

Lontras Shale (Paraná Basin, Brazil): Insightful analysis and commentaries on paleoenvironment and fossil preservation into a deglaciation pulse of the Late Paleozoic Ice Age



Lucas D. Mouro^{a,b,*}, Mírian Liza Alves Forancelli Pacheco^{c,d}, João H.Z. Ricetti^{e,f}, Ana K. Scmazzone^e, Rodrigo S. Horodyski^g, Antonio C.S. Fernandes^b, Marcelo A. Carvalho^b, Luiz C. Weinschutz^e, Mateus S. Silva^h, Breno L. Waichel^a, Claiton M.S. Scherer^e

^a Pós-Graduação em Geologia, Departamento de Geologia, Universidade Federal de Santa Catarina, PFRH-PB 240, Florianópolis, SC 88040-900, Brazil

^b Departamento de Geologia e Paleontologia, Museu Nacional/Universidade Federal Rio de Janeiro, Rio de Janeiro, RJ 20940-040, Brazil

^c Laboratório de Estudos Paleobiológicos, Departamento de Biologia, Universidade Federal de São Carlos, Campus Sorocoba, Rodovia João Leme dos Santos - até km 104, 000, Parque Reserva Fazenda Imperial, 18052780 Sorocaba, SP, Brazil

^d Departamento de Física Nuclear, Instituto de Física, Universidade de São Paulo, R. do Matão, 1371 – Butantã, 05508-090 São Paulo, SP, Brazil

^e Departamento de Paleontologia e Estratigrafia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS 91501-970, Brazil

^f Centro Paleontológico da Universidade do Contestado, Universidade do Contestado, Mafra, SC 89300-000, Brazil

^g Geology Graduate Program, Universidade do Vale do Rio dos Sinos, São Leopoldo, Rio Grande do Sul 93022-750, Brazil

^h Universidade Federal de Santa Catarina, PFRH-PB 240, Florianópolis, SC 88040-900, Brazil

ARTICLE INFO

Keywords:

Late Paleozoic
Western Gondwana
Fjord Bay
Fossilization

ABSTRACT

The Lontras Shale is a fossil site located in Mafra, Santa Catarina, south of Brazil. This Late Paleozoic (Pennsylvanian - Cisuralian) stratum holds an important place with great potential for the synthesis of knowledge about paradigmatic events that happened on Gondwana. This marine fossil site, preserved into a 1.1 m black shale, comprises a combination of different kinds of preservation, in broad taphonomical spectra, including hard and/or soft-tissues of aquatic (e.g., fishes, poriferans and ammonoids) and terrestrial biotas (e.g., insect and woods), among other organisms that were well preserved under still unrevealed process and conditions. Considering the prevailing depositional settings and aiming to present fossil diagenetic aspects that led to some special preservation modes, we performed chemical analyses of sponges and insects by means of energy-dispersive spectroscopy (EDS), synchrotron micro-X-ray fluorescence (micro-XRF) and Raman spectroscopy. To date, we have identified the majority of fossils preserved as carbonaceous compressions or phosphatized forms. The well-preserved fossils have so far permitted new insights into metazoan evolution, especially regarding Insecta, Porifera, and Conodonta. Our findings not only allow suggestions regarding the chemical remains of soft tissues on these specimens but also can provide background data for future analyses of these groups in similar depositional settings.

1. Introduction

Understanding the evolutionary history of life on Earth is one of the main goals of paleontologists, and the key combination to achieve this objective is mixing multiproxy analyses with well-preserved (or even exceptionally well-preserved: Fossil-Lagerstätten – FL – cf. Seilacher, 1970) paleobiotas. These outstanding deposits occur among different sedimentary environments (e.g., lacustrine and marine) documented over billions of years on geological time, and, more than telling the tale

of extinct organisms, research on modes and types of preservation can provide information on factors, conditions, and geobiological processes that affect fossil record information (e.g., Allison and Briggs, 2011; Laflamme et al., 2011). Despite their importance, well-preserved and diverse paleobiotas are rare, normally found in clusters of deposits with similar ages, depositional settings and geographical locations (Muscente et al., 2017; Cardoso et al., 2020). Many worldwide special deposits do not necessarily need to fill the FL parameters once they provide reliable information to address evolution, modes of

* Corresponding author at: Pós-Graduação em Geologia, Departamento de Geologia, Universidade Federal de Santa Catarina, PFRH-PB 240, Florianópolis, SC 88040-900, Brazil.

E-mail addresses: lucas.delmouro@gmail.com, ldmouro@outlook.com (L.D. Mouro).

<https://doi.org/10.1016/j.palaeo.2020.109850>

Received 6 March 2019; Received in revised form 6 April 2020; Accepted 5 June 2020

Available online 10 June 2020

0031-0182/ © 2020 Elsevier B.V. All rights reserved.

preservation and paleogeographic distribution. Therefore, considering the rare circumstances for having well-preserved paleobiotas, it is reasonable to say that knowledge obtained from “underdog” special sites is priceless, especially in certain time range and geographic places (for example, Late Paleozoic – Western Gondwana).

One of those special fossil sites presented herein is the Lontras Shale macrofossil horizon (LSMH), which was discovered in 1908 by Jay Backus Woodworth and Euzébio Paulo de Oliveira during prosecutions for glacial beds in southern Brazil (funded by the Shaler Memorial Fund, USA; see Woodworth, 1912; Ruedemann, 1929; Oliveira, 1930; Mouro et al., 2018). Attracting little attention for about one century, the presence of well-preserved fishes, insects and sponges has led to many authors claiming this deposit as a FL (Scomazzon et al., 2013; Ricetti et al., 2016; Mouro et al., 2016, 2017). Recent multiproxy research (paleontological, palynological, paleoecological and geochemical) has brought novel information regarding the LSMH. Its deposition occurred in a restricted marine environment with prolonged periods of seafloor anoxia/euxinia and intermittent photic zone euxinia. Such environments have provided a suitable scenario for the preservation of hard and possibly soft-tissue assemblages, through still unknown mechanisms (Scomazzon et al., 2013; Ricetti et al., 2016; Mouro et al., 2016, 2017).

Although part of the paleoecological data (fossil assemblage and environmental aspects) have already being analyzed, the fossil diagenetic aspects that lead to special fossil preservation have never been addressed. Therefore, in order to understand better this complex fossil assemblage, we present the taphonomic and paleoenvironmental potential of LSMH, based on a brief chemical overview from sponges and insects. We provide insightful analysis and commentary on a new way of looking at this deglaciation deposit, a possible Late Paleozoic Lagerstätten.

2. Stratigraphy and location

The intracratonic Paraná Basin (about 1,700,000 km²) is located in southern Brazil and north/northwestern Uruguay, parts of Paraguay and Argentina (Fig. 1). The basin has a NE-SW elongated shape. Its sedimentary fill was influenced by tectonic-eustatic cycles linked to the evolution of Western Gondwana during Paleozoic and Mesozoic. Six second-order depositional sequences, or supersequences (Late Ordovician to Late Cretaceous), compose the basin filling (Milani and Ramos, 1998; Milani et al., 2007). The stratigraphic interval herein studied is situated in the third supersequence, named “Gondwana I” (Late Carboniferous to Early Triassic).

The lower deposit of the Gondwana I sequence is represented by the Itararé Group, which is composed by a complex stratigraphy, comprising subglacial and proglacial deposits of the Late Paleozoic Ice Age (Carvalho et al., 1942; Rocha-Campos, 1967; Schneider et al., 1974; Milani, 1997; Milani et al., 2007; Vesely, 2006; Rocha-Campos et al., 2008; D’Ávila, 2009; Holz et al., 2010; Vesely et al., 2015; Aquino et al., 2016; Valdez Buso et al., 2019; Fallgatter and Paim, 2017). Based on subsurface data, this group is subdivided into three formations, i.e., Lagoa Azul, Campo Mourão, and Taciba (França and Potter, 1988).

The stratigraphic interval herein corresponds to the Lontras Shale, an uppermost unit of the Campo Mourão Formation (França and Potter, 1988). The Lontras Shale is a basin-scale stratigraphic marker, related to a maximum marine flooding event (França and Potter, 1988). According to Valdez Buso et al. (2019), this interval represents a second Deglaciation System Tract (DST2 from sub-cycle II of Cycle II, a 3rd-order or high-frequency, orbital-driven glacial cycles), comprising marine proglacial deposits and representing cycles of ice retreat, which result in a relative sea-level rise. The DST2 records marine proglacial sedimentation, derived from distal low concentration turbidity plumes and hemipelagic sediments (Valdez Buso et al., 2019).

Regionally (Mafra region, Santa Catarina state), the Lontras Shale is approximately 50 m thick, comprising a series of thin varved shales

alternating with siltstone and mudstone packages (Weinschütz and Castro, 2005). The deglaciation processes are evident in the Campaleo section, composed basally by a microvarved shale with striated dropstones, decreasing in size upward and overlain by an ichnofossiliferous siltstone package; the maximum transgression is reached at the LSMH, a 1.1 m-thick macrofossil-rich black shale (Castro, 1999; Weinschütz and Castro, 2005; Hamel, 2005; Mouro et al., 2016; Ricetti et al., 2016; Mouro et al., 2017).

The age of the strata is currently under discussion. Based on U–Pb zircon dating, Cagliari et al. (2016), Valdez Buso et al. (2019), Griffis et al. (2019a, 2018), and Griffis et al. (2019b) have assigned the upper portion of the Itararé Group as Upper Carboniferous. The contact with its superior unit, the Rio Bonito Formation, marks the Carboniferous/Permian transition.

Otherwise, LSMH biostratigraphic data obtained through palynology and conodonts (*Mesogondolella* spp. Zone and *Vittatina costabilis* Zone) suggest a Cisuralian age to the Lontras Shale (Petri and Souza, 1993; Dino and Rösler, 2001; Souza, 2005; Holz et al., 2010; Scomazzon et al., 2013; Wilner et al., 2016a). This dating is supported by initial Rb–Sr analysis from LSMH samples (Koester et al., 2016). The age distinction between chronologic techniques allows insight into the possibility of diachronous deglaciation within the Itararé Group in Brazil, as seen in the Paganzo Basin, Argentina (Moxness et al., 2018). However, considering the last data published on absolute dating (Cagliari et al., 2016; Valdez Buso et al., 2019; Fedorchuk et al., 2019; Griffis et al., 2019b), we may consider a Pennsylvanian age for the Campaleo Outcrop.

The LSMH excavation site referred to herein, known as the Campaleo outcrop (S 26°09' 30.22", W 49°48' 52.82" - Fig. 1), is located along road BR 280, 2 km from the junction with BR 116, in the city of the Mafra urban area, northern Santa Catarina State, southern Brazil. Basally, the site contains the first 10 m of the LSM, overlain by the macrofossiliferous, 1.10 m-thick black shale (LSMH), followed by a nonfossiliferous, 7 m-thick shelly rhythmite layer (Fig. 2). Based on pyrite concentration, rock features, and fossil content, Ricetti et al. (2016) divided the LSMH into four levels, including sublevels.

3. Brief review of Lontras Shale

3.1. Biota

- Fishes: at least two hundred completed lower actinopterygian fishes have long been described (Fig. 3) (Malabarba, 1988; Richter, 1991; Hamel, 2005), including juvenile and adult specimens. According to Hamel (2005), these fishes are either uncompressed on phosphatic concretions or flattened on shale matrix. On the other hand, the Chondrichthyes are represented mainly by *Symmoriformes* teeth and other Chondrichthyes teeth (Pauliv et al., 2014), and hitherto no body is preserved. This group is still undergoing detailed taphonomic and diagenetic characterization, but first results have indicated they are phosphatized.
- Conodonts: dozens of articulated conodont apparatuses and hundreds of isolated specimens of conodont elements *Mesogondolella* spp. (Scomazzon et al., 2013; Wilner et al., 2016a; see Electronic Supplementary Material), have been recovered in five different sublevels, alternating the preservation of P1 and ramiform elements. These elements still under study, however according to Scomazzon et al. (2013), they are all composed of calcium phosphate (phosphatized).
- Poriferans: Articulated hexactinellid specimens *Microhemidiscia greineri* (Mouro et al., 2014a) are the most abundant (almost 100 complete specimens) and are well delimited with the presence of hemidiscs (microscleres composed of SiO₂), hexactins, pentactins, and root tufts (Fig. 4a,b). Mouro (2017) also reported the possible demospongid occurrence by describing a sample collected by Oliveira (1927), which is housed at New York State Museum, and

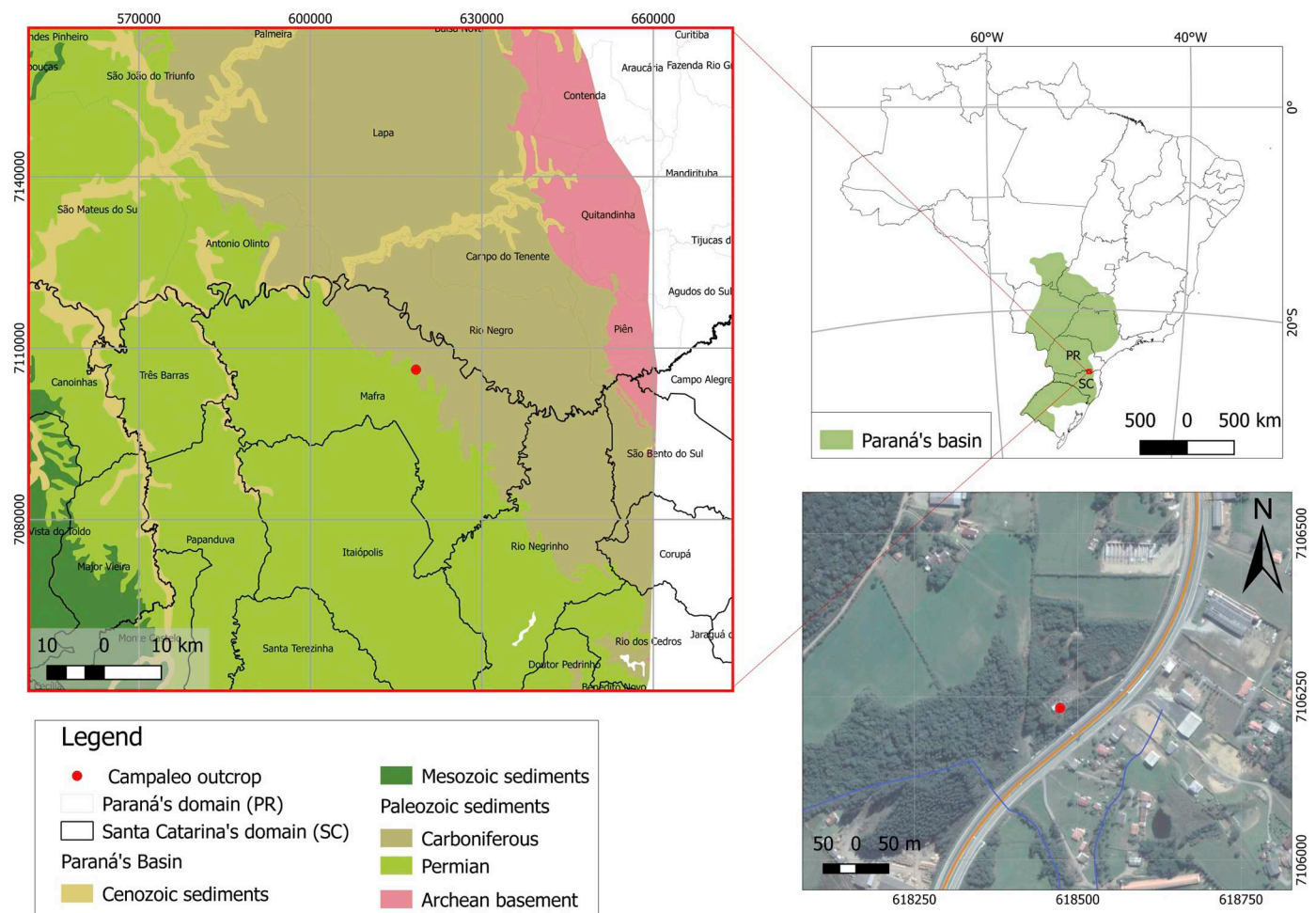


Fig. 1. Regional extent map within the Paraná Basin and the Campaleo site location.

other uncompleted specimens. Mouro et al. (2017) have recognized two taphofacies: T1- which comprises the hexactinellid specimens, where the specimens were flattened, articulated, with siliceous spicules (3D) and a possible outer layer preserved showing a calcium phosphate composition; and T2 – flattened demospongid with loose spicules, mainly substituted by pyrite.

- Brachiopods: one of the first fossils identified and described at the LSMH (Woodworth, 1912). This group comprises at least 40 specimens, mainly composed by small *Langella imbituvensis*, *Chonetes rionegrensis*, *Biconvexiella roxoi*, *Quinquenella?* sp., *Beecheria?* sp., and *Orbiculoidea guaraunensis* (Oliveira, 1930; Neves et al., 2017; see Electronic Supplementary Material). This group still under detailed taphonomical study. However, preliminary results for these specimens have shown that they have minor sizes, are isolated and are normally found parallel to the bed plane. Also, they are mainly preserved kerogenized, but a few specimens are pyritized or phosphatized.
- Annelids: the annelids (Polychaeta) are represented by more than 20 scolecodont articulated feeding apparatuses recovered inside phosphatic concretions and sparse elements in the shale layers. In the referred concretion, cylindrical segmented structures with chaeta-like rays are perceptible, suggesting the preservation of the Polychaeta body structure with probably a carbonaceous composition (Ricetti and Weinschütz, 2011; Ricetti et al., 2014; Mouro, 2017).
- Crustaceans: samples of crustacean assigned to the Malacostraca have been recovered mostly as fragments with a few rare complete body fossils (Adami-Rodrigues et al., 2012). A small cluster of

Ostracoda has also been identified with a calcium phosphate smooth carapace by MEV (Kallen et al., 2014). The ostracods are still under study, and the presence of calcium phosphate is an interesting point, since it can register as globules from the epidermal layer (see Keyser and Walter, 2004).

- Insects: the oldest known caddisfly larval cases, related to orders Trichoptera or Permotrichoptera, are known from this outcrop. This includes less resilient tissues of larval cases associated with carbonized cuticles or impressions attached to the silk (Mouro et al., 2014b; Fig. 4I-J). Insect body fossils are here represented by more than one hundred specimens assigned to the orders Blattodea and Grylloblattodea (Martins-Neto, 2005; Pinto and Sedor, 2000). Approximately 54% of this fauna is composed of Phylloblattidae (Blattodea) *Anthracoblattina mendesi*, among which some specimens preserved details with high fidelity (e.g., antennae flagellomeres, thoracic sclerites, and even epicuticular patterns; see Ricetti et al., 2012, 2016). Other specimens herein have wing microtrichia perceptible and even possible soft tissues preserved by phosphatization (Fig. 4C-H).
- Plants: scattered well-preserved carbonaceous wood specimens have been reported. According to Gnaedinger et al. (2012) and Urban et al. (2012), the fossil woods are from genera described as *Agathoxylon* Hartig and *Abietopitys* Kräusel. *Abietopitys* is characteristic of the Carboniferous and Permian of Argentina, Brazil, and Africa, whereas *Agathoxylon* has a wider distribution (Carboniferous-Tertiary). Stem carbonaceous compressions are also present at the LSMH, as well as one amber-like structure that is currently under description (Wilner et al., 2016b).

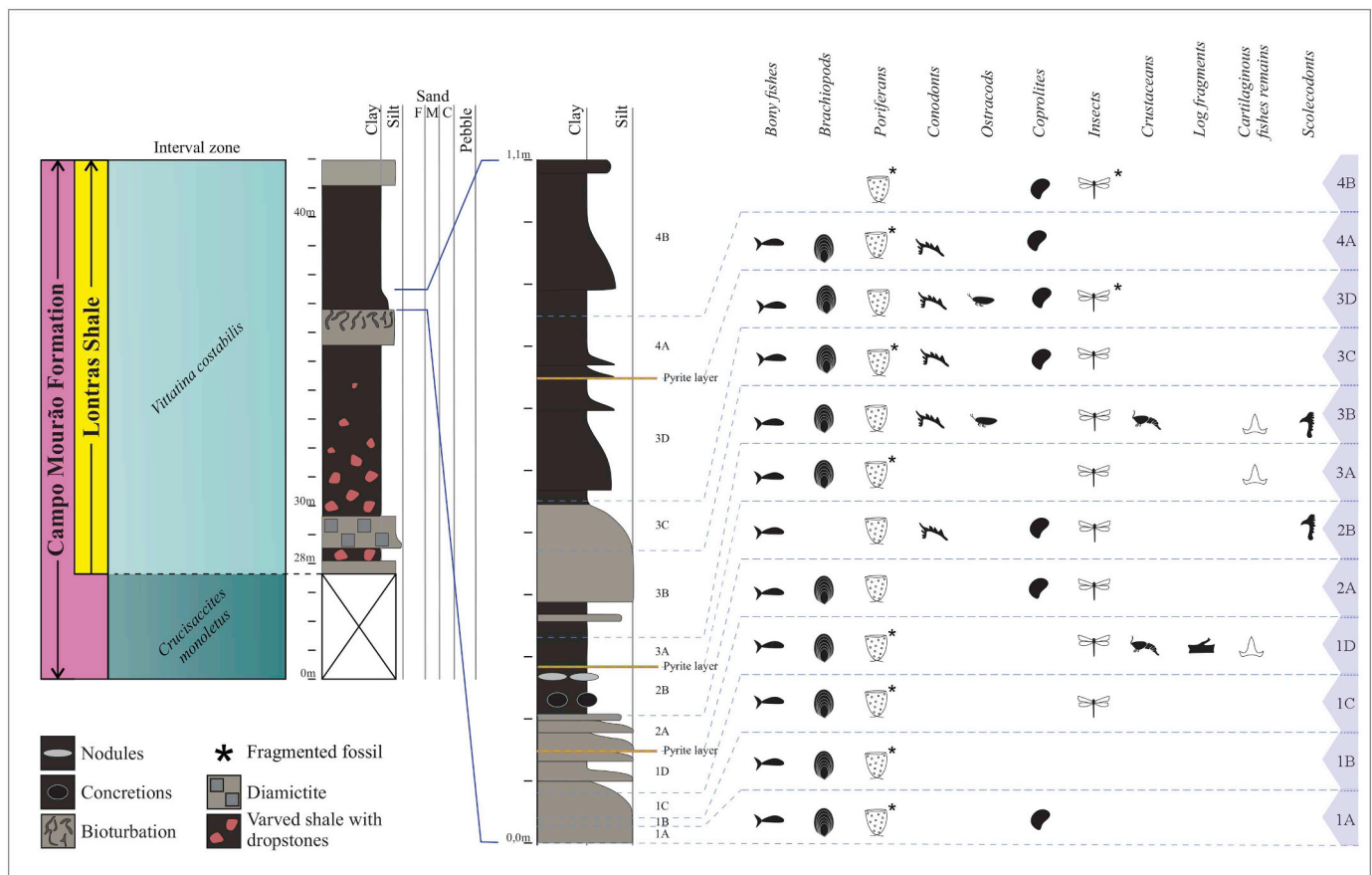


Fig. 2. Stratigraphic column of the Lontras Shale macrofossiliferous horizon (Campo Mourão Formation, Paraná Basin, Brazil) with fossil occurrences.



Fig. 3. A well-preserved Palaeoniscidae fish (CP. V 5202 a).

- Ichnofossils: At lower levels of the LSMH, few heteropolar coprolites and enterospire have been recognized. The coprolites have a rounded and cylindrical shape and are an average of approximately 24 mm in length and 13 mm in width. Some have a diameter of around 6 mm. In certain samples, it is possible to observe a concentric internal bedding, and in others it is possible to notice radial cracks (Muller et al., 2017). A SEM analysis has been performed, but no preserved fossil inclusion has been observed. Two enterospires were identified in a petrographic study but are still under study.

Given the above information, the LSMH is a rich and complex fossil assemblage. Here, we offer a brief chemical characterization of two significant groups, representing terrestrial and aquatic paleobiotas: sponges and insects.

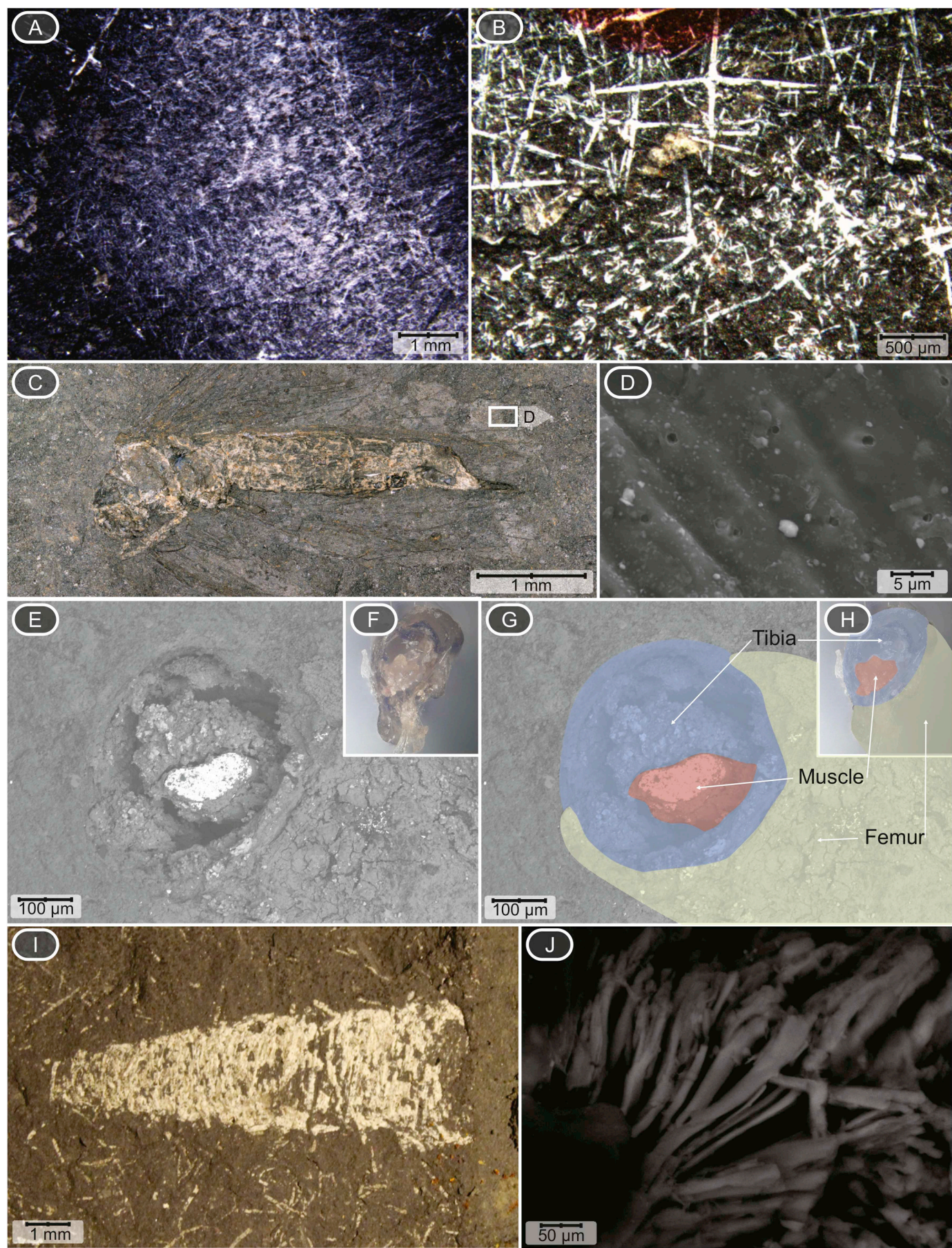
3.2. Paleoenvironmental settings

During the Carboniferous until the Cisuralian, the Gondwana

continent was mostly under deglacial conditions related to the end of the Late Paleozoic Ice Age. The distribution pattern of ice sheets in the southeastern portion of Gondwana is still uncertain, but the glacial presence left remarkable units, such as the Itararé Group in the Paraná Basin and its related units (Scotese, 1997; Ziegler et al., 1997; Buggisch et al., 2011; Isbell et al., 2012; Montañez and Poulsen, 2013; Fedorchuk et al., 2018, 2019). According to recent research, the southern portion of Brazil during the Late Carboniferous–Early Permian was shaped by multilobed glacial fronts forming fjord-like incised valleys probably controlled by topographic paleohighs (Lopes et al., 1986; Lavina and Lopes, 1987; Dias, 1993; Machado, 1994; Santos et al., 1996; Holz et al., 2010; Silveira, 2000; Vesely et al., 2015; Tedesco et al., 2016).

Fallgatter and Paim, 2017, have recognized three glacial cycles and a paleovalley from Alfredo Wagner to Vidal Ramos in the central portion of Santa Catarina State, which farther north may have been connected to the Rio do Sul embayment (see Canuto, 1999; Fig. 8). According to them, at the end of the first cycle, as the ice margin retreated toward the SE, a deep fjord was established due to progressive marine flooding. The sediments deposited during this final interval correspond to the well-known Itararé stratigraphic marker Lontras Shale Member (Schneider et al., 1974; França and Potter, 1988; Fallgatter and Paim, 2017). Insofar the deglaciation process prevailed in northern Santa Catarina, the warmer conditions may have allowed the microenvironmental conditions necessary for a hotspot of biodiversity, as seen in the modern midlatitude fjords of New Zealand. Then, even though no paleohighs have yet been identified in the vicinity of LSMH at Campaleo outcrop, we believe in a fjord bay context for the Lontras Shale.

Mouro et al. (2017) indicated that deposition of the LSMH occurred in a restricted marine environment with two alternating system tracts (a transgressive system tract and a highstand system tract), probably with depths of 200–400 m. Still, they also inferred a recurrently euxinic



(caption on next page)

Fig. 4. Well-preserved fossils from the LSMH. (a) Hexactinellid with a possible dermal layering. (b) Hexactinellid spicules with hemidisc. (c) Three-dimensionally phosphatized insects (CP/E 3243 a), detail of in (d). (e) CP.I 2276b fossil insect 2nd leg, femur-tibia articulation dorsal view, showing the preserved muscular tissue; (f) Extant hemipteran 2nd leg femur-tibia articulation, dorsal view, and its tarsal muscle; (g) Same as “E”, denoting the femur central cuticle, tibia and tarsal muscle; (h) Same as “F”, denoting the femur position, tibia and tarsal muscle; (i) Caddisfly larval case. (h) Caddisfly-related larval case silk structure ESEM image.

photic zone (indicated by biomarkers), while the bottom-water conditions were predominantly anoxic/euxinic (according to inorganic and organic geochemical data, framboid pyrite proxy). These anoxic conditions may also be related to the absence of tides (atidally), which helps promote such conditions (see Austin & Scourse, 1997; Allison et al. 1998; Wells et al. 2005), once micro-tides can be expected to be present in a fjord paleoenvironment context. However, we cannot rule out the extremely low tide ranges during the highstands that may have helped mix water in brief moments, as seen in the Carboniferous epicontinental sea of Europe.

In spite of this persistent bottom redox condition, the presence of an autochthonous benthic life (sponges) requires at least a permissive amount of oxygen, even to Porifera, which is adapted to live in an oxygen-minimum zone or seasonal anoxia (see, Tunnicliffe, 1981; Reiswig and Miller, 1998; Bell and Barnes, 2000; Mills et al., 2014). Therefore, the poriferan presence may imply that weakly periodic intrusions of oxygenated pulses have occurred, allowing these opportunist organisms (sponges and also others random infauna such as brachiopods and ostracods) to live for a brief moment and subsequently die in anoxic conditions. Interludes of oxygenation occurred and were identified by the variation in the sizes of pyrite framboid diameters and the presence of authigenic pyrite crystals (see Mouro et al., 2017). These untraceable incursions have also been assigned in the Doushantuo Formation (see Ye et al. 2017) and Lantian Formation (see Yuan et al., 2011) and may have been produced by untraceable internal weak waves induced by the land input (paleosalinity variation is observed, see palynofacies data of Mouro et al., 2017) or by wind-driven seiches (see Sanford et al., 1990; Breitburg, 1992; Diaz & Rosenberg, 1995).

Then, combining the complex paleoenvironmental context with the paleoclimatic and paleogeographic proxies, it is acceptable that LSMH could be deposited in a deep marine fjord-like paleoenvironment. Considering punctual distinction, estuarine systems have been observed in other PermoCarboniferous well-preserved paleobiota, such as Hamilton Fossil-Lagerstätte (Cunningham et al., 1993), Mazon Creek biota (Kuecher et al. 1990), Kinney Brick pit assemblage (Archer & Feldman 1990), and Lawrence Shale (Zidek 1992).

3.3. Preservation settings

The LSMH is considered a special preservational setting due its combination of different kinds of preservation and broad taphonomical spectra, including hard and/or soft tissues of aquatic and terrestrial biotas, as seen in many important Lagerstätten, such as Mazon Creek. The preservation quality of LSMH can be related to the given conditions of the very conspicuous organic matter grade, conferring the sedimentary and geochemical conditions in the burial environment. The black shales of LSMH were deposited in a deglacial influenced calm sea. The lack of bioturbations evidence confirms an unfavorable environment for infauna through LSMH deposition during long-lasting moderate euxinic-anoxic bottom conditions (predominance of sulfidic conditions), with lower detrital input and photic zone euxinia, as denoted by Mouro (2017) and Mouro et al. (2017).

The majority of fossils are preserved at LSMH as carbonaceous compressions or phosphatized forms (Fig. 5). The phosphatization process is well known to require abundant organic matter and low oxygen content, as we see at LSMH. Despite the favorable conditions for the pyritization process (e.g., iron-rich sediment and a persistent anoxic/euxinic conditions on the bottom), fewer well-preserved fossils are found pyritized (see Mouro et al., 2017). Despite the good preservation, there is no evidences of microorganisms related to decay and

preservation of specimens from LSMH (e.g. EPS or preserved bacteriomorphs), as had being detected in some others Lagerstätten site. The presence of biofilms is related to the chemical stratification of sediments and the increase of local anoxia, triggering the exceptional preservation typical of fossil Lagerstätten (Selden and Nudds, 2004; Osés et al., 2016; Osés et al., 2017).

Regarding the burial, despite no clear evidence of turbidic flows, Hamel (2005) after a taphonomical analyses of fishes carcasses inferred that the LSMH was deposited during rapid burial events caused by episodic turbidity currents (ETC) followed by times of minimal sedimentation, and the combination of glacial conditions, ETC and minimal sedimentation was suitable to phosphatization of fishes (Brett and Baird, 1986). Usually, phosphate present in organisms is replaced by calcium carbonate. However, under low pH and anoxic conditions, carbonate does not precipitate (Briggs and Kear, 1994). These conditions are usually recognized in turbidite sequences.

4. Material and methods

4.1. Analyzed material

The fossil samples from LSMH that compound the present contribution are housed at CenPaleo (Centro Paleontológico da Universidade do Contestado) Collection, Federal University of Santa Catarina Paleontology Collection. The CenPaleo Collection samples codes are: CP 399a.b; CP.B 7196; CP/E 3243a.b; CP/E 3755a.b; CP/E 6521a.b; CP.M 122; CP.I 556a.b; CP.I 680; CP.I 877a.b; CP.I 2182a.b; CP.I 2276a.b; CP.I 5332a.b; CP.I 7220a.b.c; CP.V 7195a1,a2,b; CP.V 5202a.b.

4.2. Raman Spectroscopy

For Raman analysis, we used a Renishaw InVia microRaman spectrometer, coupled with 532, 633 and 785 nm lasers. The equipment is housed at Astrolab (University of São Paulo). Analysis was performed with static mode of measurement, with a 532 nm laser applied to investigate a broad range of organic and mineral phases, and 633 and 785 nm lasers used to verify kerogen and other organic compounds, with a minor effect of fluorescence. The intensities were adjusted from 0.1% to 50%, depending on the sample, using the 5× and 50× objectives. For static point analysis, we performed 30 accumulations of 1 s each. During mapping mode, we used only one accumulation. The software Origin Pro 8.7 was used for the visualization and processing of Raman point spectra, such as the removal of cosmic rays and scaling. The maps were later processed with WiRE software.

4.3. Energy-dispersive spectroscopy (EDS) and synchrotron micro-X-ray fluorescence (micro XRF)

In order observe superficial coverings and lighter elements, we performed SEM and EDS/X on samples. Analysis performed at Terra Mineralia, Freudenstein Schloß, Freiberg, Germany, used a JCM-5700 equipped with a Bruker AXS X flash detector 4010 (133 eV) in high vacuum, environmental and backscattered modes. Analysis performed at Centro de Estudos em Petrologia e Geoquímica of Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil used a JSM-6610LV equipped with a BRUKER Nano X flash detector 5030 (133 eV) in high vacuum, environmental and backscattered modes. Analysis performed at Centro de Petroscopia e Microanálise of Universidade Federal do Rio Grande do Sul Porto Alegre, Brazil, used a JSM-5800 equipped with

Group fossil	Preserved	Types of fossilization
Annelid - Scolecodont	parallel to bed plane / in concretions	Phosphatized
Insecta	parallel to bed plane / in concretions	*
Crustacea	parallel to bed plane	Phosphatized
Brachiopoda	parallel to bed plane	Kerogenized/pyritized/phosphatized
Conodonts	parallel to bed plane	Phosphatized
Fishes	parallel to bed plane / in concretions	Phosphatized
Foraminifera	parallel to bed plane	Unknown
Mollusca	parallel to bed plane	Unknown
Plantae	parallel to bed plane	Kerogenized
Porifera	parallel to bed plane	*
Coprolites	parallel to bed plane	Unknown

Fig. 5. Summary chart of Lontras Shale Fossils and their type of fossilization.

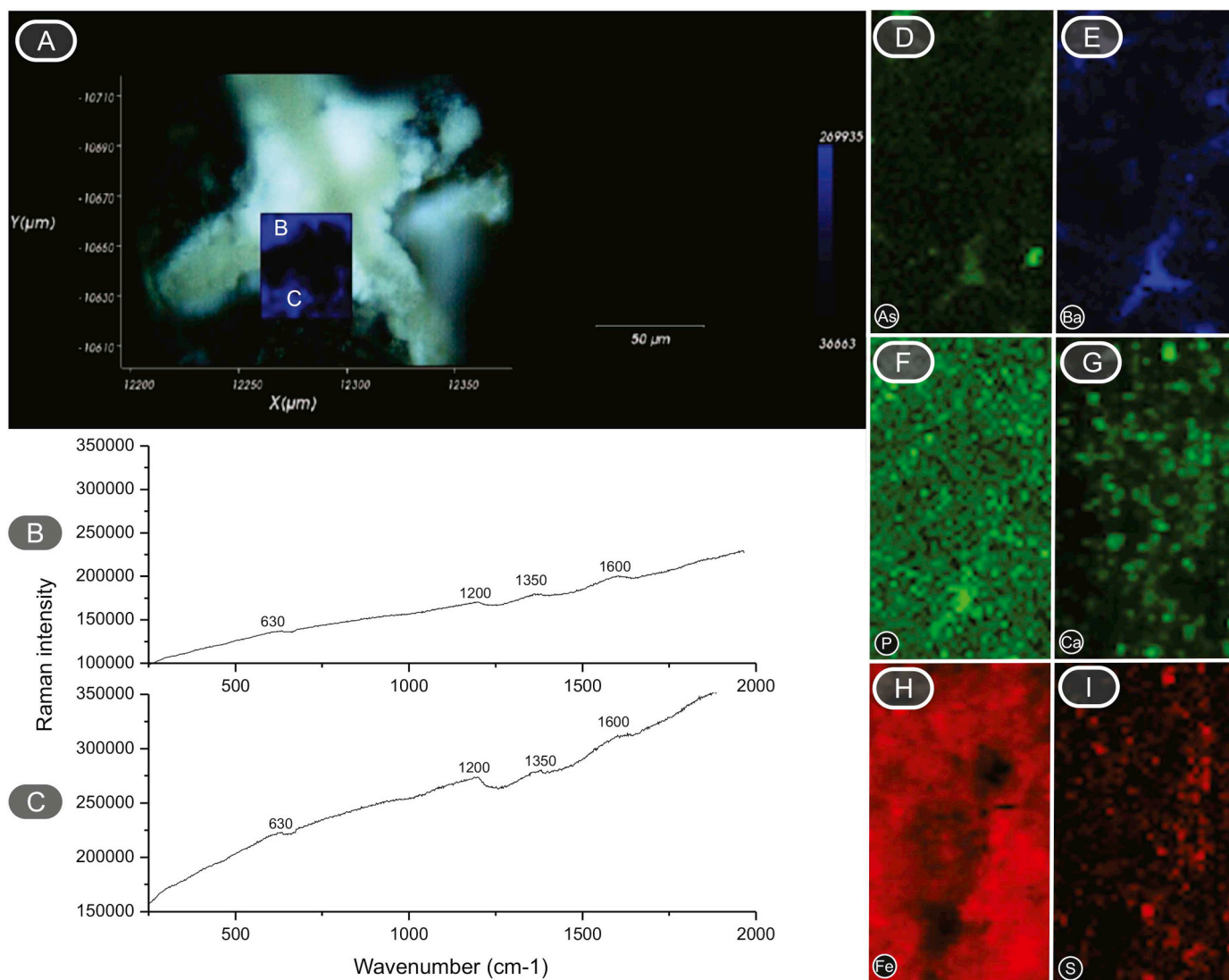
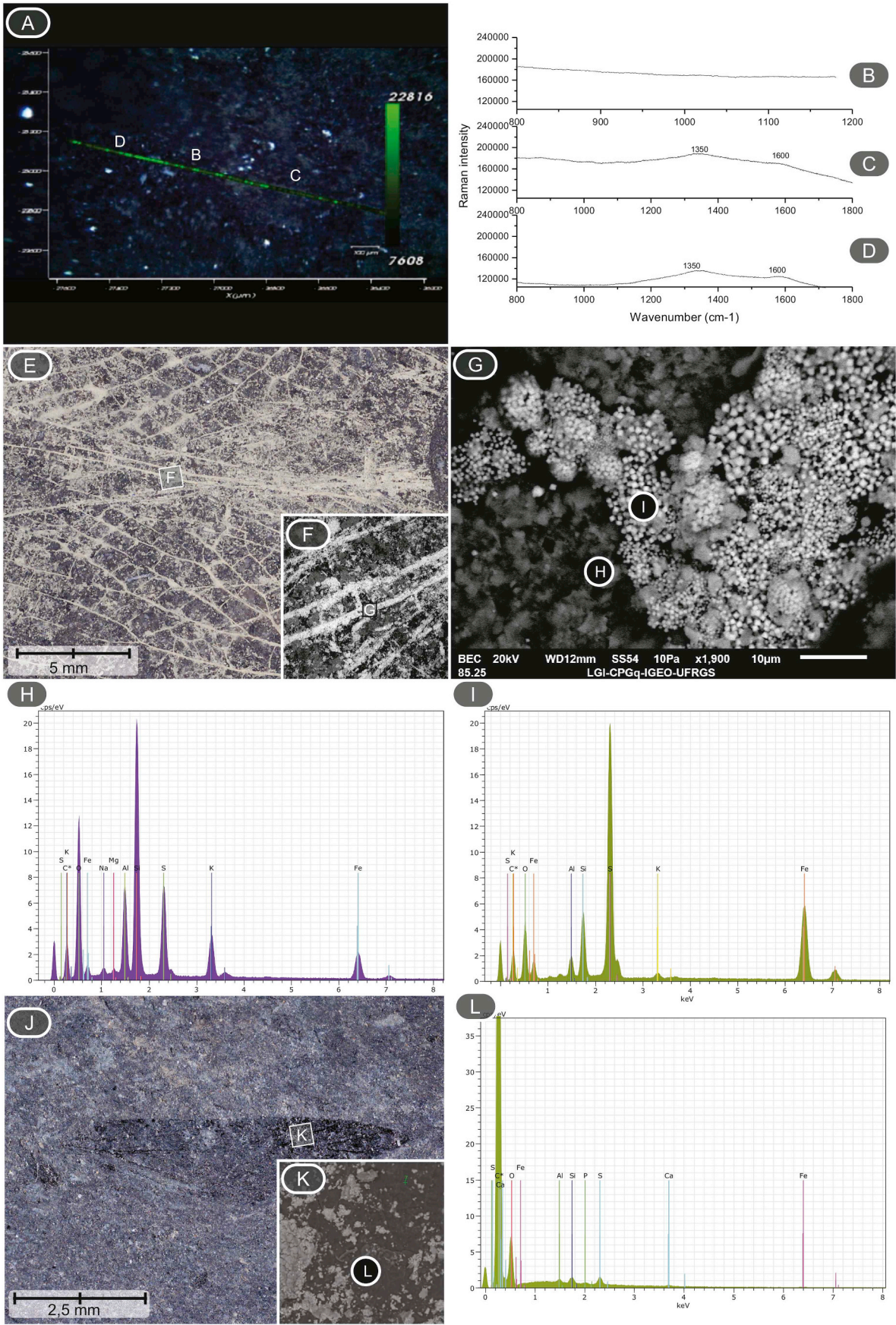


Fig. 6. Raman spectra of LSMH samples. (A) Hexactin. (B) Internal. (C) Rock matrix. Observe more pronounced kerogen bands (1350, 1600 cm^{-1}) in blue area (C and D). Laser: 633 nm, power: 100; 30 accumulations, $5\times$. (D-I) micro-XRF map of spicules and rock matrix. Notice higher intensities of As, Ba and P on spicules region, and Fe on rock matrix. Ca and S presents more homogeneous distributions.



(caption on next page)

Fig. 7. Compressed insects; (A) Raman spectra of LSMH insect wing; (B) insect wing membrane area; (C) insect wing vein; (D) rock matrix. Observe more pronounced kerogen bands in wing vein and matrix (1350, 1600 cm⁻¹). Laser: 785 nm, power: 1; 30 accumulations, 5 ×; (E) Pyritized insect CP.I 5332a photo, square indicates location of F; (F) SEM backscatter detail of CP.I 5332a hindwing vein indication the location of G (20 kV); (G) SEM backscatter detail of its vein, observe the framboidal pyrite. Indicating the location of I and J analysis (20 kV); (H) EDS point analysis of wing membrane (20 kV); (I) EDS point analysis of wing vein (20 kV); (J) Incarbonized CPI 680 wing photo, square indicates the location of K; (K) SEM backscatter detail of CP.I 680 wing vein (12 kV); (L) EDS point analysis (12 kV).

high vacuum and environmental modes. We have chosen the following tensions to perform all analysis: 5, 7, 10, 12, 15 and 20 keV.

We used Synchrotron Light X-ray Micro-Fluorescence (micro-XRF) from the Brazilian Center for Research in Energy and Materials (CNPEM, proposal 20,190,140). We performed the analyses using a 4 mm collimator, step 0.05. The maps were later processed with PyMca software.

We tested and compared the complementary parameters and limitations between EDS and synchrotron micro XRF through the investigation of labile tissues. Synchrotron light techniques have been shown to be more powerful in analyses that seek sensitivity and penetration, especially for heavier elements.

5. Results

5.1. Sponges

Poriferans are an interesting case at LSMH. In some samples, a white layer among the megascleres and microscleres is observable. Synchrotron micro-XRF data showed higher intensities of phosphorus, arsenic and barium in the spicule region. However, phosphorus also proved to be an important element in the region among the spicules skeletal-net, along with sulfur, iron and calcium (Fig. 6). SEM/EDS analysis revealed that the fossilized sponge spicules contain higher intensities of calcium, phosphorous, fluorine and carbon when compared with the surrounding matrix, with stronger intensities of iron (Fig. 6). Raman signs of kerogen were also detected on and among spicules (Fig. 6).

5.2. Insects

Insects exhibit the most exceptional preservation at LSMH. Their body remains are preserved in two distinct manners: (1) compressed in the layers of the shale, as flattened carbonaceous or pyritized forms; and (2) three-dimensionally phosphatized, concretized and non-concretized forms.

Intensities of kerogen were detected on an insect wing. The more pronounced intensities of organic matter were on insect veins and rock matrix. Detectable kerogen was not observed on the membrane area.

Sparse points of detectable sulfur intensities, as well as framboidal pyrite, were observed in an insect wing (Fig. 7A-L). The compressed pyrite forms are associated with the preservation of submillimetric body structure morphologies, such as tibia spines, tarsomeres and flagellum segments (Ricetti et al., 2016).

Some of the three-dimensionally phosphatized non-concretized insects were preserved not only with highly detailed sclerotized tissues and their microstructures but also possible muscular soft tissue (Fig. 4C-H). Evidence of pyritized muscular-like structures is perceptible in a few specimens, such as in the proximal/ventral portion of the tibia of the specimen CP.I 2276b (2nd left leg; Fig. 4E-H). This anatomical area is known by the presence of the tarsal muscles in current insects. SEM/EDX analyses show a predominance of phosphorus, mostly coinciding with calcium (Fig. 8A-B).

The epicuticular micro pattern is also perceived in the concretized phosphatized insects (Fig. 9D-E). The EDS area analysis shows few differences between fossil and concretion matrix, mainly regarding a high intensity of phosphorus and calcium in the fossil content relative to other elements (like sulfur and silicon - Fig. 8).

5.3. Caddisflies

The possible oldest known caddisfly larval cases, related to orders Trichoptera or Permtrichoptera, were recognized from this outcrop. These fossils are composed of whitish strips with possible silk-like structures. Mouro et al. (2016), analyzing the larval cases at the LSMH through energy-dispersive spectroscopy (EDS), identified thread-like structures similar to the silk of recent Trichoptera larvae, mainly enriched in calcium and sulfur (Fig. 4I-J, see also Mouro et al., 2016). Raman signs were strongly influenced by the effect of fluorescence. In this sense, it was only possible to detect overlays of oxides and organic matter. No signs of gypsum were detected.

6. Discussion

6.1. Fossil preservation: some considerations

The white layer among the megascleres and microscleres of poriferans seems to be a remnant of fossilized sponge tissue (Figs. 4A, 6). The phosphatization process of these structures is reinforced by the detected intensities of sulfur, fluorine and phosphorus (Fig. 6D-I). Even the tissue itself could be the source of phosphate and phosphatized remains. Additionally, some species of recent sponges have calcium phosphate as their main mesohyl compound, so we cannot rule out the possibility of a remnant and/or phosphorus contributions from the original mesohyl (see, Zhang et al., 2015; Colman, 2015).

Iron, detected outside the spicule region (Fig. 6H), may reinforce a scenario that favored the incorporation of sulfur by-products into organic molecules by sulfate-reducing bacteria. It is known that sponge-associated bacteria can mineralize arsenic and barium on intracellular vesicles (Keren et al., 2017). However, we also detected the intensities of those elements, especially barium, on other fossils from LSMH, such as insects (Fig. 6E). Barium is a paleoproductivity proxy related to the formation of barite from seawater and the deposition of organic matter as well (Dymond et al., 1992). Arsenic, on the other hand, could be indicative of sulfate reduction bacteria in iron-rich environments. Sometimes, arsenic can be precipitated as iron-arsenic-sulfide (Rittler et al., 1995).

The Raman sign of kerogen (Fig. 6B-C) indicates the influence (or even a remnant) of organic matter. An orange material was observed filling the axial canal region of spicules, which was very different from the rest of the spicules (lighter). Raman spectroscopy revealed kerogen bands compatible with traces of organic matter in this axial canal region of the spicule and in the space among spicules. The remnant soft tissue is reinforced by the spicules organization in a skeletal-net arrangement. In fact, the geochemical results compiled here demonstrate that there were feasible conditions for the preservation of organic compounds in and between the spicules, as well as mineral replacements.

It is important to underline that insect wings, similar to poriferan spicules, present aromatic forms of carbonaceous material (1350 and 1600 cm⁻¹) (Fig. 9). This is strong evidence that organic material underwent a transformation from their original composition (Gupta et al., 2006a, 2006b). Only in the case of poriferan spicules, we have detected Raman signs that also should be compatible with aliphatic chains (630 and 1200 cm⁻¹). This could corroborate the notion that the organic component encountered in fossil tissues is a product of incorporation of lipids present in the organism itself, resulting in a process of in situ polymerization (Gupta et al., 2006a, 2006b). However, there is still the

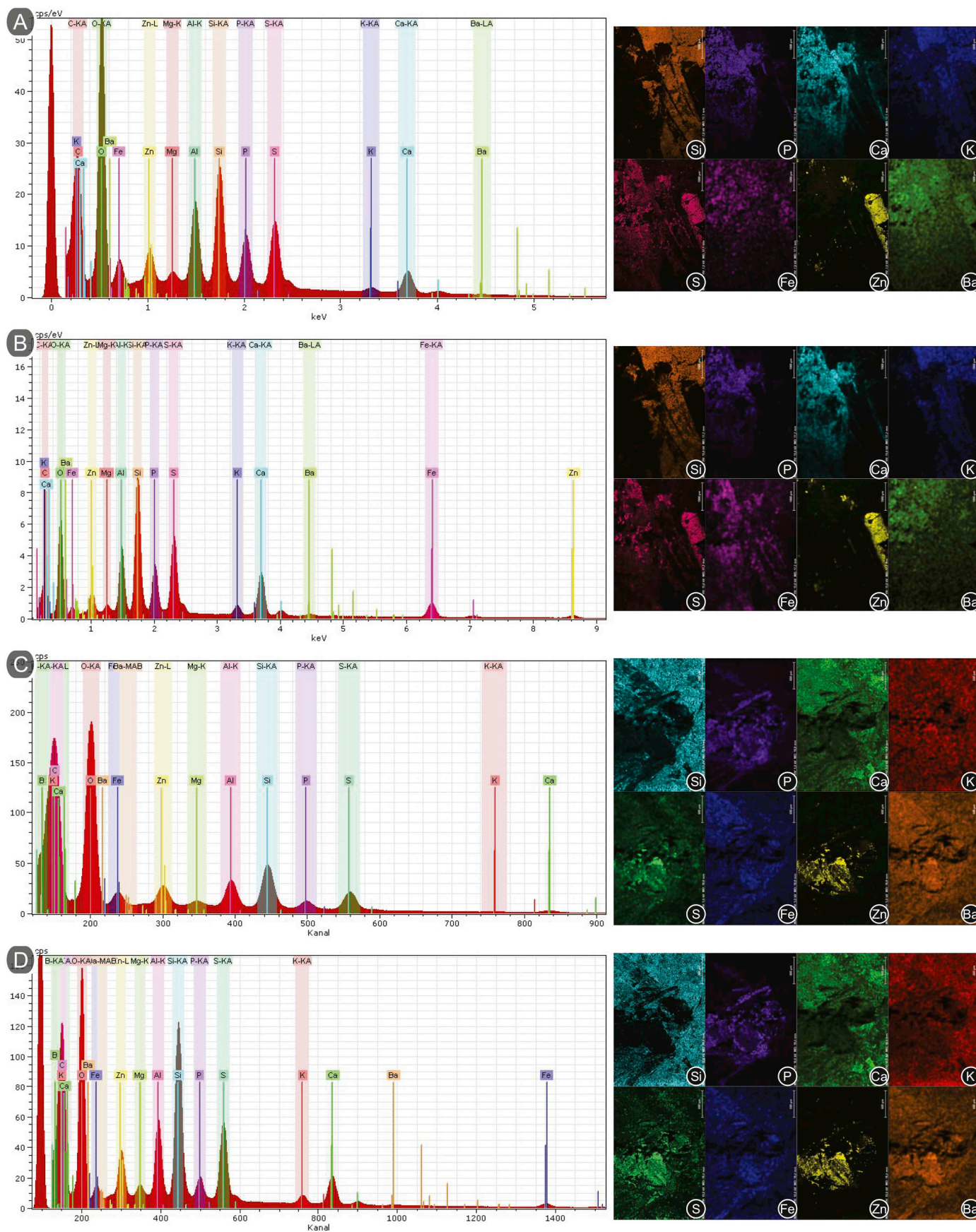


Fig. 8. EDX mapping of fossil insects; (A-B) CPI 2276a, elementary map of proximal portion of 3rd leg and part of thorax and abdomen. Notice wing veins crossing the matrix between the leg and the thorax/abdomen. 7 kV and 15 kV, respectively; (C-D) CP/E 3243b, elementary map of anterior portion of the insect. 5 kV and 10 kV, respectively.

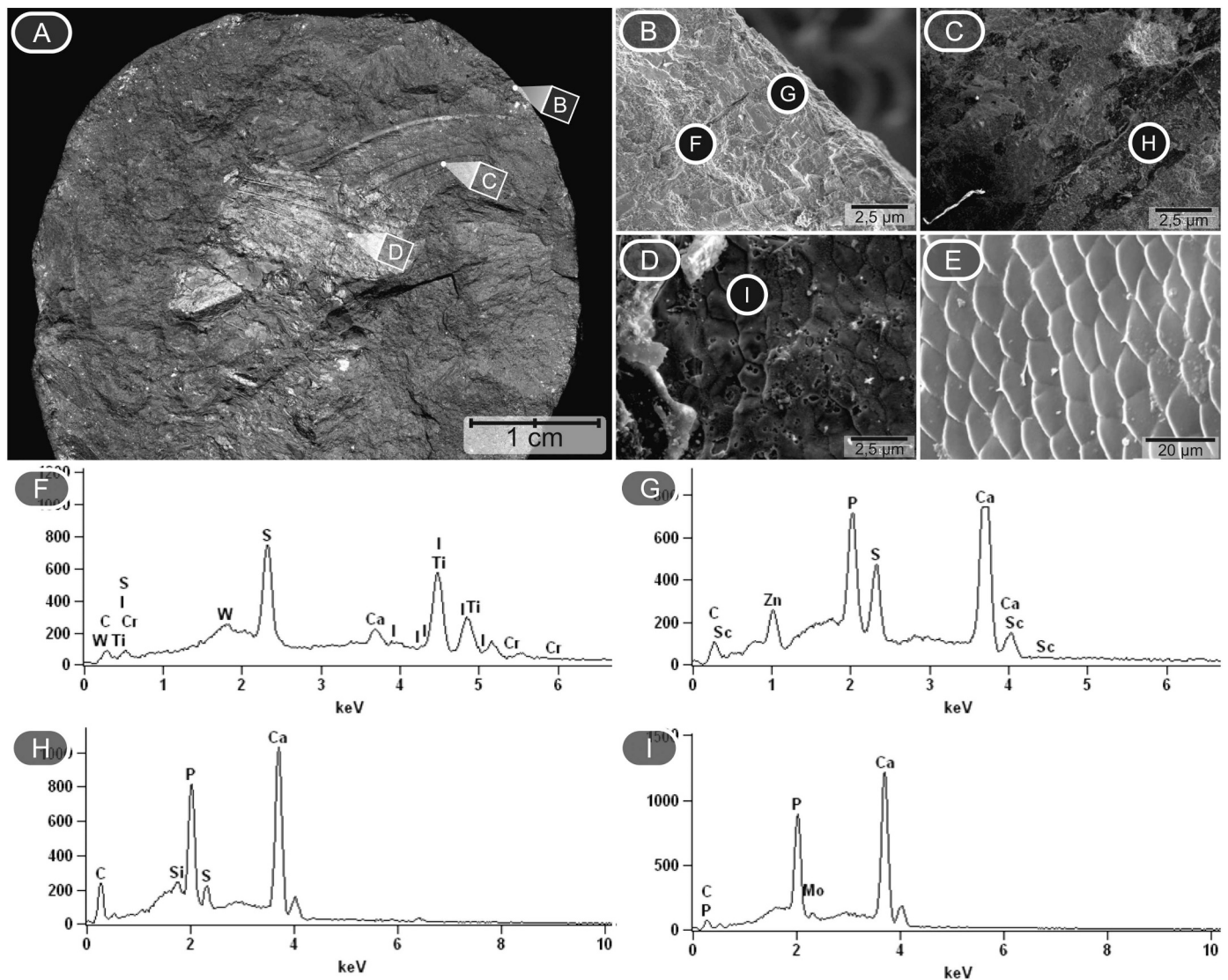


Fig. 9. (A) *Anthracoblattina mendesi* cockrochoid insect preserved inside concretion (CP/E 3755b). Squares indicating the location of SEM imaging B-D; (B) SEM image of border of CP/E 3755b concretion (5 kV). Letters in a white circle indicate the location of EDS analysis; (C) SEM image of the CP/E 3755b *Anthracoblattina* forewing (5 kV). Letter in a white circle indicates the location of EDS analysis; (D) SEM image of the cuticle of the *Anthracoblattina* wing preserved on CP/E 3755b concretion (5 kV). Letter in a white circle indicates the location of EDS analysis; (E) Nowadays cockroach epicuticle pattern (from Gupta and Summons, 2011); (F–I) EDS area analysis of concretion CP/E 3755b, location indicated in the previous images (5 kV).

possibility that the composition organic parts of these fossils are the result of the incorporation of organics from the sediment (see Briggs and McMahon, 2016), and once we also found bands of kerogen in rock matrix.

It is possible that the precipitation of framboidal pyrite in an insect wing (Fig. 7G–I (compressed insects)) was a result of anaerobic decomposition events by sulfate reducing bacteria in regions of accumulation of organic matter in the organism. The compressed pyrite forms are associated with the preservation of submillimetric body structure morphologies, such as tibia spines, tarsomeres and flagellum segments (Ricetti et al., 2016; Fig. 4). The presence of sphalerite and barite crystals in regions of the fossils denotes their preservation in an anoxic/euxinic environment, very likely with the action of bacterial films.

Regarding the concretized phosphatized insects (Fig. 7), there was a high intensity of phosphorus and calcium in the fossil content in comparison to other elements (like Sulfur and Silicon - Fig. 7). Several works have already reported the fundamental role of microbial activity in concretization, mainly sulfate-reducing bacteria. Through the decomposition of organic matter, microbial activity facilitates the creation

of a microenvironment favorable to the precipitation of minerals (Dickson and Barber, 1976; Arning et al., 2009). Concretization is also a mitigating factor in the alteration of organisms during the fossilization process by reducing the effects of weathering (Landman and Klofak, 2012).

It is possible that the granulometry pattern, between siltic and clayish, could eventually establish different degrees of permeability and/or porosity, reflected in the differential time intervals and their environmental particularities between both processes of fossilization (concretization and non-concretization). Recent experimental studies (McCoy et al., 2015a, 2015b) have corroborated the low permeability of sediments and initial decomposition as a positive feedback mechanism that leads to the low porosity and early mineralization of organisms in concretions. It was also observed that the lower the permeability of the environment, the less diffusion of oxidants that favor the decomposition of organisms and, therefore, the better conditions for the preservation of soft tissues (Gaines et al., 2005, 2012). Likewise, low permeability can inhibit the diffusion of compounds related to decomposition, creating optimum conditions for mineral precipitation

(which further decreases the permeability of the sediment). In the process of concretization, the low permeability of the sediment and the precipitation of minerals function as a mechanism of self-regulation, increasing the potential for preservation of the organisms (McCoy et al., 2015a). In future analyses, we will proceed in petrographic thin sections for studies to perform a mineralogical and microstructural characterization of matrix and fossils in the different preservational bias that is presented. The data obtained through these techniques will allow the interpretation of aspects of preservation of micro- and ultra-structures of concretized and non-concretized insects from LSHM, as well as the preservation environment of these animals.

7. Conclusions

This work applied geochemical analyses to provide data on fossil diagenetic patterns of the three most abundant fossils of the Lontras Shale, Pennsylvanian – Cisularian of Paraná Basin.

The biota assemblage of Lontras Shale provides a good opportunity to comprehend taphonomic pathways, which lead to special preservation during the Carboniferous-Early Permian interval. The encompassing data on EDS intensities of phosphorus and fluorine, micro-XRF intensities of sulfur, as well as framboidal pyrite detected by SEM/EDS make it plausible to recognize the rule of phosphatization and pyritization processes in information retention for specimens from LSMH.

By means of Raman spectroscopy, we were able to investigate the nature of some carbonaceous material detected in our samples. Lasers at 514 nm or 633 nm tend to produce stronger fluorescence background. Therefore, we also tried to move the near-infrared region (using 785 nm laser), where the fluorescence effect tends to disappear. However, the fluorescence interference was still very strong for all obtained spectra. This may be due to the compounds analyzed or the fluorescent impurities in the rocks and fossils. Even so, we were able to detect the above discussed pictures of organic matter. In future studies, we intend to irradiate the samples with intense laser light, a process known as photobleaching, which is very effective for mitigating the fluorescence effect.

No Raman signs of apatite (related to EDS intensities of phosphorus and fluorine) or pyrite (related to micro-XRF intensities of sulfur, and framboidal pyrite detected by SEM/EDS) were observed. These preservation pathways, herein perceived, were enabled by the anoxic-euxinic conditions of the burial zone (sulfidic persistent), possibly associated with microorganismal biofilms. Even with constant burial conditions, no preferential fossil diagenetic pathway has been observed in the samples; on the contrary, the pathways appear species-specific. Despite not yet being considered a Lagerstätten, the LS site can provide rich data regarding ancient ecosystems. Moreover, research focusing on the characterization of geobiologic and fossil diagenetic taphonomical windows can help distinguish a pattern of similar occurrences in distinct age geologic deposits.

Declaration of Competing Interest

None.

Acknowledgments

This work had the financial support of Programa de Formação em Recursos Humanos em Geologia da Petrobras (PFRH-PB 240), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), processo 140446/2016-8. We appreciate and are thankful for the support of the Museu Nacional, Universidade Federal de Santa Catarina, Universidade Federal do Rio Grande do Sul, Universidade do Contestado during all work phases. We also acknowledge the AstroLab (Laboratory of Astrobiology – Institute of Chemistry, USP) for providing research facilities to conduct the Raman spectroscopic analysis. We

would like to thank LNLS/CNPEM for technical support and for providing infrastructure, in particular for allowing the use of the XRF beamline (proposal 20190140). To Neal S. Gupta for the kind permission of image use. To Katrin Treppow and the Terra Mineralia for providing access to the facilities.

References

- Adami-Rodrigues, K., Pazinato, P.G., Correa, R.C., Ricetti, J.H.Z., Weinschütz, L.C., 2012. Malacostraca da Formação Rio do Sul, Grupo Itararé, Bacia do Paraná, Mafra, SC, Brasil. In: Ghilardi, R.P., Scheffler, S.M. (Eds.), *Simpósio Brasileiro De Paleoinvertebrados*, 1, Bauru, 2012. Boletim de Resumos, Bauru, UNESP.
- Allison, P.A., Ford, R., Corfield, R.M., 1998. Stratification and oxygen isotopes in the Paleozoic: is paleothermometry in hot water? Stable isotopes in geology. *Palaeontol. Soc. Spec. Publ.* 4, 244–254.
- Allison, P.A., Briggs, D.E.G., 2011. Taphonomy: Bias and process of through time. In: Allison, P.A., Briggs, D.E.G. (Eds.), *Taphonomy: Bias and process of through time*. Springer, Netherlands, pp. 1–17 (17 pp).
- Archer, A.W., Feldman, H.R., 1990. Tidal rhythmites within the Lawrence Formation (Pennsylvanian, Virgilian) of Kansas: Kansas Academy of Science. *Abstracts* 9, 4.
- Arning, E.T., Lückge, A., Breuer, L.C., Gussone, N., Birgel, D., Peckmann, J., 2009. Genesis of phosphorite crusts of Peru. *Mar. Geol.* 262 (1), 68–81.
- Aquino, C.D., Valdez, B.V., Faccini, U.F., Milana, J.P., Paim, P.S.G., 2016. Facies and depositional architecture according to a jet efflux model of a late Paleozoic tidewater grounding line system from the Itararé Group (Paraná Basin), southern Brazil. *J. S. Am. Earth Sci.* 67, 180–200.
- Evolution of seasonal stratification in the Celtic Sea during the Holocene. *J. Geol. Soc.* 154, 249–256.
- Bell, J.J., Barnes, D.K.A., 2000. A sponge diversity within a 'marine island' *Hydrobiologia* 440, 55–64.
- Breitburg, D.L., 1992. Episodic hypoxia in Chesapeake Bay: interacting effects of recruitment, behavior, and physical disturbance. *Ecol. Monogr.* 62, 252–546.
- Briggs, D.E.G., Kear, A.J., 1994. Decay and mineralization of shrimps. *Palaios* 9, 431–456.
- Brett, C.E., Baird, G.C., 1986. Comparative taphonomy: a key for paleoenvironmental reconstruction. *Palaios* 1, 207–227.
- Briggs, D.E., McMahon, S., 2016. The role of experiments in investigating the taphonomy of exceptional preservation. *Palaeontology* 59 (1), 1–11.
- Buggisch, W., Wang, X.D., Alekseev, A.S., Joachimski, M., 2011. Permo-Carboniferous carbon isotope stratigraphy of sections from China (Yangtze platform), USA (Kansas) and Russia (Moscow Basin and Urals). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 301, 18–38.
- Cagliari, J., Philipp R.P., Valdez B.V., Netto, R.G., Hillebrand P., Lopes C.R., Basei, M.A.S., Faccini, U.F., 2016. Age constraints of the glaciation in the Paraná Basin: evidence from new U–Pb dates. *J. Geol. Soc.* 173, 871–874.
- Canuto, J.R., 1999. Facies e ambientes de sedimentação da Formação Rio do Sul (Permiano), Bacia do Paraná, na região de Rio do Sul, Estado de Santa Catarina. Unpublished Ph.D Thesis. Universidade de São Paulo (184 pp.).
- Cardoso A.R., Romero, G., Osés, G.L., Nogueira, A.C.R., 2020. Taphonomy of lacustrine fish fossils of the Parnaíba Basin, northeastern Brazil: Spatial and causative relations of Konservat Lagerstätten in West Gondwana during Jurassic-Cretaceous. *Palaeogeography, Palaeoclimatology, Palaeoecology* 542, 21. <https://doi.org/10.1016/j.palaeo.2020.109602>.
- Carvalho, P.F., Miranda, J., Alvim, P.A., 1942. Geologia de Mafra. 105 Rio de Janeiro, Ministério da Agricultura, Departamento Nacional da Produção Mineral, Divisão de Geologia e Paleontologia, Boletim (41 p).
- Castro, J., 1999. Estratigrafia de seqüências das formações Campo Mourão (parte superior) e Taciba, Grupo Itararé, leste da Bacia do Paraná Rev. Brasil. Geosci. 29 (2), 255–260.
- Colman, A.S., 2015. Sponge symbionts and the marine P cycles. *PNAS* 112 (14), 4191–4192.
- Cunningham, C.R., Feldman, R.H., Frankseen, E.K., Gastaldo, R.A., Mapes, G., Maples, C.G., Schutze, H.P., 1993. The Upper Carboniferous Hamilton Fossil-Lagerstätte in Kansas: a valley-fill, tidally influenced deposit. *Lethaia* 26, 225–236 Oslo. ISSN 0024-1164.
- D'Ávila, R.S.F., 2009. Sequências deposicionais do Grupo Itararé (Carbonífero a Eopermiano), Bacia do Paraná, na área de Dr. Pedrinho e cercanias, Santa Catarina, Brasil: turbiditos, pelitos e depósitos caóticos. Ph.D Thesis. Programa de Pós Graduação em Geologia, Universidade do Vale do Rio dos Sinos, São Leopoldo, pp. 192.
- Dias, M.E.R., 1993. Palinologia do Grupo Itararé no Rio Grande do Sul. Porto Alegre. Ph.D Thesis. Universidade Federal do Rio Grande do Sul, Porto Alegre, pp. 227.
- Diaz, R.J., Rosenberg, R., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanogr. Mar. Biol. Annu. Rev.* 33, 245–303.
- Dickson, J.A.D., Barber, C., 1976. Petrography, chemistry and origin of early diagenetic concretions in the Lower Carboniferous of the Isle of Man. *Sedimentology* 23 (2), 189–211.
- Dino, R., Rösler, O., 2001. Significado estratigráfico e paleoambiental da palinoflora de concreções da Formação Rio do Sul (Neopaleozóico da Bacia do Paraná) na região de Mafra, SC. *Revista Brasileira de Paleontologia*. 2. pp. 148–149.
- Dymond, J., Suess, E., Lyle, M., 1992. Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. *Paleoceanography* 7, 163–181.
- Fallgatter, C., Paim, P.S.G., 2017. On the origin of the Itararé Group basal nonconformity

- and its implications for the Late Paleozoic glaciation in the Parana Basin, Brazil. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* <https://doi.org/10.1016/j.palaeo.2017.02.039>.
- Fedorchuk, N.D., Isbell, J.L., Griffis, N.P., Montañez, I.P., Vesely, F.F., Iannuzzi, R., Mundil, R., Yin, Q.Z., Pauls, K.N., Rosa, E.L., 2018. Origin of paleovalleys on the Rio Grande do Sul Shield (Brazil): implications for the extent of late Paleozoic glaciation in west-central Gondwana. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 531, 108738.
- Fedorchuk, N.D., Isbell, J.L., Griffis, N.P., Vesely, F.F., Rosa, E.L.M., Montañez, I.P., Mundil, R., Yin, Q.Z., Iannuzzi, R., Roesler, G., Pauls, K.N., 2019. Carboniferous glaciotectioned sediments in the southernmost Paraná Basin, Brazil: Ice marginal dynamics and paleoclimate indicators. *Sediment. Geol.* 389, 54–72.
- França, A.B., Potter, P.E., 1988. Estratigrafia, ambiente deposicional e análise de reservatório do Grupo Itararé (Permocarboífero), Bacia do Paraná (Parte 1). *Rev. Geoci. Petrobras* 2 (2/4), 147–191.
- Gaines, R.R., Kennedy, M.J., Droser, M.L., 2005. A new hypothesis for organic preservation of Burgess Shale taxa in the middle Cambrian Wheeler Formation, House Range, Utah. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 220 (1–2), 193–205.
- Gaines, R.R., Hammarlund, E.U., Hou, X., Qi, C., Gabbott, S.E., Zhao, Y., Peng, J., Canfield, D.E., 2012. Mechanism for Burgess Shale-type preservation. *Proc. Natl. Acad. Sci.* 109 (14), 5180–5184.
- Gnaedinger, S., Kloster, A.C., Adami-Rodrigues, K., Urban, C., Scmazzon, A.K., 2012. Permineralized Woods from Upper Carboniferous – Lower Permian of the Itararé Group, Brazil. *Encontro Pan-Americano da IAWA, Recife*. pp. 58–59.
- Griffis, N.P., Mundil, R., Montañez, I.P., Isbell, J., Fedorchuk, N., Vesely, F., Iannuzzi, R., Yin, Q.Z., 2018. A new stratigraphic framework built on U-Pb single-zircon TIMS ages and implications for the timing of the penultimate icehouse (Paraná Basin, Brazil). *GSA Bull.* 130 (5–6), 848–858.
- Griffis, N.P., Montañez, I.P., Fedorchuk, N., Isbell, J., Mundil, R., Vesely, F., Weinschultz, L., Iannuzzi, R., Gulbranson, E., Taboada, A., Pagani, A., Sanborn, M.E., Huyskens, M., Wimpenny, J., Linol, B., Yin, Q.Z., 2019a. Isotopes to ice: constraining provenance of glacial deposits and ice centers in west-central Gondwana. *Palaeo.* <https://doi.org/10.1016/J.PALAEO.2018.04.020>.
- Griffis, N.P., Montañez, I.P., Mundil, R., Richey, J., Isbell, J., Fedorchuk, N., Yin, Q.Z., 2019b. Coupled stratigraphic and UP-Pb zircon age constraints on the Late Paleozoic Icehouse to greenhouse turnover in south-central Gondwana. *Geology* 47 (12), 1146–1150.
- Gupta, N.S., Summons, R.E., 2011. Fate of chitinous organisms in the geosphere. In: Gupta, N.S. (Ed.), *Chitin Formation and Diagenesis*. Springer, Dordrecht, pp. 173.
- Gupta, N.S., Collinson, M.E., Briggs, D.E.G., Evershed, R.P., Pancost, R.D., 2006a. Reinvestigation of the occurrence of cutan in plants: implications for the leaf fossil record. *Paleobiology* 32, 432–449.
- Gupta, N.S., Michels, R., Briggs, D.E.G., Evershed, R.P., Pancost, R.D., 2006b. The organic preservation of fossil arthropods: an experimental study. *Proc. R. Soc. B* 273, 2777–2783.
- Hamel, M.H., 2005. A new actinopterygian from the Early Permian of the Paraná Basin, Brazil. *J. Vertebr. Paleontol.* 25 (1), 19–26.
- Holz, M., França, A.B., Souza, P.A., Iannuzzi, R., Rohn, R., 2010. A stratigraphic chart of the Late Carboniferous/Permian succession of the eastern border of the Paraná Basin, Brazil. *Southern America. J. S. Am. Earth Sci.* 29, 381–399.
- Isbell, J.L., Henry, L.C., Gulbranson, E.L., Limarino, C.O., Fraiser, M.L., Koch, Z.J., Ciccioli, P.L., Dineen, A.A., 2012. Glacial paradoxes during the late Paleozoic ice age: evaluating the equilibrium line altitude as a control on glaciation. *Gondwana Res.* 22, 1–19.
- Kallen, C.V.D., Scmazzon, A.K., Urban, C., Adami-Rodrigues, K., 2014. Novo registro de ostracodes do grupo Itararé, Formação Taciba, Membro Rio do Sul, Mafra, Santa Catarina. 23rd Congresso de Iniciação Científica da Universidade Federal de Pelotas. pp. 32.
- Keren, R., Mayzel, B., Lavy, A., Polishchuk, I., Levy, D., Fakra, S.C., Pokroy, B., Ilan, M., 2017. Sponge-associated bacteria mineralize arsenic and barium on intracellular vesicles. *Nat. Commun.* 8, 14393.
- Calcification in Ostracodes. *Revista Española de Micropaleontología* 36 (1), 1–11.
- Koester, E., Scmazzon, A.K., Weinschütz, L.C., Wilner, E., Moutinho, L.P., Nascimento, S., 2016. Idade Rb-Sr do Folhelho Lontras, Grupo Itararé, Bacia do Paraná, na Região de Mafra, SC, Brasil. *Anais do 48º Congresso Brasileiro de Geologia*. pp. 955.
- Kuecher, G.J., Woodland, B.G., Broadhurst, F.M., 1990. Evidence of deposition from individual tidal cycles from the Francis Creek Shale (host rock to the Mazon Creek Biota), Westphalian D (Pennsylvanian), northeastern Illinois. *Sedimentary Geology* 68, 211–221.
- Laflamme, M., Schiffbauer, J.D., Narbonne, G.M., Briggs, D.E.G., 2011. Microbial biofilms and the preservation of the Ediacara biota. *Lethaia* 44, 203–213.
- Landman, N.H., Klofak, S.M., 2012. Anatomy of a concretion: life, death, and burial in the Western Interior Seaway. *Palaio* 27 (10), 671–692.
- Lavina, E.L.C., Lopes, R.D.C., 1987. A transgressão Marinha do Permiano Inferior e a Evolução Paleogeográfica do Supergrupo Tubarão no estado do Rio Grande do Sul. *Paula Coutina* 1, 51–103.
- Lopes, R.D.C., Lavina, E.L.C., Signorelli, N., 1986. Fácies sedimentares e Evolução Paleambiental do Supergrupo Tubarão na Borda Leste da Bacia do Paraná: uma seção regional nos estados do Rio Grande do Sul e Santa Catarina. In: *Brazilian Geological Congress*, 24, Goiânia, SBG. 1. pp. 206–208.
- Machado, M.A.P., 1994. O Degelo final permiano e o seu registro geológico na borda sudeste da Bacia do Paraná (Paleoval de Candiota-RS). *Dissertação*. Universidade Federal do Rio Grande do Sul, Porto Alegre (165 p).
- Malabarba, M.C.S.L., 1988. A new genus and species of stem group actinopteran fish from the Lower Permian of Santa Catarina State, Brazil. *Zool. J. Linnean Soc.* 94, 287–299.
- Martins-Neto, R.G., 2005. Estágio atual da paleoartropodologia brasileira: hexápodes, miriápodes, crustáceos (Isopoda, Decapoda, Eucrustacea e Copepoda) e quelicerados. *Arquivos do Museu Nacional* 63 (3), 471–494.
- McCoy, V.E., Young, R.T., Briggs, D.E.G., 2015a. Factors controlling exceptional preservation in concretions. *Palaio* 30, 272–280.
- McCoy, V.E., Young, R.T., Briggs, D.E.G., 2015b. Sediment permeability and the preservation of soft-tissues in concretions: an experimental study. *Palaio* 30, 608–612.
- Milani, E.J., 1997. Evolução Tectono-estratigráfica da Bacia do Paraná e seu relacionamento com a geodinâmica fanerozoica do Gondwana sul-occidental. Universidade Federal do Rio Grande do Sul, Tese de doutorado, pp. 255.
- Milani, E.J., de Melo, J.H.G., de Souza, P.A., Fernandes, L.A., França, A.B., 2007. Bacia do Paraná Boletim de Geociências da Petrobras 15 (2), 265–287.
- Milani, E.J., Ramos, V.A., 1998. Orogenias Paleozóicas no domínio Sul-Occidental do Gondwana e os ciclos de subsidência da Bacia do Paraná *Revista Brasileira de Geologia* 28 (4), 473–484.
- Mills, D.B., Ward, L.M., Jones, C., Sweeten, B., Forth, M., Treusch, A.H., Canfield, D.E., 2014. Oxygen requirements of the earliest animals. *Proc. Natl. Acad. Sci. U.S.A.* 111, 4168–4172. <https://doi.org/10.1073/pnas.1400547111>.
- Muller, C., Mouro, L.D., Silva, M.S., Vieira, L.D., 2017. Coprolites of Campaleo outcrop, Lontras Shale, Campo Mourão Formation, in Mafra-SC. In: XXV CONGRESSO BRASILEIRO DE PALEONTOLOGIA. 1 Boletim de Resumos, Ribeirão Preto 211–211.
- Montañez, I.P., Poulsen, C.J., 2013. The Late Paleozoic ice age: an evolving paradigm. In: Jeanloz, R. (Ed.), *Annual Review of Earth and Planetary Sciences*. 41. pp. 629.
- Mouro, L.D., 2017. Paleoeologia do Folhelho Lontras, Formação Campo Mourão, Cisulário, Brasil. Programa de Pós-graduação em Geologia, Universidade Federal do Rio de Janeiro, Tese de Doutorado (213 pp.).
- Mouro, L.D., Fernandes, A.C.S., Rogério, D.W., Fonseca, V.M.M., 2014a. First articulated sponge from the Paleozoic of Brazil, and a new organization of the Order Hemidiscosa. *J. Paleontol.* 88 (1), 171–178.
- Mouro, L.D., Fernandes, A.C.S., Zaton, M., Flach, M.K., Mouro Junior, J.C., 2014b. Marine Caddisflies larval cases from the Permian of Brazil. In: 4th International Paleontological Congress, Mendoza. Abstracts, pp. 759.
- Mouro, L.D., Zaton, M., Fernandes, A.C.S., Waichel, B.L., 2016. Larval cases of caddisfly (Insecta: Trichoptera) affinity in Early Permian marine environments of Gondwana. *Nature Science Reports* 6, 1–7. <https://doi.org/10.1038/srep19215>. 14 January 2016. www.nature.com/scientificreports/.
- Mouro, L.D., Rakocinski, M., Marynowski, L., Piszarszewska, A., Musabellu, S., Zaton, M., Carvalho, M.A., Fernandes, A.C.S., Waichel, B.L., 2017. Benthic anoxia, intermittent photic zone euxinia and elevated productivity during deposition of the Lower Permian, post-glacial fossiliferous black shales of the Paraná Basin, Brazil. *Glob. Planet. Chang.* 158, 155–172.
- Mouro, L.D., Fernandes, A.C.S., Carvalho, M.A., Weinschutz, L.C., 2018. O Folhelho Lontras (Permiano, Bacia do Paraná) e seus Fósseis: Descoberta, Identificação e Conhecimento Atual. *Anuário do Instituto de Geociências*, pp. 636–646 41–2 / 2018.
- Moxness, L.D., Isbell, J.L., Pauls, K.N., Limarino, C.O., Schenckman, J., 2018. Sedimentology of the mid-Carboniferous fill of the Olta paleovalley, eastern Paganzo Basin, Argentina: implications for glaciation and controls on diachronous deglaciation in western Gondwana during the late Paleozoic Ice Age. *J. S. Am. Earth Sci.* 84, 127–148.
- Muscente, A.D., Schiffbauer, J.D., Broce, J., Laflamme, M., O'Donnel, K., Boag, T.H., Meyer, M., Hawkins, A.D., Huntley, J.W., McNamara, M., MacKenzie, L.A., Stanley Jr., G.D., Hinman, N.W., Hofmann, M.H., Xiao, S., 2017. Exceptionally preserved fossils assemblages through geologic time and space. *Gondwana Res.* 48, 164–188. <https://doi.org/10.1016/j.jgr.2017.04.02>.
- Neves, J.P., Taboada, A.C., Weinschutz, L.C., Simões, M.G., 2017. Brachiopods of the Itararé Group from Mafra County, Southern Brazil, and their geological significance. In: Langer, M.A., Al Halabi, W.A., Ferreira, G.S., Hermanson, G., Marsola, J.C.A., Onary-Alves, S.Y. (Eds.), *Congresso Brasileiro de Paleontologia*, 25, Ribeirão Preto. 2017. Boletim de Resumos. Boletim de Resumos, Paleontologia em Destaque, Ano 32, Edição Especial pp. 222.
- Oliveira, E., 1930. Fósseis marinhos na Série Itararé no Estado de Santa Catharina. *An. Acad. Bras. Cienc.* 2 (1), 17–21.
- Geologia e recursos minerais do Estado do Paraná. Serviço Geológico e Mineralógico do Brasil. Monografia VI, Rio de Janeiro, pp. 172 fotos e mapas.
- Osés, G.L., Petri, S., Becker-Kerber, B., Romero, G.R., Rizzutto, M.d.A., Rodrigues, F., Galante, D., da Silva, T.F., Curado, J.F., Rangel, E.C., Ribeiro, R.P., Pacheco, M.L.A.F., 2016. Deciphering the preservation of fossil insects: a case study from the Crato Member, Early Cretaceous of Brazil. *PeerJ* 4, e2756. <https://doi.org/10.7717/peerj.2756>.
- Oses, G.L., Petri, S., Voltani, C.G., Prado, G.M.E.M., Galante, D., Rizzutto, M.A., Rudnitzki, I.D., da Silva, E.P., Rodrigues, F., Rangel, E.C., Sucerquia, P.A., Pacheco, M.L.A.F., 2017. Deciphering pyritization-kero-genization gradient for fish soft-tissue preservation. *Sci. Rep.* 7, 1468. <https://doi.org/10.1038/s41598-017-01563-0>.
- Pauliv, V.E., Dias, E.V., Sedor, F.A., Weinschutz, L.C., 2014. Elasmobranchii teeth from the Late Carboniferous-Early Permian Itararé Group (Paraná Basin), Southern Brazil. *Society of Vertebrate Paleontology 74th Annual Meeting*, Berlin. pp. 202.
- Petri, S., Souza, P.A., 1993. Síntese dos conhecimentos e novas concepções sobre a bioestratigrafia do Subgrupo Itararé, Bacia do Paraná, Brasil. *Rev. Inst. Geol.* 14 (1), 7–18.
- Pinto, I.D., Sedor, F.A., 2000. A new Upper Carboniferous Blattoid from Mafra Formation Itararé Group, Paraná Basin, Brazil. *Pesquisa em Geociências* 27, 45–48.
- Reiswig, H.M., Miller, T.L., 1998. Freshwater sponge gemmules survive months of anoxia. *Invertebrate Biology* 117, 1–8.
- Ricetti, J.H.Z., Weinschutz, L.C., 2011. Ocorrência de escolecodontes (Annelida, Labidognatha) nas formações Mafra e Rio do Sul, Permo-Carbonífero da Bacia do Paraná, Brasil. In: *Reunião Regional de Paleontologia dos Estados do Paraná e Santa Catarina*, 12, PALEO, Cascavel, 2010. Paleontologia em Destaque. 64. pp. 31–32.
- Ricetti, J.H.Z., Adami-Rodrigues, K., Weinschutz, L.C., 2012. Blattidas (Insecta) do

- Folhelho Lontras, base da Formação Rio do Sul da Bacia do Paraná In: Ghilardi, R.P., Scheffler, S.M. (Eds.), *Simpósio Brasileiro de Paleontologia*, 1, Bauru, 2012, pp. 66. *Boletim de Resumos*, Bauru, UNESP. Paleontologia em Destaque, Edição Especial.
- Ricetti, J.H.Z., Wilner, E., Weinschütz, L.C., 2014. Novos escolocodontes do contato Carbonífero-Permiano (Grupo Itararé) da Bacia do Paraná na cidade de Mafra, Santa Catarina. In: XVI Encontro Regional de Paleontologia dos Estados do Paraná e Santa Catarina - PALEO, 2014, Florianópolis. *Paleontologia em Destaque*, 2014. 68. pp. 76–77.
- Ricetti, J.H.Z., Schneider, J.W., Iannuzzi, R., Weinschütz, L.C., 2016. *Anthracoblattina mendesi* Pinto et Sedor (Blattodea, Phylloblattidae): the most completely preserved South American Palaeozoic cockroach. *Rev. Brasil. Paleontol.* 19, 181–194.
- Richter, M., 1991. A New Marine Ichthyofauna from the Permian of the Paraná Basin of Southern Brazil. King's College London, University of London (Ph.D. Thesis, 233 pp.).
- Rittle, K.A., Drever, J.I., Colberg, P.J.S., 1995. Precipitation of arsenic during bacterial sulfate reduction. *Geomicrobiol. J.* 13 (1), 1–11. <https://doi.org/10.1080/01490459509378000>.
- Rocha-Campos, A.C., 1967. The Tubarão Group in the Brazilian portion of the Paraná Basin. In: Bigarella, J.J., Becker, R.R., Pinto, I.D. (Eds.), *Problems in Brazilian Gondwana Geology*. IG/UFPR, Curitiba, pp. 27–102.
- Rocha-Campos, A.C., dos Santos, P.R., Canuto, J.R., 2008. Late Paleozoic glacial deposits of Brazil: Parana Basin. In: Fielding, C.R., Frank, T.D., Isbell, J.L. (Eds.), *Resolving the Late Paleozoic Ice Age in Time and Space*. 441. pp. 97–114.
- Ruedemann, R., 1929. Fossils from the Permian tillite of São Paulo, Brazil, and their bearing on the origin of tillite. *Bull. Geol. Soc. Am.* 40, 417–426.
- Sanford Sellner, L.P., 1990. Covariability of dissolved-oxygen with physical processes in the summertime Chesapeake Bay. *J. Mar. Res.* 48 (3), 567–590.
- Santos, P.R., Rocha-Campos, A.C., Canuto, J.R., 1996. Patterns of Late Palaeozoic deglaciation in the Paraná Basin, Brazil. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 125, 165–184.
- Schneider, R.L., Muhlmann, H., Tommazi, E., Medeiros, R.A., Daemon, R.F., Nogueira, A.A., 1974. Revisão estratigráfica da Bacia do Paraná In: *Congress Brasileiro de Geologia*, 28, Porto Alegre, 1974. *Anais, Porto Alegre, SBG*, 1, pp. 41–66.
- Scomazzon, A.K., Wilner, E., Purnell, M.A., Nascimento, S., Weinschütz, L.C., Lemos, V.B., de Souza, F.L., da Silva, C.P., 2013. First report of conodont apparatuses from Brazil – Permian of Paraná Basin, Itararé Group, Lontras Shale – Evidence of Gondwana deglaciation. In: *Conodont from the Andes. 3rd International Conodont Symposium. Publicación Especial N° 13. Paleontological Note*, pp. 99–102.
- Scotese, C.R., 1997. *Continental Drift*, 7th edition. PALEOMAP Project, Arlington, Texas (79 pp.).
- Seilacher, A., 1970. Begriff Und bedeutung der Fossil-Lagertätten. In: *Neues Jahrbuch für geologie und Paläontologie, Jahrgang Heft*, pp. 34–39.
- Selden, P., Nudds, J., 2004. *Evolution of Fossil Ecosystems*. Manson Publishing, London, pp. 160 (ISBN 1 84076 040 0; 1 84076 041 9).
- Silveira, A.S., 2000. *Estratigrafia de Sequências e Evolução Paleoambiental da Sucessão Permiana (Sakmariano – Eokazaniano) da Bacia do Paraná, entre Rio Pardo e Mariana Pimentel (RS)*. M.S. Dissertation. Univ. do Vale do Rio dos Sinos (140 pp.).
- Souza, P.A., 2005. Late Carboniferous palynostratigraphy of the Itararé Subgroup northeastern Paraná Basin, Brazil. *Rev. Palaeobot. Palynol.* 138, 9–29.
- Tedesco, J., Cagliari, J., Coitinho, J.R., Lopes, R.C., Lavina, E.L.C., 2016. Late Paleozoic paleofjord in the southernmost Parana Basin (Brazil): geomorphology and sedimentary fill. *Geomorphology* 269, 203–214.
- Tunnicliffe, V., 1981. High species diversity and abundance of the epibenthic community in an oxygen-deficient basin. *Nature* 294, 354–356. <https://doi.org/10.1038/294354a0>.
- Urban, C., Gnaedingr, S., Rodrigues, K.A., Scomazzon, A.K., 2012. *Primer Registro de maderas fósiles del Grupo Itararé, Carbonífero Superior-Permiano Inferior, Brasil. II Simpósio Argentino de Melisopalinologia*, Buenos Aires. pp. 126.
- Valdez Buso, V., Aquino, C.D., Paim, P.S.G., Souza, P.A., Mori, A.L., Fallgater, C., Milana, J.P., Kneller, B., 2019. Late Palaeozoic glacial cycles and subcycles in western Gondwana: Correlation of surface and data of the Paraná Basin, Brazil. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 531 (Part B), 108435. <https://doi.org/10.1016/j.palaeo.2017.09.004>.
- Vesely, F.F., 2006. *Dinâmica sedimentar e arquitetura estratigráfica do Grupo Itararé (Carbonífero-Permiano) no centro-leste da Bacia do Paraná*. Ph.D. Thesis. Universidade Federal do Paraná, Curitiba (226 pp.).
- Vesely, F.F., Trzaskos, B., Kipper, F., Assine, M.L., Souza, P.A., 2015. Sedimentary record of a fluctuating ice margin from the Pennsylvanian of western Gondwana: Paraná Basin, southern Brazil. *Sediment. Geol.* 326, 45–63.
- Weinschütz, L.C., Castro, J., 2005. A Sequência Mafra Superior/Rio do Sul Inferior (Grupo Itararé, Permocarboneífero) em sondagens testemunhadas da região de Mafra, SC, margem leste da Bacia do Paraná Geociências 24, 131–141.
- Wells, M.R., Allison, P.A., Hampson, G.J., Piggott, M.D., Pain, C.C., 2005. Modelling ancient tides: the Upper Carboniferous epi-continental seaway of Northwest Europe. *Sedimentology* 52, 715–735.
- Wilner, E., Lemos, V.B., Scomazon, A.K., 2016a. Associações naturais de conodontes Mesogondolella spp., Grupo Itararé, Cisuraliano da Bacia do Paraná GAEA J. Geosci. 9 (1), 30–36.
- Wilner, E., Ricetti, J.H.Z., Weinschütz, L.C., 2016b. Comunicado de possível primeiro ambar paleozoico da Bacia do Paraná. *Paleontologia em Destaque. Boletim informativo da SBP* 31 (69), 136.
- Woodworth, J.B., 1912. Geological expedition to Brazil and Chile, 1908–1909. *Bull. Museum Compar. Zool.* 56 (1), 3–137.
- Ye, Y., Wu, C., Zhai, L., 2017. Pyrite morphology and episodic euxinia of the Ediacaran Doushantuo Formation in South China. *Sci. China Earth Sci.* 60, 102–113. <https://doi.org/10.1007/s11430-016-0066-0>.
- Yuan X., Chen Z., Xiao S., Zhou C., Hua H., 2011. An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature* 470, 390–393.
- Zhang, F., Blasiak, L.C., Karolin, J.O., Powell, R.J., Geddes, C.D., Hill, R.T., 2015. Phosphorus sequestration in the form of polyphosphate by microbial symbionts in marine sponges. *PNAS* 112 (14), 4381–4386.
- Geology and paleontology of the Kinney Brick Quarry, Late Pennsylvanian, central New Mexico. In: Zidek, J. (Ed.), *New Mexico Bureau of Mines and Mineral Resources Bulletin*. 138. pp. 1–242.
- Ziegler, A.M., Hulver, M.L., Rowley, D.B., 1997. Permian world topography and climate. In: Martini, I.P. (Ed.), *Late Glacial and Postglacial Environmental Changes: Quaternary, Carboniferous-Permian and Proterozoic*. Oxford University Press, Oxford, pp. 111–146.