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First Tithonian record of perforated *Pediastrum* Meyen *s.l.* species within early-diagenetic carbonate concretions from the Vaca Muerta Formation, Neuquén Basin, Argentina. Implications for the palynological analysis of fine-grained rocks

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FIRST TITHONIAN RECORD OF PERFORATED *PEDIASTRUM* MEYEN *S.L.* SPECIES WITHIN EARLY–DIAGENETIC CARBONATE CONCRETIONS FROM THE VACA MUERTA FORMATION, NEUQUÉN BASIN, ARGENTINA. IMPLICATIONS FOR THE PALYNOLOGICAL ANALYSIS OF FINE-GRAINED ROCKS

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Abstract. The perforated *Pediastrum* Meyen *s.l.* species are recorded for the first time in the basal levels of the Tithonian Vaca Muerta Formation, extending its first stratigraphical record to ages as old as Late Jurassic times. Based on the ecological requirements of *Pediastrum simplex* var. *clathratum* and *P. simplex* var. *biwaense*, the previously warm paleoclimatic conditions suggested by the Late Jurassic of Neuquén Basin, are reinforced. The co-occurrence of the different mechanisms that interacted during the transport, accumulation, and early diagenesis of these sediments and their organic content would have allowed for the excellent preservation of the *Pediastrum* Meyen *s.l.* species.

Key words. *Pediastrum* Meyen *s.l.* Vaca Muerta Formation. Tithonian. Neuquén Basin. Argentina.

Resumen. PRIMER REGISTRO TITONIANO DE ESPECIES PERFORADAS DE *PEDIASTRUM* MEYEN *S.L.* EN CONCRECIONES CARBONÁTICAS DE LA FORMACIÓN VACA MUERTA, CUENCA NEUQUINA, ARGENTINA. IMPLICANCIAS EN EL ANÁLISIS PALINOLÓGICO DE ROCAS DE GRANO FINO. En esta contribución se da a conocer el hallazgo de especies de *Pediastrum* Meyen *s.l.* con cenobios perforados provenientes de los niveles basales de la Formación Vaca Muerta, extendiendo su primer registro estratigráfico a edades tan antiguas como el Titoniano. Los requerimientos ecológicos de *Pediastrum simplex* var. *clathratum* y *P. simplex* var. *biwaense*, sugieren el desarrollo de cuerpos de agua dulce bajo condiciones cálidas, lo cual refuerza las interpretaciones paleoclimáticas previamente propuestas para el Jurásico Tardío de la Cuenca Neuquina. La buena preservación de este material es interpretada como resultado de la co-ocurrencia de diferentes mecanismos que interactuaron durante el transporte, la acumulación y la diagénesis temprana de estos sedimentos y las especies de *Pediastrum* Meyen *s.l.* reconocidas.

Palabras clave. *Pediastrum* Meyen *s.l.* Formación Vaca Muerta. Titoniano. Cuenca Neuquina. Argentina.

The Chlorophyceae green algae, a class of the Division Chlorophyta, include both unicellular and colonial species. Its members show a wide variation in morphology, habit, and habitat (Batten, 1996). *Pediastrum* Meyen *s.l.* is a typical colonial form of green algae (Hydrodictyaceae) mainly found in freshwater environments (*e.g.*, ponds, swamps, lakes), rarely reported from brackish waters (Kowalska & Wołowski, 2010; Xiang *et al.*, 2021). Some species are endemic, others are cosmopolitan, and some of them are restricted to cold, temperate, or warm regions (Zamaloa & Tell, 2005). Studies of modern environments show that the global distribution of *Pediastrum* Meyen *s.l.* mainly depends on the temperature, whereas its regional distribution seems to be more likely controlled by the water chemistry, *e.g.*, some species such as *P. angulosum* (Ehrenberg) ex Meneghini are favored by warm and alkaline waters (Tell, 2004). The phylogeny of the Hydrodictyaceae family traditionally was based on morphology. However, a recent phylogenetic analysis of rDNA data indicated that *Pediastrum* Meyen *s.l.* is not a monophyletic taxon (Buchheim *et al.*, 2005). Following these molecular phylogenetic studies, several authors proposed a subdivision of this genus into six genera: *Stauridinium* (Printz) Hegewald, *Monactinus* (Turpin) Hegewald, *Pediastrum* Meyen, *Parapediastrum* Hegewald, *Pseudopediastrum* Hegewald, and *Lacunastrum* McManus (Buchheim *et al.*, 2005; McManus & Lewis, 2005, 2011; McManus *et al.*, 2011). However, the present study follows the scheme proposed by Komárek & Jankovská (2001), who considered *Pediastrum* Meyen *s.l.* This criterion is based on that only some selective taxa have been subjected to the phylogenetic studies, so we considered that it was necessary to improve this new system to avoid mistakenly applying these taxonomy categories. This viewpoint was followed by other authors such as Lenarczyk (2015), Nader & Kddo (2018), and Xian *et al.* (2021).

The present contribution is part of a major study focused on carbonate ($CaCO_3$) concretions located within the lowermost (~100 m) section of the Upper Jurassic Vaca Muerta Formation (Weaver, 1931) of several central localities of the Neuquén Basin (Otharán *et al.*, 2022). This multidisciplinary approach involved stratigraphy, sedimentology, organic geochemistry, and palynofacies analyses. The aims of this work are: i) to present the register of the freshwater micro-algae *Pediastrum* Meyen *s.l.* in the Upper Jurassic Vaca Muerta Formation; ii) to highlight its relevance for the biostratigraphy and paleoclimatology of southern South America; iii) to understand the mechanisms that control the excellent preservation of these freshwater algae, even after a long transport history towards distal marine depositional environments; and iv) to reevaluate the palynological proxies for the paleoenvironmental interpretation of fine-grained sedimentary rock units.

GEOLOGICAL SETTING

The Neuquén Basin is a triangular-shaped basin located in west-central Argentina (32°–40° S), that covers more than 160.000 km^2. It is a back-arc basin developed during the Mesozoic on the western margin of Gondwana (Mosquera *et al.*, 2011). Its sedimentary infill comprises at least 7.000 m of siliciclastic, carbonate, and evaporite deposits accumulated in a wide range of continental and marine depositional environments mainly controlled by tectonic activity and repeated sea-level oscillations that conditioned the basin connection with the palaeo-Pacific Ocean (Legarreta & Uliana, 1991; Mutti *et al.*, 1994). The tecto-sedimentary history of the basin was controlled by three stages: syn-rift, back-arc, and foreland (Howell *et al.*, 2005; Casadío & Montagna, 2015). The former comprises volcaniclastic and epiclastic continental sedimentation in several isolated depocenters accumulated during the Late Triassic to Early Jurassic (Carbone *et al.*, 2011). The back-arc stage, characterized by multiple transgressions and regressions, pointed out the establishment of Andean volcanism and extensive subsidence from the Early Jurassic to the Early Cretaceous (Howell *et al.*, 2005; Casadío & Montagna, 2015). The last stage, dominated by continental sedimentation in a foreland basin, started in the Late Cretaceous after the final disconnection of the basin with the Pacific Ocean (Tunik *et al.*, 2010).

The Vaca Muerta Formation corresponds to the distal facies of a shallowing-upward marine sedimentary cycle known as the VM-Q system (Veiga & Spalletti, 2007). The VM-Q system is a marine depositional cycle composed of subaqueous muddy clinoforms accumulated between the early Tithonian and the early Valanginian in the southwest of Gondwana. During the accumulation of the VM-Q system, the Neuquén Basin was an epicontinental sea connected to the west with the Pacific Ocean. To the west, the basin boundary was defined by a contemporary volcanic island arc, whereas the southern and eastern/northeastern margin was established by the North Patagonian Massif and the Sierra Pintada System, respectively. According to the most recent chronostratigraphic framework of the VM-Q system, seven major seismic horizons with regional distribution across a wide area of the Neuquén Basin were recognized (Desjardins *et al.*, 2016). These horizons separated six seismic units named U1–U6 *sensu* Desjardins *et al.* (2016). The maximum time range for the accumulation of the Vaca Muerta Formation is from early Tithonian (*Virgatosphinctes mendozanus* Zone) to early Valanginian (earliest part of the *Lissonia riveroi* Zone) based on ammonite data (in Olivera *et al.*, 2018). Tithonian deposits, comprised between the *Virgatosphinctes mendozanus* Ammonite Zone and the lower part of the *Windhauseniceras internispinosum* Ammonite Zone, correspond to Unit 1 (see also Minisini *et al.*, 2020).

The lowermost interval of the VM-Q system is a

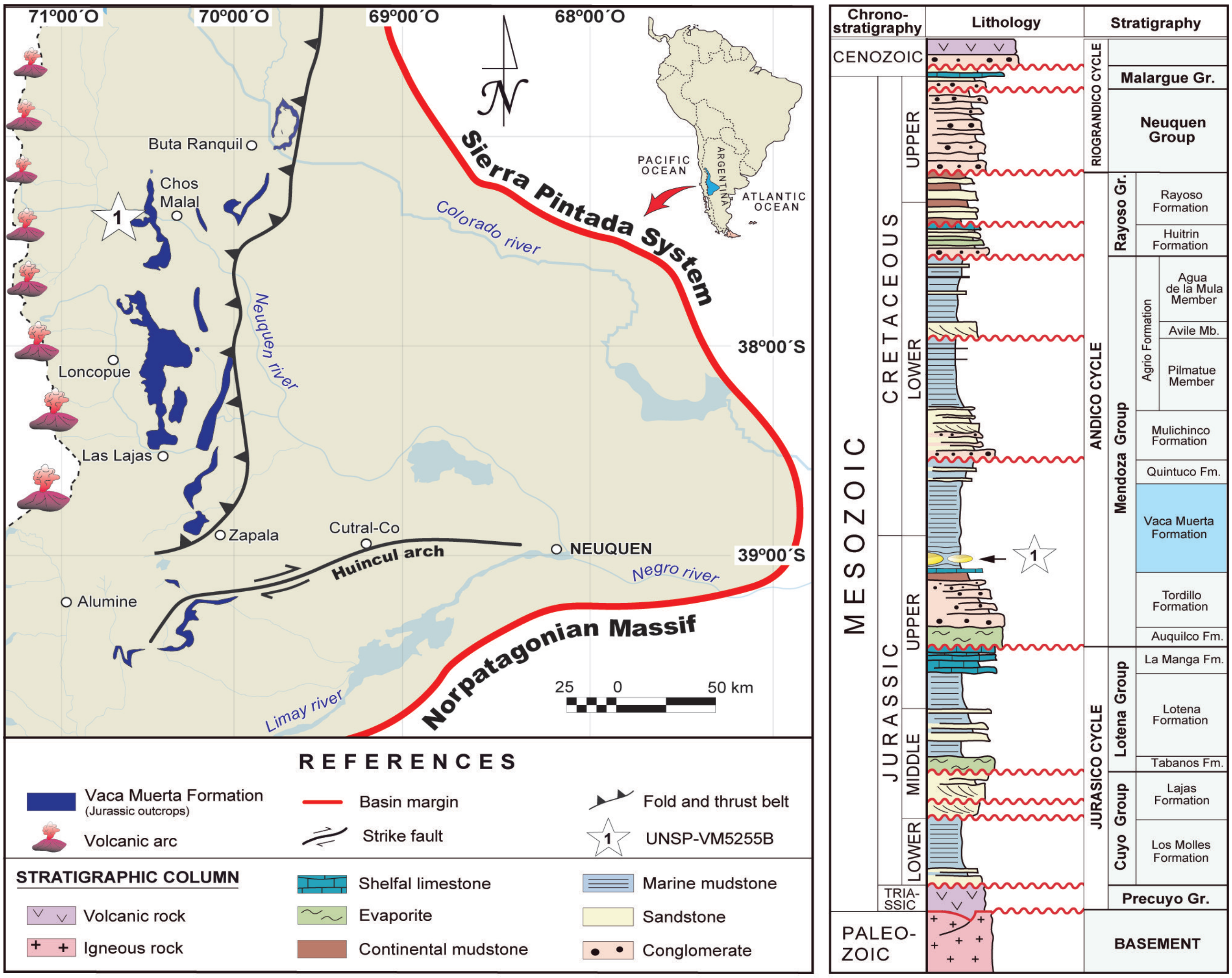

Figure 1. Geologic map and generalized stratigraphic column of the Neuquén Basin with indication of the analyzed palynological sample (modified after Otharán *et al.*, 2022).

transgressive deposit with a basal condensed section that accumulated during a period of high productivity of organic carbon and a high sea level that led to reduced siliciclastic input. The basal condensed section, overlaid by prograding carbonate–siliciclastic clinoforms, was developed due to of the gradual increase in sediment supply and the limited accommodation space in the shallow-marine shelf.

MATERIAL AND METHODS

Studied interval

The sample studied herein (UNSP-VM5255B) was collected from the basal deposits of the Vaca Muerta Formation at the central basin depositional locality (Fig. 1). Particularly, the lowermost ~50 m of the Vaca Muerta Formation is composed of organic carbon-rich mudstones and commonly exhibits multiple horizons bearing laterally persistent early-diagenetic carbonate concretions. Field relationships point out that the sample analyzed in this study belongs to Unit 1 of the VM-Q system.

Sample preparation

The physical and chemical extraction of palynological organic matter from the inorganic matrix was carried out using standard non-oxidative palynological techniques (Volkheimer & Melendi, 1976; Tyson, 1995). The slide was examined using a TWL microscope (Nikon eclipse50i). Palynomorphs were evaluated under RFL microscopy (Olympus BH2) since the blue ultraviolet radiation has proven to be a valuable tool in ordinary taxonomic palynological determinations (Tyson, 1995). The palynological slide is housed in the Instituto Geológico del Sur-Universidad Nacional del Sur, Bahía Blanca, Buenos Aires Province, Argentina. It is identified by catalog number preceded by the abbreviation UNSP-VM. Specimen locations are referred to England Finder coordinates.

Institutional acronyms. INGEOSUR, Instituto Geológico del Sur, Bahía Blanca, Argentina; **UNS,** Universidad Nacional del Sur, Bahía Blanca, Argentina; **UNSP-VM,** Universidad Nacional del Sur, Palynology-Vaca Muerta Formation.

Other abbreviations. EPS, extracellular polymeric substances; **POM,** palynological organic matter; **RFL,** reflected fluorescence light; **TWL,** transmitted white light; **VM-Q,** Vaca Muerta-Quintuco.

RESULTS

SYSTEMATIC PALEONTOLOGY

Class CHLOROPHYCEAE Kützing, 1843
Order SPHAEROPLEALES Deason *et al.*, 1991
Family HYDRODICTYACEAE Dumortier, 1829 *emend.* Deason *et al.*, 1991

Genus ***Pediastrum*** Meyen, 1829

Type species. *Pediastrum duplex* Meyen, 1829.

Pediastrum simplex cf.
P. simplex var. ***clathratum*** (Schröter) Chodat, 1902
Figures 2.1–2.6, 3.1

Studied material. UNSP-VM5255B: W26/2.

Description. Coenobium originally circular in outline, secondarily distorted by compression, with holes of irregular shape and dimensions (Figs. 2.1–2.6, 3.1). Cells arranged in concentric circles. At least 14 marginal cells with one conical lobe, terminating with a cylindrical *processus* (horn), with a pilate or blunt ending. In some marginal cells, this cylindrical *processus* is missing (Fig. 2.1). The lobe is situated in the middle of the outer margin of a marginal cell. Cell wall is finely granular. The boundaries of the marginal cells are not clearly visible, except in one part of the coenobium (Fig. 2.1). Under RFL microscopy, the joining of each cell with its neighboring cell shows a stronger and more brightened fluorescence in yellow color that the rest of the coenobium (Fig. 2.4–2.6).

Dimensions. Maximum diameter coenobium: 100 μm; marginal cell without *processus*: up to 10 μm; marginal cell with *processus*: up to 19 μm; distance between horns: 25–35 μm.

Comparison. This specimen is closely resembled to *P. simplex* var. *clathratum* in having the large holes in the coenobium that characterize this taxon. However, the preservation degree of this specimen does not allow to distinguish all its morphological features preferring to compare rather than identify it.

Geographic distribution and stratigraphic occurrence. *Pediastrum simplex* is recorded worldwide since the Late Triassic (Nader & Kddo, 2018), but the most abundant registers come from Cretaceous to Cenozoic deposits (*e.g.*, Songtham *et al.*, 2003; Sha, 2007; El-Noamani & Saleh, 2018). In southern South America, the oldest previous record of this taxon comes from the Late Miocene of the Calchaquí Valley, Salta Province (Starck & Anzótegui, 2001). *Pediastrum simplex* var. *clathratum* is a scarcely registered species in the fossil record. This taxon was identified in the Neogene deposits of China as *P. clathratum* (El-Noamani & Saleh, 2018). In Argentina, it was only recognized in modern lakes of the Mesopotamia region (Tell, 2004). This record, in Tithonian carbonate concretions, constitutes the oldest mention of this taxon.

Pediastrum simplex cf.
P. simplex var. ***biwaense*** Fukushima 1956
Figures 2.7–2.12, 3.2

Studied material. UNSP-VM5255B: B30/1.

Description. Coenobium subcircular in outline (Figs. 2.7–2.12, 3.2), with many large perforations concentrically arranged (under RFL microscopy, Fig. 2.10–2.12). At least 23 marginal cells can be recognized, with one lobe and a blunt terminal *processus* (Figs. 2.11, 3.2). The *processi* of two adjacent cells are arcuate one to another (Figs. 2.7–2.8, 2.10, 3.2). Cell wall is granular. Under blue light fluorescence

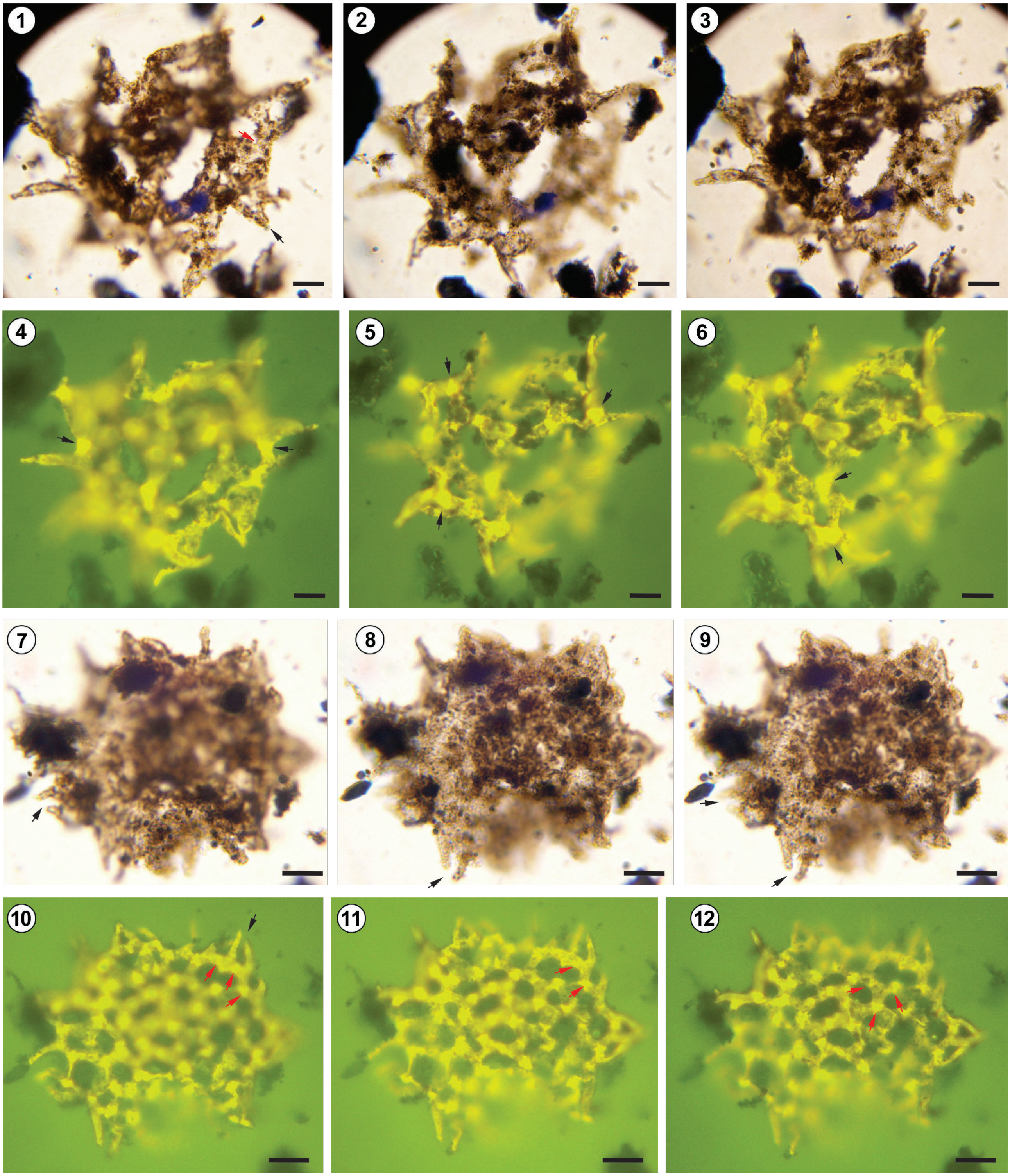

Figure 2. 1–6, ***Pediastrum simplex*** cf. ***P. simplex*** var. ***clathratum*** Schröter, **UNSP-VM5255B: W26/2**; **1,** black arrow points out a missing *processus* and red arrow indicates the V-shaped incision formed in the joining of two adjacent cells; **4–6,** black arrows show the stronger and brightened fluorescence of the joining between neighboring cells; **7–12,** ***Pediastrum simplex*** cf. ***P. simplex*** var. ***biwaense*** Fukushima **UNSP-VM5255B: B30/1**; **7–10,** black arrows indicate two adjacent arcuate *processi*; **10–12,** the stronger and brightened fluorescence of the joining between neighboring cells are indicated by red arrows. Photomicrographs 1–3 and 7–9 were taken with transmitted white light microscopy. Photomicrographs 4–6 and 10–12 are fluorescence light photomicrographs. Scale bars= 10 µm.

microscopy, the joining of each cell with its neighboring cells shows a stronger and more brightened fluorescence in yellow color than the rest of the coenobium (Fig. 2.10–2.12).

Dimensions. Maximum diameter coenobium: 75 µm; marginal cell with *processus*: up to 12 µm; wide cell wall: 2–3 µm; distance between horns (in same marginal cell): 2–3 µm; clathrations: up to 8 µm.

Comparison. The studied material closely resembles *P. simplex* var. *biwaense* in its high number of large holes, which are always larger than the cell´s size, and by its finely granulate wall (Komárek & Jankovská, 2001). Nonetheless, since the major part of the perforations in the coenobia were identified under the RFL microscope and only one specimen was recovered, we prefer compared to, rather than firmly identified this specimen with *Pediastrum simplex* var. *biwaense*.

Geographic distribution and stratigraphic occurrence. This species was described from recent lakes in Japan (Komárek & Jankovská, 2001). It was also mentioned in recent environments of eastern and north-eastern India (Jena & Adhikary, 2007). This taxon was scarcely registered in fossil deposits, and it was previously mentioned in the Upper Triassic strata of Iraq (Nader & Kddo, 2018). In Argentina, *P. simplex* var. *biwaense* was not previously identified.

ECOLOGICAL REQUIREMENTS

Pediastrum simplex is reported in freshwater eutrophic to mesotrophic environments with neutral to alkaline waters (Komárek & Jankovská, 2001; Tell, 2004). *Pediastrum simplex* var. c*lathratum* is mainly developed in temperate an even in warm waters but is absent in cold and circumpolar regions (*e.g.*, Komárek & Jankovská, 2001; Tell, 2004; Zamaloa & Tell, 2005; Xiang *et al.*, 2021). This taxon is particularly common in tropical lakes (Komárek & Jankovská, 2001). *Pediastrum simplex* var. *biwaense* was described from Yokohama, Japan. This region is characterized by a temperate climate with hot summers (Cfa climate type *sensu* the Köppen-Geiger criterion, in Peel *et al.*, 2007). *Pediastrum simplex* var. *biwaense* also occurs in temperate to tropical regions: Andulasia in Spain (Fanés Treviño, 2008), Andhra Pradesh in the southern coastal region of India (Naidu *et al.*, 2018), Nasser Lake in the northeast of Africa (El-Otify *et al.*, 2003), among others.

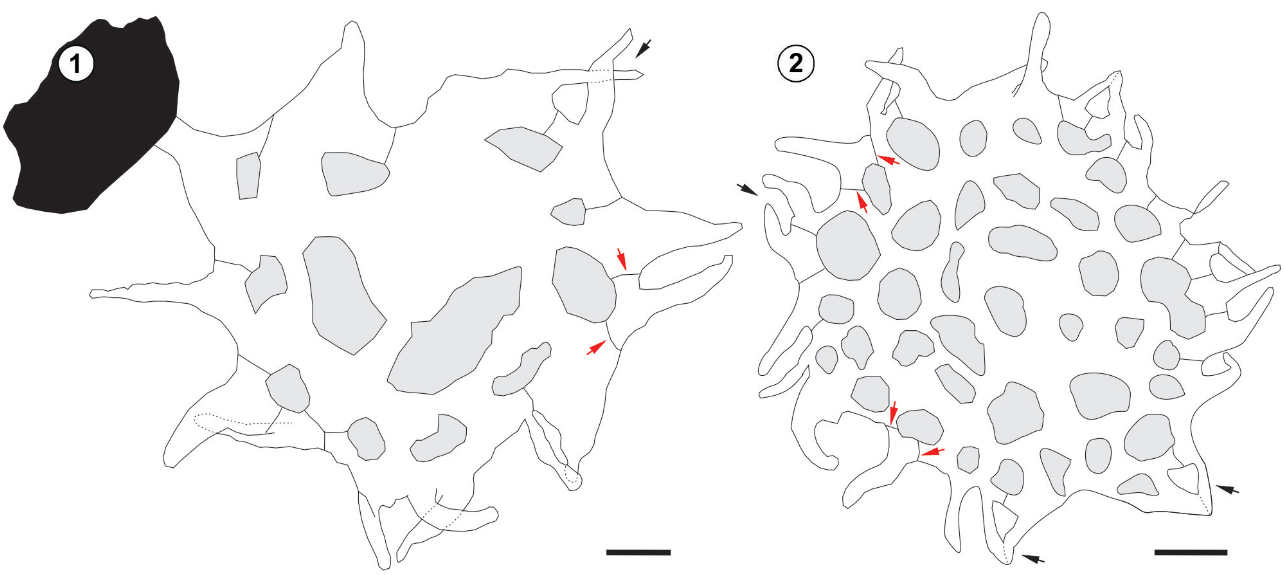

Figure 3. Sketches based on studied specimens of ***Pediastrum*** *s.l.* under reflected fluorescence light microscope; **1, *Pediastrum simplex*** cf. ***P. simplex*** var. ***clathratum*** Schröter, see large holes (gray) in the coenobium characteristic of this taxon. In upper left corner, a large phytoclast (black) partially covers a horn; **2, *Pediastrum simplex*** cf. ***P. simplex*** var. ***biwaense*** Fukushima. Red arrows show boundaries between neighboring cells, black arrows show *processi* of two adjacent cells arcuate one to another. Scale bars= 10µm.

DISCUSSION

In this contribution, specimens of *Pediastrum* Meyen *s.l.* were recovered from the interior of concretion samples from the Vaca Muerta Formation. The overall stacking pattern trend and sedimentary features described in the intervals bearing early-diagenetic concretions suggest that these deposits were accumulated in distal depositional settings (Otharán *et al.*, 2022). The excellent preservation state of *Pediastrum* Meyen *s.l.* in such a basinal position is very noteworthy and was interpreted by Otharán *et al.* (2022) as the result of a complex mechanism in which the EPS played a superlative role, involving the transport, accumulation, and preservation of organic carbon-rich mud in distal environments. The EPS is produced by microbes (*i.e.*, bacteria, archaea, microeukaryotes) as secretions of biofilms which secure attachment and enhance their local anoxic micro-environment and/or as excess metabolic waste products (Decho & Gutierrez, 2017). EPS broadly acts as a substance that binds, traps, and concentrates organic and inorganic particles as microplankton and clastic grains, making floccules. These aggregates would have been supplied by dilute buoyant river plumes that sporadically reached distal marine environments. This encapsulation into an anoxic microenvironment would have preserved the POM from degradation (*i.e.*, chemical oxidation in aerial and subaerial environments *sensu* Delcourt & Delcourt, 1980) and mechanical damage (*i.e.*, the breakage and/or wrinkling of palynomorphs *sensu* Delcourt & Delcourt, 1980) during the transport. The recognition of *Pediastrum* Meyen *s.l.* coenobia in distal marine deposits from the Vaca Muerta Formation calls for a critical reappraisal of the palynological proxies traditionally used to interpret proximal/distal settings in fine-grained rock units. Based on the morphology and excellent preservation state of these freshwater algae, the environment of deposition could be misinterpreted. Thus, for a comprehensive understanding of organic carbon storage in fine-grained sedimentary successions it is essential to conduct multidisciplinary studies and to focus neither on the organic or the inorganic components of these rocks but to use the entire available information in the stratigraphic record. Considering this, an interesting question emerges: is the presence of these floccules the only condition that could explain the appearance of these taxa in Upper Jurassic sediments? Otharán *et al.* (2022) pointed out that the early diagenetic carbonate concretions provide a record of the uncompacted primary sedimentary fabrics and the organic particles of some fine-grained rocks. These concretions could have protected the palynomorphs, avoiding post-depositional mechanical damage, compaction, and possible reworking. The co-occurrence of these two factors, the development of floccules and the early diagenetic concretions could explain the presence and good preservation of *Pediastrum* Meyen *s.l.* specimens in these deposits. Therefore, further studies focused on concretion samples are necessary to confirm or reject this hypothesis.

During the Late Jurassic, a great part of southern South America was under extremely arid and warm conditions (Volkheimer *et al.*, 2008). This paleoclimate agrees with the desert biome proposed by Rees *et al.* (2000) for this paleolatitude during this time. The presence of the identified *Pediastrum* Meyen *s.l.* species, which are successful colonizers of warm freshwater bodies, reinforces this paleoclimatic interpretation.

It is important to highlight this register in Upper Jurassic deposits of freshwater algae assigned to *Pediastrum* Meyen *s.l.* genus (Figs. 2, 3). Coenobia of *Pediastrum* Meyen *s.l.* are commonly mentioned worldwide as part of the Cretaceous and Cenozoic palynological assemblages. The pre–Cretaceous registers of *Pediastrum* Meyen *s.l.* are very scarce, with the oldest mentions coming from Triassic strata of China and Iraq (*e.g.*, Ji *et al.*, 2010; Nader & Kddo, 2018). In Argentina, the only pre-Cretaceous record of this taxon comes from the Lower Jurassic Nestares Formation (Zavattieri *et al.*, 2008), registered as indeterminate forms of this genus. It is worth mentioning that the specimens registered in the present contribution show an excellent state of preservation, allowing its assignment to perforated coenobia of different varieties of *Pediastrum simplex* (Fig. 2.3–2.6, 2.10–2.12). Following Zamaloa & Tell (2005) perforated *Pediastrum* Meyen *s.l.* species were not recognized in southern South America until the Miocene. Therefore, this finding of Late Jurassic *Pediastrum* Meyen *s.l.* species with perforated coenobia constitutes the first stratigraphic record in southern South America.

CONCLUSION

This record of perforated coenobia of *Pediastrum* Meyen *s.l.* genus from the Upper Jurassic (Tithonian) deposits in southern South America constitutes a significant finding from a stratigraphic, palynological, and paleoclimatic standpoint.

The mention of *Pediastrum simplex* cf. *P. simplex* var. *clathratum* and *P. simplex* cf. *P. simplex* var. *biwaense* in the Upper Jurassic Vaca Muerta Formation represents the oldest stratigraphic record of *Pediastrum* Meyen *s.l.* with perforated coenobia in southern South America.

The ecological requirements of these *Pediastrum* Meyen *s.l.* specimens suggest that the Vaca Muerta Formation accumulated under warm paleoclimatic conditions, which agree with the previously paleoclimatic conditions proposed for the Neuquén Basin during Late Jurassic.

The excellent preservation of the delicate structure of these freshwater algae probably responds to two main factors: 1) the mechanism of clay-floccule formation that binds and traps the organic matter would preserve the *Pediastrum* Meyen *s.l.* coenobia of the mechanical damage and degradation during transport and; 2) the nucleation of the early diagenetic carbonate concretions, which would have "frozen" the original packing of these condensed intervals, would avoid the post-depositional mechanical damage and compaction of the palynomorphs.

The finding of this freshwater alga in distal marine deposits from the Vaca Muerta Formation highlights the importance of applying interdisciplinary studies for a comprehensive understanding of organic carbon-rich mudstone deposits. Based on the morphology and the excellent preservation state of *Pediastrum* Meyen *s.l.* coenobia, the basinal facies of the Vaca Muerta Formation could be misinterpreted as accumulated in proximal depositional settings. However, when the complete information available in the rock record is analyzed, these mudstones show a much more complex depositional history than previously assumed. This work demonstrates the importance of carrying out multidisciplinary studies to arrive at a more accurate interpretation of the depositional and burial history of the sediments and their organic content and the long-term preservation of the palynological matter in organic carbon-rich mudstones.

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