

A Permian methane seep system as a paleoenvironmental analogue for the pre-metazoan carbonate platforms

Um sistema de exudação de metano permiano como um análogo paleoambiental para plataformas carbonáticas pré-surgimento dos metazoários

Lucas Veríssimo Warren^{1,2*}, Fernanda Quaglio³, Marcello Guimarães Simões^{2,4},
Mario Luis Assine^{1,2}, Luciano Alessandretti³, George Luiz Luvizotto¹,
Claudio Riccomini^{2,5}, Nicolás Misailidis Stríkis⁶

ABSTRACT: Following the rise of metazoans, the beginning of bioclasticity and substrate competition, the saga of microbial mats was in a fluctuating decline in the end of the Neoproterozoic era. Increases in diversity during the Phanerozoic and punctual upturns in the microbial carbonate production occurred after the events of global mass extinctions. Gradually along the Phanerozoic, the microbial colonies occupied isolated niches and grazers-free environments, characterized by physically and/or geochemically stressful conditions, such as those found in saline bays, alkaline lakes and hydrothermal or cold seep vents. Here we report one of the oldest occurrences of a vent camp coupled with cold seepage of methane in the geological record, associated with well-preserved microbialites and elephant skin structures. During the seep activity, oxygen depletion and high salinity conditions are prohibitive for complex animal life, clearing the way to microbial colonies to flourish. Due to the co-occurrence of high adaptability and low competitiveness of microbial forms, they became highly specialized in stressful conditions. We argue that the sporadic microbial mat upturns in Earth's history are not restricted to geological periods, following massive death of metazoan species; they also may occur in response to punctual paleoenvironmental conditions that enable microbial colonies to grow. Indeed, the Phanerozoic geological record is punctuated of these examples, in a kind of hide-and-seek game of Precambrian times.

KEYWORDS: Methane cold seeps; microbial mats; ecospace; Permian; Irati Formation.

RESUMO: Após o aparecimento dos metazoários, o início da bioclasticidade e a competição pelo substrato marinho, a saga das esteiras microbiais é marcada por um progressivo declínio. Pontuais aumentos em sua diversidade e na produção de carbonatos durante o Paleozoico em geral estão associados a eventos globais de extinção em massa. Ao longo do Fanerozoico, as colônias microbiais ocuparam nichos ecológicos específicos e ambientes livres de organismos predadores caracterizados por condições ecológicas extremas, como aqueles encontrados em baías hipersalinas, lagos alcalinos e locais sujeitos a hidrotermalismo. Neste trabalho é reportada uma das mais antigas ocorrências de um campo de exudação de metano no registro geológico associado com microbialitos e estruturas sedimentares induzidas por atividade microbiana. Nesse sistema, durante a atividade de exalação de metano, instalaram-se condições de extrema anoxia e alta salinidade, proibitivas para a manutenção da vida animal, permitindo, desse modo, o florescimento de colônias microbiais. Por causa das severas imposições do ambiente, os organismos microbiais tornaram-se altamente adaptáveis às condições adversas então vigentes. Nós sustentamos a hipótese de que aumentos na diversidade e na quantidade de colônias microbiais na história da Terra não estão apenas restritos a períodos que sucedem à extinção em massa de organismos predadores de esteiras, mas ocorrem em resposta a condições ambientais localizadas que proporcionam o crescimento de colônias microbiais. De fato, o registro geológico Fanerozoico é pontuado de exemplos semelhantes ao aqui reportado, simulando uma espécie de jogo de esconde-esconde das condições ambientais vigentes no Éon Pré-cambriano.

PALAVRAS-CHAVE: sistema de exudação de metano; esteiras microbiais; ecospaço; permiano; Formação Irati.

¹Departamento de Geologia Aplicada, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista – UNESP, Rio Claro (SP), Brazil. E-mails: warren@rc.unesp.br; assine@rc.unesp.br; georgell@rc.unesp.br

²Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq, Brasília (DF), Brazil. E-mails: warren@rc.unesp.br; profmgsimoes@gmail.com; assine@rc.unesp.br; ricomin@usp.br

³Curso de Geologia, Instituto de Geografia, Universidade Federal de Uberlândia – UFU, Uberlândia (MG), Brazil. E-mails: quaglio@gmail.com; luciano.geors@gmail.com

⁴Departamento de Zoologia, Instituto de Biociências, Universidade Estadual Paulista “Júlio de Mesquita Filho” – UNESP, Botucatu (SP), Brazil. E-mail: profmgsimoes@gmail.com

⁵Instituto de Energia e Ambiente, Universidade de São Paulo – USP, São Paulo (SP), Brazil. E-mail: riccomin@usp.br

⁶Departamento de Geoquímica, Universidade Federal Fluminense – UFF, Niterói (RJ), Brazil. E-mail: strikis@gmail.com

*Corresponding author

Manuscript ID: 20170125. Received on: 10/11/2017. Approved on: 10/17/2017.

INTRODUCTION

The end of the Ediacaran period was characterized by several biological novelties and key paleoenvironmental changes, including the rise of metazoans, the origin of bioclast-enriched substrates and the emergence of the first reef ecosystems, as well as the decline of stromatolites (Pratt 1982; Riding 2006; Warren *et al.* 2013; Penny *et al.* 2014). These events mark the onset of Phanerozoic-like benthic ecosystems during the Ediacaran-Cambrian transition (Seilacher 1999; Droser *et al.* 2002); that is, a change from marine carbonate platforms primarily dominated by horizontal bioturbation and extensive microbial mats (Grotzinger 1989) to those with vertical bioturbation and the absence of microbial mats. Such changes played a key role in the evolution of stem and crown groups of metazoan phyla and are associated with the Cambrian substrate revolution (Bottjer 2010), which created new benthic microenvironments and dramatically altered the ecology of shallow subtidal seafloors after the early Cambrian (Seilacher 1999; Bottjer *et al.* 2000; Meyer *et al.* 2014).

During the Neoproterozoic, the low rates of dissolved oxygen prevailed on the carbonate platform substrates (Grotzinger & Knoll 1999), which was covered by microbial-dominated communities (Grotzinger 1989). Extensive microbial mat coverage of photosynthetic organisms, such as cyanobacteria, formed a barrier to burrowers and other living organisms, inhibiting them from accessing the substrate (a sharp sediment-water interface). Two ecological novelties at the end of the Ediacaran could cause the decline of cyanobacterial communities and create a new opportunity for organisms to penetrate the substrate, leading to a diffuse sediment-water interface. The first one appears to be tied to the rise of the earliest bilaterians at c. 580 Ma, whose ability to disrupt and burrow through the mats (Seilacher & Pflüger 1994) lead to the Cambrian Substrate Revolution (Bottjer *et al.* 2000; Bottjer 2010; Orr *et al.* 2003). The second one is linked to the beginning of bioclasticity, which caused the biomineralized remains of dead metazoan skeletons to enrich the microbial mat-dominated sea floor with more durable, biogenic scraping remains (Awramik 1971; Pratt 1982; Porada & Bouougri 2007). Combined with the origin of bioclasts, expansion of grazing benthos and the competition for eco-space, these innovations also significantly contributed to the pronounced decrease in microbial-induced sedimentary structures (MISS) during the Ediacaran-Cambrian transition. As a rule, the abundance and diversity of MISS and microbialites have never been the same (Riding 2006; Porada & Bouougri 2007) and are considerably scarce in younger Phanerozoic records.

The geological record indicates that the development of microbial-rich sea floors took place in stressful conditions including seepage of hydrogen sulphide, methane and other hydrocarbon-rich fluids and/or where penetrative bioturbation was suppressed (Buatois *et al.* 2013).

Here we report the discovery of an uncommon high-stress aquatic environment formed by a singular Permian methane seep system in south-eastern Brazil, where microbial communities developed profusely around vents that are now silicified. Despite its relative abundance in the Mesozoic record, the occurrence of vents associated with methane seepage is rare in the Paleozoic (Campbell 2006). This is the oldest evidence of this type of exudation structure in the geologic record of South America and represents an unusual occurrence of methane seepage system in an intra-continental context.

GEOLOGICAL SETTING

The Irati Formation is a 60 m thick mixed sedimentary succession subdivided into two distinct units, the Taquaral and Assistência members (Fig. 1). The lower Taquaral Member is a monotonous succession of black shales deposited in offshore conditions (>50 m). The upper Assistência Member has rhythmic intercalations of shales and white dolomites, suggesting deposition in reduced bathymetries in respect to Taquaral Member. Spheroidal siliceous concretions and aggregates of pyrite crystals occur sporadically throughout the Assistência Member. Laterally irregular chert levels are also present. Preserved salt pseudomorphs are sometimes present. The high organic matter concentration in the black shales, with mean total organic carbon content (TOC) values of 11%, the presence of disseminated pyrite and the occasional occurrence of bitumen indicate that the rocks were deposited under reducing (anoxic) conditions (Araújo *et al.* 2000).

The fossil content of the Assistência Member includes endemic, aquatic mesosaurid reptiles, insects and crustacean remains (Ricardi-Branco *et al.* 2008) that sometimes form dense mass accumulations (Matos *et al.* 2013). Bioturbation and trace fossils of benthic invertebrates are absent. Kerogen is common in the Assistência Member, which indicates that the water was stagnant and hypersaline (Faure & Cole 1999). Hypersaline conditions are also supported by the preservation of mesosaurid soft tissues (Piñeiro *et al.* 2012a; Piñeiro *et al.* 2012b).

Based on the co-occurrence of mesosaurid reptiles, the Irati Formation has been correlated to the Artinskian White Hill Formation of the main Karoo Basin in South Africa (Oelofsen & Araújo 1987). Radiometric zircon ages from

volcanic ash in the oil-rich succession of the Taquaral Member, in São Matheus do Sul, Paraná, confirmed a Kungurian age (278 Ma, Araújo *et al.* 2006). Similar zircon ages of ~275 Ma from an ash level (Rocha-Campos *et al.* 2011) confirm that the top of the Irati Formation was deposited during the Kungurian stage.

To the north, nearly 130 km from the study area, the Irati Formation preserves remarkable giant domed stromatolitic bioherms reaching up to 3 m in height (Suguio & Sousa 1985; Soares 2003). Other microbialites in the Assistência Member include domed stromatolites and microbial laminated facies described near the study area (Calça & Fairchild 2012), in some cases recording organic-walled microfossils such as coccoidal cyanobacteria and palynomorphs. Other limestone dome structures associated with

dolostones of the Irati Formation have been interpreted as small and localized salt domes (Hachiro 2000).

MATERIAL AND METHODS

The study area is located in the District of Paraisolândia, Charqueada town, state of São Paulo, Brazil. The vents occur in the upper section of the Irati Formation (Assistência Member), along the left bank of the Paraíso creek. Detailed measurement and description of 153 individual mounds and vents was carried out in the field and included characterization of lithotypes, sedimentary structures, bed thicknesses, contact relationship and geometry, as well as gas scape structures. Morphometric measurements included diameter,

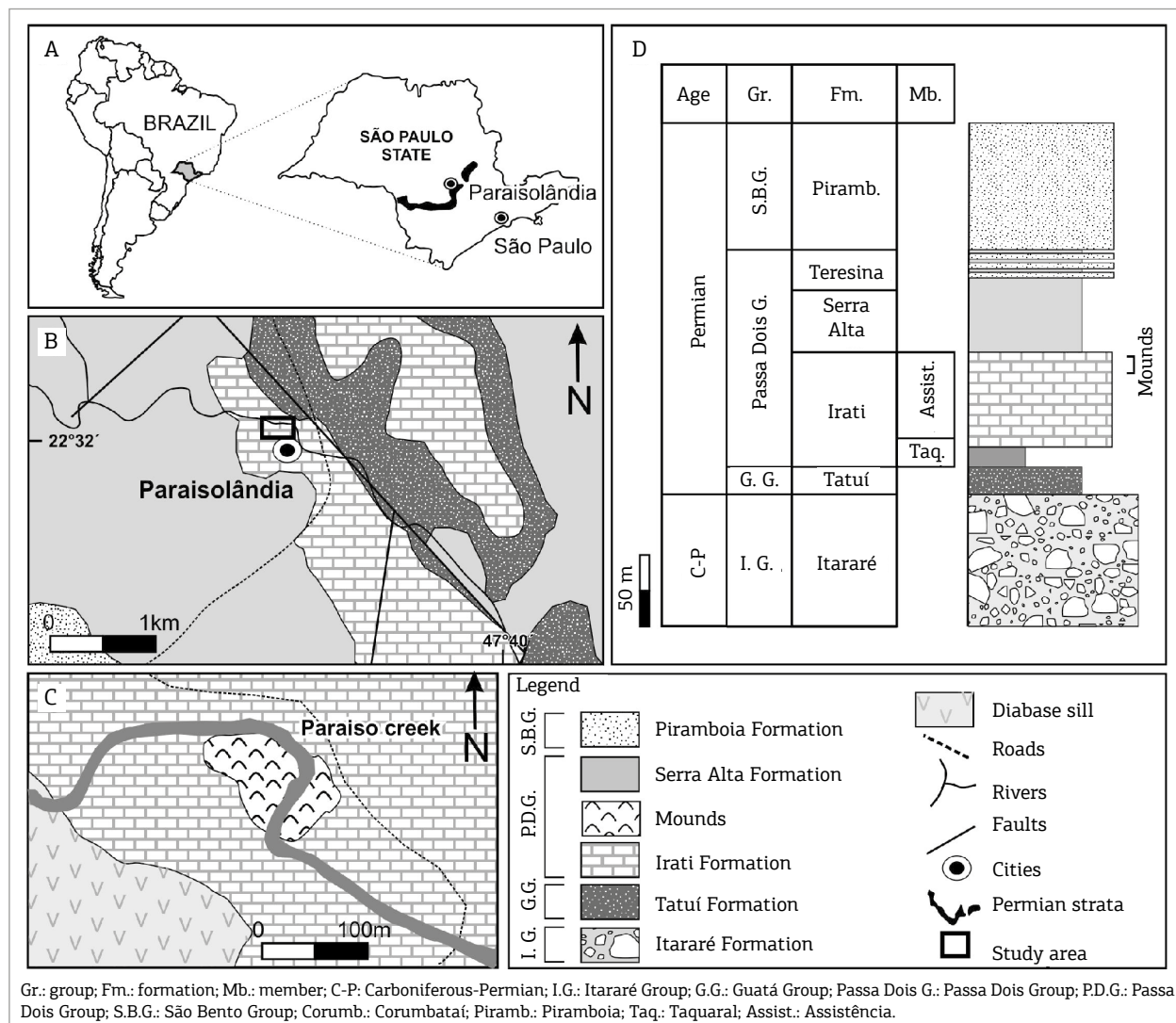


Figure 1. (A) Location of São Paulo state highlighting the Permian rocks of the Paraná Basin; (B) geologic map of the Paraisolândia district with the location of the study area (map by Lucas V. Warren); (C) detail of the Paraíso Creek area and the dome camp; (D) lithostratigraphic column of the Carboniferous and Permian succession of the Paraná Basin with the stratigraphic location of the domes (vents).

longest and shortest axes, height, margin thickness and wall thickness. The occurrence of MISS, stromatolites, collapsed areas, mud spill features and coalescent forms was also documented. After removal of incrusting sediments, the collected samples (30 in total) were analyzed in details under stereoscopic lupe. Twenty-two petrographic thin sections of chert and carbonates were investigated under normal and polarized light using a Zeiss AxioLab petrographic microscope at the Unespetro Research Center of the Institute of Geosciences and Exact Sciences, São Paulo State University “Júlio de Mesquita Filho” (IGCE-UNESP). Rock samples and thin sections are housed in the Laboratory of Sedimentology of the IGCE-UNESP.

The stable isotope analyses ($d^{13}\text{C}$ and $d^{18}\text{O}$) were carried out in five microbial carbonate samples in the Stable Isotope Laboratory at Geosciences Institute of University of São Paulo (IGC-USP). Carbon and oxygen isotope ratios are expressed in δ notation, the per mil deviation from the Vienna Pee Dee Belemnite (VPDB) standard (*e.g.*, for oxygen, $\delta^{18}\text{O} = [((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{VPDB}}) - 1] \times 1000$). For each measurement, approximately 200 mg of powder was drilled from the sample and analyzed with an on-line, automated, carbonate preparation system linked to a Finnigan Delta Plus Advantage. Reproducibility of standard materials is 0.1‰ for $\delta^{18}\text{O}$ and 0.05‰ for $\delta^{13}\text{C}$.

THE PERMIAN METHANE SEEP SYSTEM IN THE PARANÁ BASIN

Near the Paraisolândia district, Charqueada town, state of São Paulo (Fig. 1), several aligned domes and mounds are

recorded over the banks of the Paraíso creek, covering an area of at least 10,000 m² (Figs. 1A-1C). As discussed ahead, these are interpreted as seep structures and are stratigraphically located in the upper portion of the Irati Formation, or nearly two meters below the abrupt contact with grey mudstones of the Permian Serra Alta Formation (Fig. 1D). They occur in two distinct dolostone beds intercalated with bituminous black shales, occasionally containing pyrite crystals. The carbonate layers are 10–25 cm thick and have subtle wave ripples and microbial laminations intercalated with submillimetre layers of white and dark (organic-rich) mudstones. Centimetre-thick silicified claystone beds intercalate with these carbonate beds. The domes and mounds outcrop is composed of 153 chert structures, most of which are NE orientated (Fig. 2A). Notice that the dome camp occurs near to well documented NW-SE normal faults. The individual irregular mounds (or vents, *sensu* Milkov 2005) have the average length of 79.9 cm, height of 26.2 cm and width of 56.8 cm (Figs. 2A and 2B). They have steep-sided walls and occasionally merge with other domes (29%) forming clusters of two, three or four structures (Fig. 2B).

Half of the mounds (52%) have a typical central crater with partially collapsed walls and irregular hemispherical depressions (Figs. 3A and 3B). Ninety per cent of the mounds have the outer surface of thin (1–3 mm) laminated micritic carbonate or dolomitized grainstone. Some of them show flow and collapse features, such as corrugations and bubbles (Fig. 3C), as well as radial fractures filled by microcrystalline quartz preserved in their external walls. The inner conduits of the mounds are filled by massive mudstone (Figs. 3D and 3E), and the internal portion of the walls is composed of completely silicified black chert with fluidal

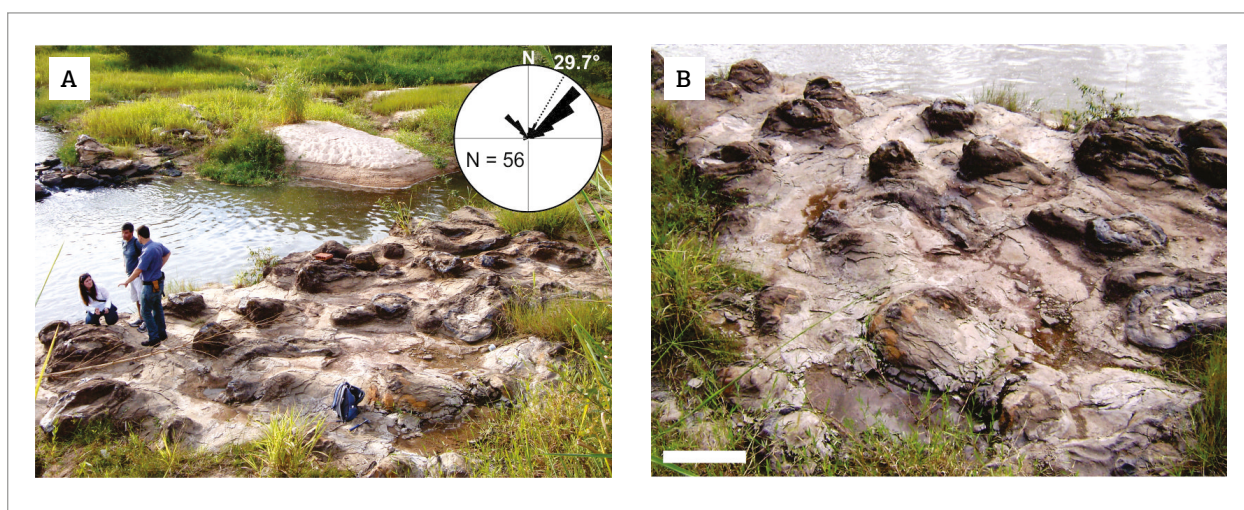


Figure 2. (A) Overview of the Permian vents of the Irati Formation, Paraisolândia district, Brazil. The rose-diagram shows NE-SW preferential orientation of the elongation axis of the vents (mean direction of 29.7°); (B) view of several individual domes (some of them coalesced) showing a central depression.

structures, bifurcated tubes (Fig. 3F) and fenestral vesicles filled by microcrystalline silica, pyrite and rarely vivianite (Fig. 3F). These structures are commonly ovoid in shape and connected to other vesicles, forming a fenestral fabric.

The external walls of some cones (24%) are completely covered and have interconnected centimetre- to submillimetre-scale cracks that form a reticulate pattern covering a very thin silicified grainstone bed (Figs. 4A and 4B).

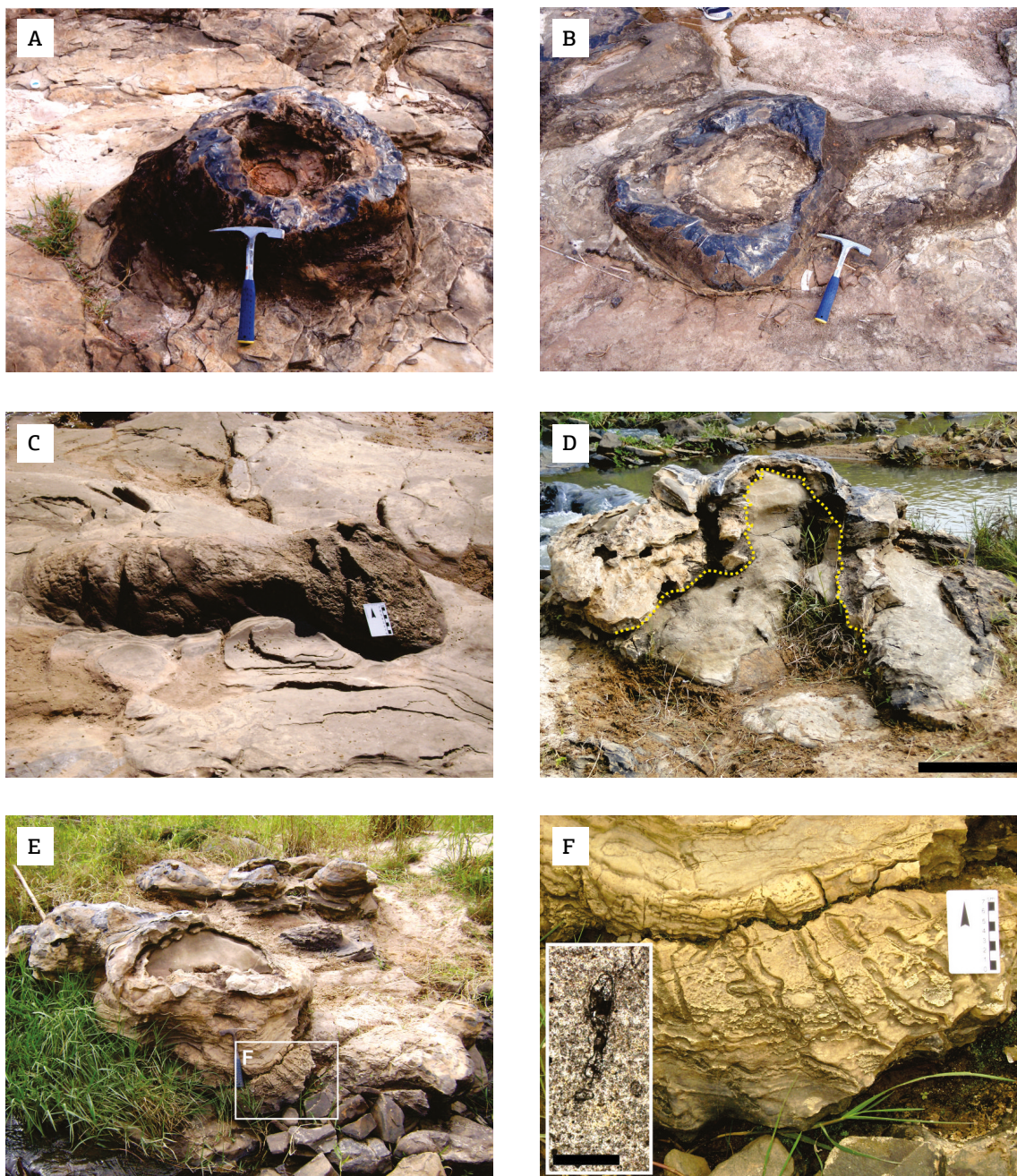


Figure 3. (A) Close-up of a silicified mound with a circular central crater; (B) coalescent silicified domes with central depressions; (C) collapsed mound showing mudflow features; (D) section of two coalescent silicified mounds showing the inner conduit filled by massive mudstone; (E) silicified mound with central crater filled by massive mudstone; (F) detail of branched tubes interpreted as degassing structures in E. Detail of photomicrograph of vesicles and bubbles filled by microcrystalline silica as seen in petrographic thin section. Scale bars = 200 μ m in F and 0.5 m in D.

The crack dimensions vary between 0.3 and 1.8 cm, and some have millimetre-scale areas of relief that correspond

to negative wrinkle structures defined as elephant skin microscopically, the cracks are associated with thin layers

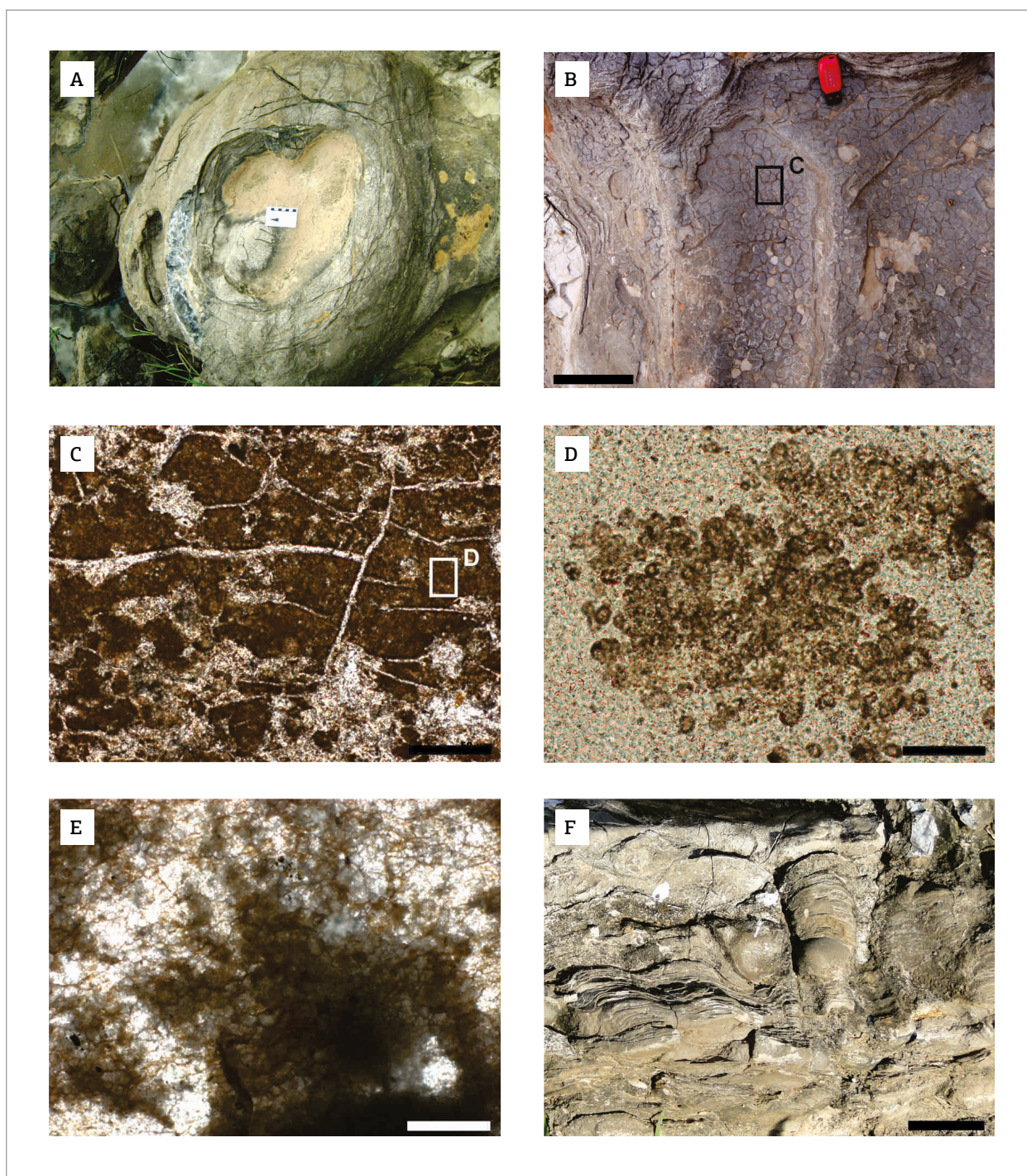


Figure 4. Microbialites and microbial-induced sedimentary structures (MISS) structures. (A) Mounds with irregular central crater completely covered by a thin layer of mudstone with elephant skin structures (ESS); (B) ESS developed on a silicified outer surface of mounds forming a typical reticulate pattern. The rectangle indicates the photo C position; (C) photomicrograph of elephant skin structures showing the polygonal array formed by cracks. Dark grey material is mainly composed of amorphous organic matter and subspheroidal cells. The rectangle indicates the photo D position; (D) detail of the dark grey organic matter showed in D. Notice the cluster or coccoidal cyanobacteria in a planar arrangement; (E) subspheroidal cells observed in thin sections of the chert; (F) centimeter size dome and columnar stromatolites developed between the domes. Scale bars = 5 cm in B and F, 100 μ in C and 50 μ in D and E.

of amorphous organic matter and organic-walled microfossils (Figs. 4C-4E). Hundreds of subspheroidal spheroids found in the chert wall of the domes (Figs. 4D and 4E) form poorly organized clusters of coccoidal cyanobacterial colonies. The spheroids are commonly unornamented, sometimes preserving the outer ring of the walls. The clusters are irregularly segregated and form protuberances. Successive mat layers are intercalated in a reticulate configuration in which the cracks form a polygonal network with pinnacles at the junction points (Porada & Bouougru 2007). It is important to notice that well preserved coccoidal cyanobacterial cells were also found in chert samples from Paraisolândia outcrops (Calça and Fairchild 2012). Rare centimetre-size dome and columnar stromatolites are also associated and occur within the space between the domes (Fig. 4F). These structures constitute concrete evidence of biologic-induced mineralization (organomineralization), and the presence of metabolic activity of cyanobacteria induces the direct precipitation of microbialites.

The C isotope ratios of the laminites and MISS samples show average $\delta^{13}\text{C}$ values of -2.4‰ (Tab. 1).

THE ORIGIN OF THE SEEP STRUCTURES AND THE PERMIAN METHANE EXUDATION

Nowadays the number of vents and mounds associated with methane exudation on Earth exceeds the hundreds (Campbell 2006; Milkov 2005), but they are rare in the Phanerozoic and Precambrian geological record (Gehling 1999; Peckmann *et al.* 2001; Allison *et al.* 2008). Several features that are typical of modern vent camps associated with methane exudation are present within the Irati Formation, including:

- The general morphology of the domes and mounds, together with their collapsed walls and central conduit;
- The high organic matter content of the clay sequence, as indicated by elevated TOC values;

- The close association with regional tectonic features (Mellors *et al.* 2007);
- The presence of trapped bubbles in the chert, degassing and spill structures and pyrite-filled conduits, which strongly suggests gas (methane) activity.

In addition, some of the structures in the external portions of the Irati mounds, including depressions, corrugations and bubbles, are interpreted as high viscosity spill structures or collapsed mound walls (Fig. 3C). Some (corrugations, bubbles) are particularly common in the outer walls of modern vents and mud volcanos (Riccomini *et al.* 1992). In the internal portion of the mounds, the ovoid fenestral vesicles probably correspond to primary biogenic structures associated with degassing (Figs. 3E and 3F).

Modern cold seep vents and domes are commonly triggered by sediment extrusion caused by diapirism, dewatering processes associated with compaction and pore fluid expulsion (in compressional zones), or even episodic thermogenic and/or biogenic methane exhalations due to fractures induced by seismic activity along faults (Campbell 2006; Mellors *et al.* 2007; Moore *et al.* 1990). In some cases, two of these trigger processes co-occur. For instance, seismicity and hydrocarbon generation can together cause migration of fluid and mud due to lateral tectonic compression and gas pressure (Milkov 2005). Thermogenic methane is a product of hydrocarbon maturation, whereas biogenic methane is produced by microbial respiration. Again, though, both processes can occur in combination (Campbell 2006).

In the Permian example of the Paraná Basin, the evidence cited before suggests an eruption triggered by gas generation, which caused fluidized sediment to emerge along faults or fractures with or without seismic influence. The origin of the vents is probably associated with biogenic methane exhumation following hydrocarbon maturation. Several lines of evidence support this interpretation:

- The vents occur in association with (and above) potential biogenic methane sources (the bituminous-rich black shales), which are the main hydrocarbon sources in the

Table 1. Stable carbon and oxygen isotopes values for microbial carbonates samples from the Permian Paraisolândia mud volcano camp (Irati Formation, Paraná Basin), Brazil.

Sample code	STABLE ISOTOPES			
	$\delta^{13}\text{C}$ (‰, VPDB)	Error- $\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ (‰, VPDB)	Error- $\delta^{18}\text{O}$ ‰
MV 4	-1.76	0.04	-6.21	0.12
MV 5	-4.36	0.05	-7.91	0.13
MV 6	-1.32	0.05	-6.79	0.13
MV 8	-2.29	0.13	-6.56	0.15

VPDB: Vienna Pee Dee Belemnite.

sedimentary succession of the Paraná Basin (Milani & Zalán 1999; Mateus *et al.* 2014);

- Microbial mats composed of cyanobacterial colonies occur around the cones;
- Trapped bubbles, veins, vesicles and tubes preserved in the chert of the inner mound walls could have served as conduits for degassing, and these were later filled by microcrystalline silica and pyrite during early diagenesis;
- Slightly negative C isotope values in the carbonates can indicate methanogenic activity (Tab. 1).

In addition to the methanogen hypothesis, the influence of seismicity as a mechanism for creating fractures and moving the gas/fluidized mud to the surface cannot be ruled out. The vents and mounds are clearly aligned with a preferential orientation to the northeast (a mean direction of 30°) and secondarily to NW (Fig. 3A). This orientation coincides with the vast majority of local faults and large-scale deformational structures, as well as the microcrystalline silica veins recorded at the base of the Irati Formation. Several examples of syndimentary deformational structures such as seismites, faults and hydrothermal vents have been described in the Permian succession of the Paraná Basin, which points to a period of intense intraplate deformation and seismicity (Mateus *et al.* 2014; Riccomini *et al.* 1992; Rostirolla *et al.* 2003; Perinotto *et al.* 2008; Yamamoto *et al.* 2005).

THE NEOPROTEROZOIC ANALOGUE FOR A PERMIAN STRESSFUL AQUATIC SETTING

Detailed petrographic analysis of microbial mudstones and chert mounds shows smooth spheroidal structures with extracellular sheaths and typical size of coccoidal cyanobacteria, sometimes forming clusters. This pattern suggests bacterial colonies present in these rocks and includes rare and very well preserved evidence for cell division (Calça & Fairchild 2012). As with other structures putatively formed by microbial influence, such as MISS, the genesis of elephant skin is related to the interaction between sedimentary beds and microbial communities (Porada & Bouougru 2007). The reticulate pattern is produced by the alignment of motile filamentous cyanobacteria across the substratum (Shepard & Sumner 2010).

The presence of high temperature conditions and turbidity currents are unfavourable for the establishment and growth of microbial colonies in the outer surface of the vents. However, as photosynthetic organisms, cyanobacteria preferably prospers in photic environments with relatively clear water. The presence of viscous flow structures, bubbles

and vesicles at the vent walls constitutes strong evidence for mud and gas exhalations during brief eruptions (Mazzini *et al.* 2009). Immediately after these episodic periods of vent activity in the Irati paleo seafloor, the water was completely saturated by gas hydrates, and the resulting suspended mud could have blocked light from fully penetrating to the seafloor, inhibiting cyanobacterial growth. Following the return of normal conditions, bottom sediments were repopulated by microbial communities (Felden *et al.* 2013). This sequence of events explains the intercalation of organic-rich layers with stromatolites, elephant skin structures and barren chert and mudstones in the Irati Formation (Fig. 4). Hence, the deposit is a record of sudden environmental shifts between eruption periods interrupting quiescent intervals.

During the intervals between eruptions, some hydrothermal influence and degassing input would provide suitable conditions for microbial reproduction, namely stable temperatures and large quantities of energy and reduced substrates such as carbon-rich gases. A possible modern analogue is Socompa Lake in Argentina (Fariás *et al.* 2013). Because of the shape of the vent craters, the distribution of chemosynthetic habitats follows a concentric pattern, as shown by most Quaternary mounds (Fenchel 1998). The extracellular polymeric substances (EPS) production by microbial colonies formed a net-like pattern of coccoids and filaments covering the outer walls of the cones. Such mat coverage promoted the biostabilization of sediments (Taj *et al.* 2014) can result in the preservation of the vent mounds.

The absence of metazoans in physically and/or geochemically extreme environments is another relevant condition that allowed the development of microbial mats. Modern cyanobacterial mats vanish over a period of one to two weeks when exposed to grazing animals (Fenchel 1998). At the study site, the exhalation of mud and high concentrations of hydrogen sulphide nearby the vent cones would have added toxic elements to the water, precluding the presence of animals (Felden *et al.* 2013). Oxygen deficiency and high salinity are two additional limiting factors that can dampen metazoan activity. The presence of pyrite crystals, hydrocarbons and the absence of bioturbation in the rocks at the study site provide evidence for such conditions. Despite the scarcity of salt pseudomorphs in the sediments, the predominance of coccoidal over filamentous cyanobacteria is a good indicator of hypersalinity (Thomas *et al.* 2005). Grazing benthos do not tolerate salinities higher than 50‰, while cyanobacterial colonies are commonly found in environments with salinities up to 80‰ (Haas *et al.* 2006).

We notice that the seismic influence hypothesis would also imply unfavourable conditions for metazoan life. Because hydrothermal fluids are commonly enriched in solutes and sometimes silica, water toxicity would be increased

during eruption periods. The presence of silica would enhance the fossilization potential by starting the early diagenesis (cementation) immediately after the deposition. This could explain the alternating beds of microbial carbonates and barren silicified mudstones. Although plausible, this interpretation is difficult to test and remains speculative.

The subtle negative $\delta^{13}\text{C}$ values recorded in some microbial mudstones (varying from -4.4 to -1.3‰, Tab. 1) suggest the addition of very negative C to the basin, which could be related to the release of methane hydrates during eruptions (Campbell 2006). This scenario is consistent with the poor fossil content and widespread anoxic conditions of the Irati Formation (Calça & Fairchild 2012). A similar association occurs in the Permian-Triassic boundary section of the western Paleo-Tethys margin, in which a decline in the biotic content of shales is followed by an abrupt decrease in $\delta^{13}\text{C}$ values (from 0 to -4‰). Although the values for oxidation of fractionated microbial methane are typically very low [$\delta^{13}\text{C}$ -100 to -50‰ PDB, Whiticar 1999], several examples with high $\delta^{13}\text{C}$ are reported in similar environments (Wirsig *et al.* 2012; Teichert *et al.* 2014; Lash 2015). This effect can be assigned to the oxidation of diverse hydrocarbons (other than methane), or an atypically high dissolved inorganic carbon input associated with the sulfate reduction.

NEOPROTEROZOIC-LIKE BOTTOMS: AGENTS STRUCTURING MICROBIALY-DOMINATED SUBSTRATES IN PHANEROZOIC DEPOSITS

Contemporary living microbial mats and stromatolites are found in several environments, but they are much common in peculiar, stressful sedimentary settings. Blooms of cyanobacteria communities are recorded in modern alkaline lakes of the Andes, hydrothermal camps and hypersaline restricted bays in which biological activity is hampered by limiting ecological factors (Farías *et al.* 2013; Walter *et al.* 1972; Hoffman 1976; Takashima & Kano 2008). The stressful environmental conditions in these distinct settings allied with the almost complete absence of more complex life forms allow simple organisms to flourish. It suggests that very stressful conditions must exist in order to keep the substrates free of grazers, enabling microbial mats to cover the bottom in the same fashion as during most part of the Neoproterozoic. These Neoproterozoic-like bottoms can, occasionally, reappear in the Phanerozoic due to remarkable biogeochemical changes in aquatic sedimentary environments, allowing the profuse growth of microbial communities.

Because of their high adaptability, extremophile bacteria can survive under virtually any environmental conditions. Modern bacteria have developed strategies that enable them to settle on both biotic and abiotic surfaces and develop biofilms (O'Toole *et al.* 2000). These biofilms have several environmental requirements to growth, often including adequate conditions of nutrient availability, temperature, pH, and oxygen. Composition of microbial communities and substrate distribution are dependent on these conditions. Additional elements are required for carbonate precipitation by bacteria and cyanobacteria, such as high concentrations of calcium and inorganic carbon. Once a microorganism is in contact with a given surface, a shift in gene expression begins, causing differentiation of the cells so that they attach to the substrate and form a biofilm (O'Toole *et al.* 2000). Oscillations in hydrodynamic patterns and nutrient inputs will affect biofilm morphology (Stoodley *et al.* 1998). Distinct microbial forms may have associated configurations enhancing their potential for environmental usage, and additional life forms can be integrated into the biofilm to create the three-dimensional structure of a microbial mat. Hence, the vertical mat arrangement is dependent on several factors:

- Conditions prior to biofilm formation;
- Local environmental conditions during biofilm thickening and mat formation (Gerdes 2007);
- Taxonomic composition of the pioneering microbes;
- Daily environmental variations, such as sunlight incidence, which can cause vertical migration.

The microbial distribution and configuration in a mat are highly dynamic and include a relatively complex ecological community with several potential interactions that define a colonial-type arrangement. It suggests that some degree of alpha diversity is necessary to develop a proper mat. In this way, the overall microbial community works almost like an ecological specialist, as it is able to easily thrive in environmental conditions that are too severe for more complex life forms or even a few microbes alone.

Harsh conditions can be developed under authigenic control in locally restricted environments. However, the relative abundance of reef-building microbial carbonates after the rise of bilaterians at ca. 580 Ma (Yuan *et al.* 2011) is concurrent with a decline in microbial mat communities despite minor local resurgences (Riding 2006; Bottjer 2010). The link of microbial structures and stressful paleoenvironments suggests that the appearance and growth of microbial mats in the Phanerozoic could be exclusive of global extinction periods. In fact, following each of the "big five" mass extinction events in the Phanerozoic, deterioration of the trophic chain coupled with elimination of grazers led to the expansion of microbial mats on marine substrates (Riding 2006).

This proposed invasion of the ecospace is particularly noteworthy following the Late Devonian and end Permian mass extinctions. However, niche opening is thought to happen whenever severe environmental changes take place. Global environmental turnovers or local restricted conditions may be indicated by the presence of biofilms of cyanobacteria and other microorganisms in Phanerozoic deposits, mimicking global conditions of Neoproterozoic times.

CONCLUSIONS

In this contribution, we argue that the installation of a methane seep system in the central-western Gondwana region during the Permian may have significantly changed the marginal benthic ecosystems of the Paraná Basin (the largest known epeiric sedimentary

basin ever). It altered ecosystem functioning and gave rise to geochemical conditions that suppressed grazing benthos and, thus, competition for substrate. As a result, a short-lived reappearance of Precambrian-like microbial matground-rich ecosystems occurred, providing a brief return to conditions that prevailed in the Neoproterozoic carbonate platforms.

ACKNOWLEDGEMENTS

The authors thank the Brazilian National Council for Scientific and Technological Development (CNPq) (grant 444070/2014-1) for financial support. This research was made with institutional support of the UNESP, Brazil. L. V. Warren, M. L. Assine, C. Riccomini and M. G. Simões are fellows of the CNPq.

REFERENCES

- Allison P.A., Hesselbo S.P., Brett C.E. 2008. Methane seeps on an Early Jurassic dysoxic seafloor. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **270**(3-4):230-238.
- Araújo L.M., Triguês J.A., Cerqueira J.R., Freitas L.C.S. 2000. The atypical Permian petroleum system of the Paraná Basin, Brazil. In: Melo M.R. & Katz B.J. (eds.) *Petroleum systems of South Atlantic margin*. AAPG Special Volumes 73, p. 377-402.
- Araújo C.C., Yamamoto J., Rostrolla S.P. 2006. Arenitos asfálticos na Bacia do Paraná: estudo das ocorrências no Alto Estrutural de Anhembi. *Boletim de Geociências da Petrobras*, **14**:47-70.
- Awramik S.M. 1971. Precambrian columnar stromatolite diversity: Reflection of metazoan appearance. *Science*, **174**(4011):825-827.
- Bottjer D.J. 2010. The Cambrian Substrate Revolution and Early Evolution of the Phyla. *Journal of Earth Sciences*, **21**(1):21-24.
- Bottjer D., Hagadorn J.W., Dornbos S.Q. 2000. The Cambrian Substrate Revolution. *Geological Society of America Today*, **10**(9):1-7.
- Buatois L.A., Netto R.G., Mángano M.G., Carmona N.B. 2013. Global deglaciation and the re-appearance of microbial matground-dominated ecosystems in the late Paleozoic of Gondwana. *Geobiology*, **11**(4):307-317.
- Calça C.P. & Fairchild T.R. 2012. Petrographic approach to the study of organic microfossils from the Irati Subgroup (Permian, Parana Basin, Brazil). *Journal of South American Earth Sciences*, **35**(9):51-61.
- Campbell K.A. 2006. Hydrocarbon seep and hydrothermal vent palaeoenvironments and palaeontology: Past developments and future research directions. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **232**(2-4):362-407.
- Droser M.L., Jensen S., Gehling J.G. 2002. Trace fossils and substrates of the terminal Proterozoic–Cambrian transition: Implications for the record of early bilaterians and sediment mixing. *Proceedings of the National Academy of Sciences*, **99**(20):12572-12576.
- Farfás M.E., Rascovan N., Toneatti D.M., Albarracín V.H., Flores M.R., Poiré D.G., Collavino M.M., Aguilar O.M., Vazquez M.P., Polerecky L. 2013. The discovery of stromatolites developing at 3570 m above sea level in a high-altitude volcanic lake Socompa, Argentinean Andes. *PLoS One*, **8**(1):1-15.
- Faure K. & Cole D. 1999. Geochemical evidence for lacustrine microbial blooms in the vast Permian Main Karoo, Paraná, Falkland Islands and Huab basins of southwestern Gondwana. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **152**(3-4):189-213.
- Felden J., Lichtschlag A., Wenzhöfer F., de Beer D., Feseker T., Pop Ristova P., de Lange G., Boetius A. 2013. Limitations of microbial hydrocarbon degradation at the Amon mud volcano (Nile deep-sea fan). *Biogeosciences*, **10**:3269-3283.
- Fenchel T. 1998. Formation of laminated cyanobacterial mats in the absence of benthic fauna. *Aquatic Microbial Ecology*, **14**:235-240.
- Gehling J.G. 1999. Microbial mats in terminal Proterozoic siliciclastics: Ediacaran death masks. *Palaios*, **14**(1):40-57.
- Gerdes G. 2007. Structures left by modern microbial mats in their host sediments. In: Schieber J., Bose P.K., Eriksson P.G., Banerjee S., Sarkr S., Altermann W., Catuneau O. (eds.) *Atlas of microbial mat features preserved within the siliciclastic rock record*. Elsevier, p. 5-38.
- Grotzinger J.P. 1989. Facies and evolution of Precambrian carbonate depositional systems: emergence of the modern platform archetype. In: Crevello P.D., Wilson J.L., Sarg J.F., Read J.F. (eds.) *Controls on Carbonate Platform and Basin Development*. Society Of Economic Paleontologists and Mineralogists, Special Publication, 44, Tulsa, p. 79-106.
- Grotzinger J.P. & Knoll A.H. 1999. Stromatolites in Precambrian carbonates: Evolutionary mileposts or environmental dipsticks? *Annual Review of Earth and Planetary Sciences*, **27**:313-358.
- Haas J., Demény A., Hips K., Vennemann T.W. 2006. Carbon isotope excursions and microfacies changes in marine Permian–Triassic boundary sections in Hungary. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **237**(2-4):160-181.
- Hachiro J. 2000. Occurrences of evaporites in the Irati Subgroup (late Permian, Paraná Basin). *Anais da Academia Brasileira de Ciências*, **72**(4):600.

- Hoffman P. 1976. Stromatolite morphogenesis in Shark Bay, Western Australia. In: Walter M.R. (ed.) *Stromatolites*. Elsevier Scientific Publishing Company, p. 261-272.
- Lash G.G. 2015. Authigenic barite nodules and carbonate concretions in the Upper Devonian shale succession of western New York – A record of variable methane flux during burial. *Marine and Petroleum Geology*, **59**:305-319.
- Mateus A., Riccomini C., Ferreira E.J.E.C.B., Tassinari C.C.G. 2014. Permian-Triassic maturation and multistage migration of hydrocarbons in the Assistência Formation (Irati Subgroup), Paraná Basin, Brazil: Implications for the exploration model. *Brazilian Journal of Geology*, **44**(3):355-360.
- Matos S.A., Pretto F.A., Simões M.G. 2013. Tafonomia dos Pygocephalomorpha (Crustacea, Peracarida, Malacostraca), Permiano, Bacia do Paraná, Brasil, e seu significado paleoambiental. *Revista Brasileira de Paleontologia*, **16**(1):97-114.
- Mazzini A., Svensen H., Planke S., Guliyev I., Akhmanov G.G., Fallik T., Banks D. 2009. When mud volcanoes sleep: Insight from seep geochemistry at the Dashgil mud volcano, Azerbaijan. *Marine and Petroleum Geology*, **26**(9):1704-1715.
- Mellors R., Kilb D., Aliyev A., Gasanov A., Yetirmishli G. 2007. Correlations between earthquakes and large mud volcano eruptions. *Journal of Geophysical Research*, **112**:B04304.
- Milani E.J. & Zalán P.V. 1999. An outline of the geology and petroleum system of the Paleozoic interior basins of South America. *Episodes*, **22**(3):199-205.
- Meyer M., Xiao S., Gill B.C., Schiffbauer J.D., Chen Z., Zhou C., Yuan X. 2014. Interactions between Ediacaran animals and microbial mats: Insights from Lamonte trevallisi, a new trace fossil from the Dengying Formation of South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **396**:62-74.
- Milkov A.V. 2005. Global distribution of mud volcanoes and their significance in petroleum exploration as a source of Methane in the atmosphere and hydrosphere and as a geohazard. In: Martinelli G., Panahi B. (eds.) *Mud Volcano Geodynamics and Seismicity*. NATO Science Series, Springer, p. 29-34.
- Moore J.C., Orange D., Kulm L.D. 1990. Interrelationship of fluid venting and structural evolution: Alvin observations from the frontal accretionary prism, Oregon. *Journal of Geophysical Research*, **95**(B6):8795-8808.
- Oelofsen B.W. & Araújo D.C. 1987. Mesosaurus tenuidens and Stereosternum tumidum from the Permian Gondwana of both southern Africa and South America. *South African Journal of Sciences*, **83**:370-372.
- Orr P.J., Benton M.J., Briggs D.E.G. 2003. Post-Cambrian closure of the deep-water slope-basin taphonomic window. *Geology*, **31**(9):769-772.
- O'Toole G., Kaplan H.B., Kolter R. 2000. Biofilm formation as microbial development. *Annual Review of Microbiology*, **54**:49-79.
- Peckmann J., Gischler E., Oschmann W., Reitner J. 2001. An Early Carboniferous seep community and hydrocarbon-derived carbonates from the Harz Mountains, Germany. *Geology*, **29**(3):271-274.
- Perinotto J.A.J., Etchebehere M.L.C., Simões L.S.A., Zanardo A. 2008. Diques clásticos na Formação Corumbataí (P) no nordeste da Bacia do Paraná, SP: análise sistemática e significações estratigráficas, sedimentológicas e tectônicas. *Geociências*, **27**(4):469-491.
- Penny A.M., Wood R., Curtis A., Bowyer F., Tostevin R., Hoffman K.H. 2014. Early animals. Ediacaran metazoan reefs from the Nama Group, Namibia. *Science*, **334**(6191):1504-1506.
- Piñeiro G., Morosi E., Ramos A. 2012a. Pygocephalomorph crustaceans from the Early Permian of Uruguay: Constraints on taxonomy. *Revista Brasileira de Paleontologia*, **15**(1):33-48.
- Piñeiro G., Ramos A., Goso C., Scarabino F., Laurin M. 2012b. Unusual environmental conditions preserve a Permian mesosaur-bearing Konservat-Lagerstätten from Uruguay. *Acta Paleontologica Polonica*, **57**(2):299-318.
- Porada H. & Bouougri E.H. 2007. Wrinkle structures – a critical review. *Earth-Science Reviews*, **81**(3-4):199-215.
- Pratt B.R. 1982. Stromatolite decline – A reconsideration. *Geology*, **10**(10):512-515.
- Ricardi-Branco F., Caires E.T., Silva A.M. 2008. Levantamento de ocorrências fósseis nas pedreiras de calcário do Subgrupo Irati no estado de São Paulo, Brasil. *Revista Brasileira de Geociências*, **38**(1):80-88.
- Riccomini C., Chamani M.A.C., Agena S.S., Fambrini G.L., Fairchild T.R., Coimbra A.M. 1992. Earthquake-induced liquefaction features in the Corumbataí Formation (Permian, Paraná Basin, Brazil) and the dynamics of Gondwana. *Anais da Academia Brasileira de Ciências*, **64**:210.
- Riding R. 2006. Microbial carbonate abundance compared with fluctuations in metazoan diversity over geological time. *Sedimentary Geology*, **185**(3-4):229-238.
- Rocha-Campos A.C., Basei M.A., Nutman A.P., Kleiman L.E., Varela R., Llambias E., Canile F.M., Rosa O.C.R. 2011. 30 million years of Permian volcanism recorded in the Choiyoi igneous province (W Argentina) and their source for younger ash fall deposits in the Paraná Basin: SHRIMP U-Pb zircon geochronology evidence. *Gondwana Research*, **19**(2):509-523.
- Rostirolla S.P., Mancini F., Rigoti A., Kraft R.P. 2003. Structural styles of the intracratonic reactivation of the Perimbó fault zone, Paraná basin, Brazil. *Journal of South American Earth Sciences*, **16**(4):287-300.
- Seilacher A. 1999. Biomat-related lifestyles in the Precambrian. *Palaios*, **14**(1):86-93.
- Seilacher A. & Pflüger F. 1994. Bibliotheks- und Informationssystem der Carl von Ossietzky. In: Krumbein W.E., Peterson D.M., Stal L.J. (eds.) *Bio stabilization of Sediments*. Oldenburg, Universität Oldenburg, p. 97-105.
- Shepard R.N. & Sumner D.Y. 2010. Undirected motility of filamentous cyanobacterial produces reticulate mats. *Geobiology*, **8**:179-190.
- Soares M.B. 2003. A taphonomic model for the Mesosauridae assemblage of the Irati Formation (Paraná Basin, Brazil). *Geologica Acta*, **1**(4):394-361.
- Stoodley P., Dodds I., Boyle J.D., Lappin-Scott H.M. 1998. Influence of hydrodynamics and nutrients on biofilm structure. *Journal of Applied Microbiology*, **85**(1):19-28.
- Suguio K. & Sousa S.H.M.E. 1985. Restos de mesossaurídeos na Formação Corumbataí, Permiano da Bacia do Paraná, no Estado de São Paulo. *Anais da Academia Brasileira de Ciências*, **57**(3):339-347.
- Taj R.J., Aref M.A.M., Schreiber B.C. 2014. The influence of microbial mats on the formation of sand volcanoes and mounds in the Red Sea coastal plain, south Jeddah, Saudi Arabia. *Sedimentary Geology*, **311**:60-74.
- Takashima C. & Kano A. 2008. Microbial processes forming daily lamination in a stromatolitic travertine. *Sedimentary Geology*, **208**(3-4):114-119.
- Teichert B.M.A., Johnson J.E., Solomon E.A., Giosan L., Rose K., Kocherla M., Connolly E.C., Torres M.E. 2014. Composition and origin of authigenic carbonates in the Krishna-Godavari and Mahanadi Basins, eastern continental margin of India. *Marine and Petroleum Geology*, **58**(A):438-460.

- Thomas D.J., Sullivan S.L., Price A.L., Zimmerman S.M. 2005. Common freshwater cyanobacteria grow in 100% CO₂. *Astrobiology*, **5**(1):66-74.
- Walter M.R., Bauld J., Brock T.D. 1972. Siliceous algal and bacterial stromatolites in hot spring and geyser effluents of Yellowstone National Park. *Science*, **178**(4059):402-405.
- Warren L.V., Simões M.G., Fairchild T.R., Riccomini C., Gaucher C., Anelli L.E., Freitas B.T., Boggiani P.C., Quaglio F. 2013. Origin and impact of the oldest metazoan bioclastic sediments. *Geology*, **41**(4):507-510.
- Whiticar M.J. 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology*, **161**:291-314.
- Wirsig C., Kowsmann R.O., Miller D.J., Godoy J.M.O., Mangini A. 2012. U/Th-dating and post-depositional alteration of a cold seep carbonate chimney from the Campos Basin offshore Brazil. *Marine Geology*, **329-331**:24-33.
- Yamamoto J.K., Fairchild T.R., Boggiani P.C., Montanheiro T.J., Araújo C.C., Kiyohara P.K., Matos S.L., Soares P.C. 2005. A record of Permian subaqueous vent activity in southeastern Brazil. *Nature*, **438**(7065):205-207.
- Yuan X., Chen Z., Xiao S., Zhou C., Hua H. 2011. An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature*, **470**(7334):390-393.

Available at www.sbgeo.org.br
