of amorphous, globular, tubular sheaths, and twisted stalks morphologies of iron oxides-oxyhydroxides in an organic-rich matrix between the sandy grains. It indicates the syngenetic deposition of Fe, available in pore water, as a by-product of microbial metabolism. Biogenic minerals usually form nanocrystals with diverse morphologies and mineral compositions or occur as amorphous minerals (Kappler et al., 2016). The differences in the morphology and size of these structures potentially suggest that more than one group of bacteria was present in the original microbial assemblage. The structures found in the FSCs from Rio Bonito Formation are similar to those of ferruginous Betaproteobacteria (e.g., extant

Comamonadaceae and Gallionellaceae families; Fleming et al., 2011). Although it is difficult to precisely determine their taxonomy, tubular sheaths and twisted stalks structures are common among Fe-oxidizing bacteria, such as *Leptothrix* spp. and *Gallionella* spp., respectively. The globular morphology might be related to coccoid cyanobacteria, which are the first to colonize sediments at the water-sediment interface (Gyollai et al., 2015).

Leptothrix spp. and *Gallionella* spp. are the most abundant Fe-oxidizing bacteria in modern iron-rich freshwater settings (Fleming et al., 2014; McBeth et al., 2013). Estuaries have temporally unstable salinities, oscillating daily between freshwater and brackish conditions. *Leptothrix* spp. occurrence is reported only in freshwater and the *Gallionella* spp. could tolerate brackish water, but do not occur in fully marine systems (McBeth et al., 2013). Thus, the input of freshwater in the analyzed settings is essential for the growth of these two main groups of iron-synthesizing bacteria.

Leptothrix spp. and *Gallionella* spp. are common in suboxic and neutral pH coastal environments in the present day (Cowen, 1992; Emerson and Moyer, 1997; Fleming et al., 2014; Konhauser, 1998; McBeth et al., 2013). Kinetic limitations make ferrous iron relatively stable at acidic pH, even in the presence of O_2 (Stumm and Morgan, 1996), making microorganisms the main responsible for Fe (II) oxidation. However, at circumneutral pH, microorganisms have to compete with the rapid chemical oxidation of Fe (II) by molecular oxygen, making microorganisms thrive best in microoxic environments (Emerson and Moyer, 1997). In anoxic substrates, iron can be phototopically oxidized by iron-oxidizing bacteria that use light as an energy source (Widdel et al., 1993; Hegler et al., 2008). In this context, goethite and hematite with twisted stalks, tubular sheaths and globular morphologies are produced by direct microbial oxidation of Fe^{+2} to Fe^{+3}, depending on the pH and O_2 concentrations.

Leptothrix spp. and *Gallionella* spp. produce, respectively, tubular sheaths and twisted stalks to avoid the cell incrustation by direct Fe^{3+} precipitation (Chan et al. 2004, 2011, 2016). Microorganisms also produce poorly ordered ferrihydrite as a primary mineral which transforms into more ordered minerals (goethite and hematite) during diagenesis. This transformation occurs within a few months or years via dissolution-dehydration processes (Konhauser, 1998).

Cagliari et al. (2019) reported the presence of framboidal pyrite in coal layers of Capané and Iruí paleovalleys, assuming it as a signature of marine incursion in the protected settings where organic matter was accumulated. However, it is well known that the precipitation of pyrite in framboid morphology is attributed to microbiological activity (Maclean et al., 2008).

The biogeochemical cycle of iron is very complex; the processes of oxidation and reduction could not be separate in natural environments, occurring cyclically or even simultaneously (Kappler et al., 2021). In the studied crusts we also observed the occurrence of filaments that indicated the presence of remnants of the microbial activity. These filaments are generally attached and partially wounded to sand grains, indicating the original presence of EPS (e.g., Gerdes et al., 2000; Noffke et al., 2001; Porada and Bouougri, 2007; Noffke, 2010). EPS plays a key role in microbial communities, providing protection against desiccation and other extreme effects while improving surface adhesion and colony stability (Nielsen et al., 1997; Wolfaardt et al., 1999; Schieber et al., 2007). Aggregated communities of microorganisms are common in aquatic settings forming biofilms and microbial mats (e.g., Teske and Stahl, 2002). Water and nutrients provide the organic richness necessary for biofilm generation, opening the colonization window (*sensu* Pollard et al., 1993) for microbes to quickly grow up and expand the populations in the microbial community (Heim, 2010). Under favorable conditions and over time, other microbial species become part of the community, making the ecosystem complex and diverse.

The biominerals differ from chemically synthesized minerals in key aspects (Kappler et al., 2016). Compared to silicified extracellular stalks of Fe-oxidizing bacteria, abiogenic filaments are strongly oriented and show larger diameters, lack of branching patterns, Fe-rich bands, and particulate interiors (Johannessen et al., 2020). The filaments preserved in the crusts analyzed herein have diameters smaller than 1μm.

Another criterion adopted by Jones (2010) is the presence of sedimentary fabrics that can be attributed to microbial activity. Macroscopic and microscopic MISS occur on the bed tops where the FSC occur in the Rio Bonito Formation (Fig. 4a-b, Table 1). The occurrence of wrinkle structures, remnant pockets, trapping and binding and wavy tops (Fig. 4) indicated the bioestabilization of substrate. The microlaminations and sinoidal structures observed in some thin sections reveal the interactions of biofilms and the sandy deposits (Fig. 6d). The exceptional preservation of the mollusk shell's molds and the preservation of very small plant fragments in coeval storm beds in the Cambaí palleovalley (Schmidt-Neto et al., 2018) also suggest substrate stabilization and covering by biofilms and microbial mats. The biofilms quickly covered these pavements, encapsulating the shells and plant fragments preventing them from erosion and reworking by waves and currents (e.g., Hao et al., 2016; Raff et al., 2008; Martins et al., 2022). Sedimentary surfaces can be tightly bound or biostabilized by EPS (Characklis and Wilderer, 1989; Peng and Jones, 2012). The observed organic structures observed (amorphous, globular, sheath and stalks structures) are closely associated with the preserved EPS filamentous and lumpy structures (Fig. 7).

The presence of geochemical proxies considered indicative of microbe activity is the third criterium postulated by Jones (2010) to determine biosignatures. Microbial communities strongly depend on EPS for their metabolic processes and colony protection (Limoli et al., 2015). EPS is comprised of polysaccharides, proteins, nucleic acids, lipids, and humic compounds (Nielsen et al., 1997; Wolfaardt et al., 1999; Schieber et al., 2007). During burial (diagenesis and catagenesis), EPS undergoes transformations and becomes biomarkers (Brocks and Pearson, 2005; Vandenbroucke and Largeau, 2007), such as kerogen and graphite, which are present in the FSCs from the Rio Bonito Formation.

5.2. Ferruginous crusts as biomarkers of discontinuity surfaces on a high-resolution stratigraphic scale

Although diagenesis usually destroys microbial filaments, they can be preserved during depositional hiatus, where sedimentation is extremely low and compaction is minimal (e.g., García-Hidalgo et al., 2018; Préat et al., 2018). Petrophysical analyses of the studied samples of the Cambai palleovalley indicate low compaction and to substrate biostabilization (Braga, 2021), a factor that favored the preservation of filament molds.

The microscopic and geochemical biosignatures of bacteria, the presence of MISS associated with the analyzed FSCs, and the exceptional preservation of the mollusk shells in the Cambaí paleovalley corroborate with the development of microbial mats on the top of the storm beds formed in the inner portion of the estuarine systems developed in the paleovalleys at the southern border of the Paraná Basin (Cagliari et al., 2014, 2016, 2019; Schmidt-Neto et al., 2018; Fritzen et al., 2019; Villegas-Martin et al., 2020; Mello et al., 2021). The Paraná Basin was affected by an increase in humidity and temperature in the Early Permian caused by the demise of glaciation in western Gondwana (Cagliari et al., 2016). It is likely that the deglaciation process enhanced the availability of iron in the hydrologic systems due to greater chemical weathering, especially when considering the proximity to the source area. After storms ceased, the hydrodynamic conditions in the estuary returned to normal, characterizing a calm Fe-rich environment, especially in protected, low-energy settings. According to Tucker (2001), ironstone formation is favored by low sedimentation rates.

The occurrence of FCSs is restricted to certain stratigraphic levels in the middle portion of the Rio Bonito Formation sedimentary succession (e.g., Netto, 1994; Schmidt-Neto et al., 2018; Mello et al., 2021). They represent dormancy periods in the paleovalleys, favoring the development of epibenthic microbial mats. There is strong evidence to support that these storm deposits were formed in the estuary, and not in shoreface settings, as generally interpreted by the medium portion of the Rio Bonito Formation in the Rio Grande do Sul State (e.g., Lavina et al., 1985; Lopes et al., 1986, 2003a,b,c; Elias et al., 2000; Holz et al., 2010; Cagliari et al., 2014).

Frequent fluctuations in salinity and oxygenation rates, common in estuarine settings, have been largely attested by bioturbation in the Rio Bonito Formation (e.g., Netto, 1994; Buatois et al., 2005, 2007; Tognoli, 2006; Gandini et al., 2010; Schmidt-Neto et al., 2018; Villegas-Martín and Netto, 2019; Villegas-Martín et al., 2020; Mello et al., 2021). It suggests periods of stressful ecological conditions for most burrowing macroorganisms, creating an ideal context for microbial mat growth. These stressful conditions might be enhanced by the input of humic materials eroded from the peat bogs formed in adjacent supratidal zones, creating a highly toxic environment for all organisms except microorganisms. Coal beds varying from less than a meter to up to 9 m in thickness occur in these paleovalleys (e.g., Aboarrage and Lopes, 1981; Lavina et al., 1985; Holz et al., 2010). Thus, it is feasible to suppose that the storm waves might have eroded part of the original peat bogs in some portions of the basin. This organic matter input might have served as a source for aerobic bacteria, creating oxi-reducing or poorly oxygenated conditions at the sediment-water interface in a few tens of centimeters.

The presence of FSCs on the top of sedimentary cycles indicates substrate compaction and a discontinuity surface associated with very low sedimentation rates (McLaughlin et al., 2008; García-Hidalgo et al., 2018). Typical features associated with emersion and subaerial exposure (e.g., root horizons, paleosols and/or bauxitic horizons) do not occur in the analyzed ferruginous crusts, indicating subaqueous early cementation. The presence of discrete paleosols in underlying layers in some of the studied outcrops (e.g., Gandini et al., 2010; Schmidt-Neto et al., 2018; Villegas-Martín et al., 2020; Mello et al., 2021) reinforces the existence of quiescence periods in the paleovalleys. In the Rio Bonito Formation, the FSCs are typically thin (a few centimeters), suggesting a short time available for the crust development rather than erosion by subsequent events. These aspects suggest that the depositional processes were controlled by high-order eustatic fluctuations, with the existence of repeated falls in the relative sea level during the long-term rise.

6. Conclusions

The data presented herein support a synsedimentary origin of the ferruginous crusts triggered by microbial activity in these coastal clastic environments. The biosignatures present in the ferruginous crusts indicate the original presence of organic carbon, preserved as kerogen and graphite, and remnants of microbial metabolic activity. They also indicate the presence of iron-rich minerals, filaments, lumpy structures, and wrinkle structures.

The authigenic origin of the ferruginous crusts reinforces the interpretation of deposition in protected settings affected by storm surges in the inner estuary. These storm surges locally provided conditions for the emergence of microbial mats. Crust development reveals a hiatus during minor episodes of sedimentary starvation. It demonstrates the value of biosignatures as relative proxies for reconstructing sedimentary dynamics in ancient siliciclastic environments.

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2. Síntese integradora

Com base nos resultados obtidos neste estudo é possível concluir que as crostas de ferro presentes nos depósitos arenosos da porção mediana e superior da Formação Rio Bonito foram precipitadas a partir da mediação microbiana, sendo, portanto, sinsedimentares. A metodologia adotada permitiu observar a presença de feições biogênicas, como as ocorrências grumosas e filamentosas e o registro de goetita botroidal, feições comumente observadas em ferro-bactérias como *Leptothrix* (*sheats*) e em cianobactérias cocoides. Com relação às análises geoquímicas, foi possível verificar a ocorrência predominante do mineral de goetita, seguido por hematita, além da presença de querogênio em algumas amostras. O querogênio é um importante biomarcador, indicando a origem orgânica do carbono presente nas amostras.

O desenvolvimento de esteiras microbianas ocorre em ambientes calmos, protegidos, que garantam a janela de tempo necessária para a adesão dos micróbios ao substrato e a formação dos biofilmes (horas) e para o crescimento das esteiras epibênticas (semanas). Tais contextos já foram propostos por outros autores para os depósitos analisados (Mello et al., 2021; Schmidt-Netto et al., 2018). A partir da análise integrada, envolvendo a sedimentologia e a icnologia, sabe-se que a deposição destes sedimentos ocorreu em um ambiente protegido, afetado esporadicamente por ondas de tempestade na porção interna de um estuário. A presença das crostas arenosas ferruginosas revela um hiato durante pequenos eventos de estagnação sedimentar, em escala estratigráfica de alta resolução. Logo, essas crostas biogênicas possuem valor para a reconstrução da dinâmica de depósitos siliciclásticos do passado.

Assim, considera-se que o objetivo deste estudo foi atingido, obtendo-se repostas para a pergunta-problema, permitindo validar a hipótese levantada a partir do emprego da metodologia adequada.