Trace fossils as tools to unravel oxygen conditions: A case study from Los Molles Formation (Toarcian-lower Callovian)

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ABSTRACT

The Toarcian - lower Callovian Los Molles Formation in the Chacay Melehue section (southern limb of Cordillera del Viento - Neuquén Basin) comprises offshore-shelf deposits and subordinately, channel-levee and lobe deposits produced by density currents. These deposits are characterized by two distinctive trace fossil suites: (1) Chondrites and Trichichnus in the offshore-shelf mud, and (2) Chondrites, Trichichnus, and Phycosiphon occurring in distal levee deposits. The generally low diversity and abundance of the trace fossils suggest severe environmental conditions. In particular, in the intervals containing Chondrites and Trichichnus, pyrite framboids are abundant and most likely indicate low oxygen availability within the sediment. The presence of Phycosiphon in the levee deposits implies short periods of improved oxygenation caused by the density currents originating in shallow water.

Keywords: oxygenation, Chondrites, Trichichnus, Phycosiphon, Cuyo Group.

RESUMEN

Trazas fósiles como herramienta para reconocer las variaciones de oxigenación: un caso de estudio en la Formación Los Molles (Toarciano - Calloviano inferior)

La Formación Los Molles en la sección de Chacay Melehue (Toarciano - Calloviano inferior), flanco sur de la Cordillera del Viento, Cuenca Neuquina, comprende depósitos de offshore-plataforma, y de forma subordinada, depósitos de canal-albardón y lóbulo generados por descargas de densidad. Estos depósitos están asociados a dos suites de trazas fósiles: (1) Chondrites y Trichichnus asociados a los depósitos de fango, y (2) Chondrites, Trichichnus y Phycosiphon asociados a la parte distal de los albardones generados por descargas de densidad. La baja diversidad y abundancia de trazas fósiles sugiere condiciones ambientales estresantes. En particular los intervalos que contienen Chondrites y Trichichnus poseen abundante pírita framboidal, lo que indica una baja disponibilidad de oxígeno en el sedimento. La presencia de Phycosiphon en los albardones implica cortos periodos de aumento de la oxigenación causados por el ingreso de corrientes de densidad originadas en aguas someras.

Palabras clave: Oxigenación, Chondrites, Trichichnus, Phycosiphon, Grupo Cuyo.
INTRODUCTION

Trace fossils represent autochthonous indicators of the palaeoenvironmental conditions, and thus, have been commonly used in sedimentary environment and facies analysis (Hertweck 1972, Bromley 1990, Wetzel et al. 2009). They offer key paleoecological information that helps to better characterize a depositional setting, particularly in deposits where body fossils are scarce or absent (e.g., Buatois and Mángano 2011). Many environmental parameters define the specific ecological niches utilized by organisms, while there are some limiting factors that condition the colonization and establishment of organisms (Pickerill and Brenchley 1991, Benton and Harper 2009). In marine settings, the most common limiting factors, among others, are oxygen, food content, salinity, light, substrate consistency, and temperature. Many of them are not documented in the rock record and, therefore, can only be indirectly inferred in the fossil record (Benton and Harper 2009). In particular, the oxygen level is considered as greatly affecting the activities of the benthic organisms and thus, their responses to fluctuating oxygen content may be recorded by their traces (Savrda 2007).

Los Molles Formation (Weaver 1931) in the Chacay Melehue section (Toarcian - lower Callovian, according to Gulisano and Gutiérrez Pleimling 1995) comprises a thick succession of ammonite-bearing black shales and coarse, mass-flow related sandstones that were commonly interpreted as deep-marine turbidites (Gulisano and Gutiérrez Pleimling 1995). More recently, Liambías and Leanza (2005) and Ponce et al. (2015) have recognized deposits representing offshore-shelf environments affected by density currents. There are numerous studies recognizing several intervals implying oxygen-deficient conditions both for this section (e.g., Damborenea and Manceñido 2005, Liambías and Leanza 2005) and for other localities (Manceñido et al. 2007, Al-Suwaidi et al. 2008, 2010, 2016, Ros-Franch et al. 2019) of Los Molles Formation. However, those studies focused principally on the body-fossil record and chemostratigraphic analyses. In this regard and although some studies mentioned the occurrence of some trace fossils for this locality (see Damborenea and Manceñido 1996, 2005), the ichnologic content of these deposits has not been explored in detail yet. Within this context, it is the purpose of this study (1) to describe the trace fossil content found in the Los Molles Formation in Chacay Melehue section, and (2) to outline the implications of the recognized ichnoassemblages as indicators of oxygen conditions.

GEOLOGICAL SETTING

The Neuquén Basin is located in western-central Argentina and it is bounded by Sierra Pintada Systems to the northeast, the North Patagonian Massif to the southeast, and by the Andean magmatic arc to the west (Fig. 1). The tectonic development of the basin comprises three major phases, namely (1) syn-rift, (2) post-rift, and (3) foreland basin stage (Howell et al. 2005). The syn-rift stage occurred during late Triassic–earliest Jurassic times (Legarreta and Gulisano 1989, Legarreta and Uliana 1991, Gulisano and Gutiérrez Pleimling 1995), and a series of fault-bounded half grabens and grabens with NE-SW orientation acted as depocenters and were filled with volcanic, volcanioclastic and marine materials assigned to the Pre-Cuyo Group (Gulisano and Gutiérrez Pleimling 1995, Liambías et al. 2007, Lanés et al. 2008, Riccardi 2008a, Carbone et al. 2011). During the Lower Jurassic to Lower Cretaceous post-rift phase, a subduction regime was initiated along the western margin of Gondwana in Early-Middle Jurassic times (Franzese et al. 2003, Howell et al. 2005). At the end of the Late Jurassic, the magmatic arc was almost fully developed. Back-arc subsidence gave way for the flooding of the basin from the pro-
to-Pacific Ocean through gaps in the arc (Spalletti et al. 2000, Howell et al. 2005) that allowed the deposition of thick –continental to marine successions in isolated or partially connected depocenters (Arregui et al. 2011). These deposits include the sediments of the Cuyo, Lotena, and Mendoza groups, which represent successive transgressive-regressive cycles. The foreland basin stage (Late Cretaceous to Cenozoic), including a reorganization of the Pacific plates and a decrease in the angle of slab subduction, resulted in a compressional tectonic regime (Vergani et al. 1995) that caused inversion of previous extensional structures (Legarreta and Uliana 1991, Howell et al. 2005). During this stage, the continental sediments of the Neuquén Group and the marine sediments of the Malargüe Group were accumulated, which represent the first marine transgression from the Atlantic Ocean (Howell et al. 2005).

The study area (37°16'57.17"S; 70°34'28.03"W) is located 27 km northwest of Chos Malal city, which is situated in the west-central part of the Neuquén Basin. The Cordillera del Viento domain is characterized by an uplifted block having a steep southern slope while an active volcanic center was nearby (Gulisano and Gutiérrez Pleimling 1995, Llambias et al. 2007). In this area, the Cuyo Group is represented by the La Primavera, Los Molles and Tábanos formations that together constitute a transgressive-regressive cycle (Gulisano and Gutiérrez Pleimling 1995, Rovere et al. 2004, Leanza et al. 2005, Riccardi 2008a,b, Leanza 2009, Arregui et al. 2011, Sánchez et al. 2014).

The biostratigraphy of the Jurassic to Early Cretaceous deposits of the Neuquén Basin has been extensively studied (e.g., Westermann and Riccardi 1972, 1979, Riccardi et al. 1988, 2011, Damborenea 1990, Aguirre-Urreta et al. 2005, Riccardi 2008a,b). Particularly, the Pliensbachian – Tithonian interval is characterized by an abundant and diverse paleontological content. This fauna includes mostly ammonoids, brachiopods, and bivalves, and additional groups involve gastropods, cnidarians, sponges, annelids, and echinoderms.
(Riccardi et al. 2011). The biostratigraphy of Los Molles Formation has been studied in several localities (e.g., Arroyo Lapa, Arroyo Serrucho, and Chacay Melehue). In particular, the biostratigraphy of the Chacay Melehue section is based on detailed studies on bivalves and ammonoids (Riccardi et al. 1988, 2011, Gulisano and Gutierrez Pleimling 1995, Damborenea 1990, Riccardi 2008a,b).

The Los Molles Formation consists of black shales having conglomerate levels, micritic limestones and calcareous nodules intercalated (Leanza et al. 2005), which have been interpreted to represent offshore deposits associated with turbidites, large-scale slumps and subaquatic lahars (Gulisano and Gutiérrez Pleimling 1995, Rovere et al. 2004, Llambías and Leanza 2005, Paim et al. 2008, Leanza 2009, Arregui et al. 2011, Ponce et al. 2015).

SEDIMENTOLOGY

The Los Molles Formation at the Chacay Melehue section comprises an 837 m thick succession of clastic and volcanoclastic rocks (Groebber et al. 1953, Westermann and Riccardi 1972, 1979, Damborenea 1990, Gulisano and Gutiérrez Pleimling 1995, Ponce et al. 2015; Figs. 2 and 3). The section consists of intervals with tabular beds (20–30 cm thick), mainly composed of massive and laminated dark mudrocks centimeter-thick, alternating massive and laminated dark mudrocks and sandstones that exhibit wave and lenticular lamination. Fine particulate organic matter, frambooidal pyrite, ammonites, bivalves, calcareous concretions, and some tuff levels are abundant (Figs. 2, 3 and 4a-b).

In the lower part of the section (0 - 288 m), the mudrock levels are cut by lenticular beds of medium to coarse sandstones that are massive, parallel laminated, deformed, trough-cross-stratified, or with climbing ripples, while clay chips and allochthonous clasts occur locally (Figs. 2, 3 and 4c). These lenticular beds are laterally connected with wedge-shaped beds consisting of massive and laminated dark mudrocks and sandstones exhibiting climbing ripples, parallel lamination, and wave and lenticular lamination (Figs. 2, 3 and 4).

<table>
<thead>
<tr>
<th>Facies</th>
<th>Lithology</th>
<th>Sedimentary structures</th>
<th>Trace fossils</th>
<th>Geometry</th>
<th>Origin</th>
<th>Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mm</td>
<td>Claystones with and without OM</td>
<td>Massive</td>
<td>——</td>
<td>Tabular</td>
<td>Flocculation and settling from hypopycnal or hyperpycnal buoyant plume.</td>
<td>Offshore, Shelf</td>
</tr>
<tr>
<td>MI</td>
<td>Claystones with and without OM</td>
<td>Parallel Lamination</td>
<td>Chondrites, Trichichnus</td>
<td>Tabular</td>
<td>Setting from hypopycnal or hyperpycnal buoyant plume.</td>
<td>Density currents</td>
</tr>
<tr>
<td>Sms</td>
<td>Fine to medium tuffaceous sandstones</td>
<td>Massive and Slumps</td>
<td>——</td>
<td>Tabular and lenticular</td>
<td>Continuous aggradation from density current.</td>
<td>Channel, Lobe</td>
</tr>
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<td>Sta</td>
<td>Fine to medium tuffaceous sandstones</td>
<td>Tangential cross-stratification</td>
<td>——</td>
<td>Tabular and lenticular</td>
<td>Migration of 3D large scale bed forms associated to density currents.</td>
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<td>Str</td>
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<td>Trough cross-stratification</td>
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<td>Tabular and lenticular</td>
<td>Migration of 3D large scale bed forms associated to density currents.</td>
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<td>Sl</td>
<td>Fine to medium tuffaceous sandstones</td>
<td>Parallel Lamination</td>
<td>——</td>
<td>Tabular</td>
<td>Traction processes in low to high flow rate.</td>
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<td>Fine to medium tuffaceous sandstones</td>
<td>Climbing ripples</td>
<td>——</td>
<td>Tabular</td>
<td>Traction-settling processes originated by unidirectional density currents.</td>
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<tr>
<td>Swl</td>
<td>Fine tuffaceous sandstones</td>
<td>Wave and lenticular lamination</td>
<td>Chondrites, Trichichnus, Phycosiphon</td>
<td>Tabular and wedge</td>
<td>Traction processes produced by unidirectional diluted density current.</td>
<td></td>
</tr>
<tr>
<td>Cg</td>
<td>Conglomerates</td>
<td>Massive and trough and tangential cross-stratification</td>
<td>——</td>
<td>Lenticular</td>
<td>Continuous aggradation or migration of 3D bed forms associated to density currents.</td>
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Figure 3. Description, interpretation, and occurrences of the recognized sedimentary facies in the Chacay Melehue section.
Figure 4. Facies associations encountered in the Cordillera del Viento section: a) Offshore-shelf laminated mudrocks; b) Offshore-shelf laminated mudrocks with concretions and tuff levels; c) Channel-levee density-current deposits; d) Poorly sorted debris flow sediments; e) Offshore-shelf deposits at the base of the section and channels on top; f) Conglomeratic channels produced by density currents. See in figure 2 the stratigraphic position of each facies association.
ICHNOLOGY

Within the studied section, the trace fossils occur in restricted intervals and often in clusters. In general, the biogenic structures are of low to moderate abundance and low diversity, with small sizes ranging from 0.6 mm to 3 cm. Additionally, some thin levels that do not show any primary sedimentary structures, very likely document indistinct bioturbation of very shallow burrowers producing biodeformational structures, which have no distinct outlines or identifiable morphology and, therefore prevent their classification. The biogenic sedimentary structures were analyzed in the field and six samples with trace fossils were collected for a more detailed morphologic study. They are housed at the Museo de Ciencias Naturales, Paleontología de Invertebrados, Universidad Nacional del Comahue (MUCPi 2851 - 2856), Neuquén Province, Argentina. Some samples were studied microscopically using a binocular microscope (Nikon SMZ800), optical microscope (ZEISS - AXIO Imager. A2m), and a scanning electron microscope (SEM ZEISS - EVO 15). Three ichnogenera and four ichnospecies were recognized.

Ichnogenus Chondrites von Sternberg, 1833

Chondrites consists of a regularly branching system of tunnels with a single or a small number or master shafts that open to the surface, and ramifications forming dendritic networks downward (Osgood 1970, Fürsich 1974, Wetzel and Uchman 1997, Uchman et al. 2012). The burrows are unlined and may show an active fill, and the tunnel diameters remain constant (Knaust 2017). This ichnogenus is commonly found in fine-grained substrates. In the studied section, Chondrites occurs in mudrocks of the offshore-shelf domain, and also in distal levee deposits (Fig. 5). This ichnogenus has been recognized previously in these deposits by Damborenea and Manceñido (2005).

Chondrites intricatus (Brongniart, 1823)

It consists of a tree-like system of tunnels radiating downwards. Width of the tunnels is constant within each specimen and is usually 0.8 - 1.0 mm. The angle of branching is less than 45º. Most of the specimens show two orders of branching, although third-order branching has been observed occasionally. The color of the tunnel fill is always lighter than the host rock (Fig. 5a-e). The fill is massive and consists of quartz, plagioclase, and lithics fragments smaller than 10 μm and pyrite (Fig. 5e). Macroscopically, in cross-section, some specimens appear as clusters of small circular to elliptical dots. The specimens are preserved in full relief.

Chondrites patulus Fischer-Ooster, 1858

Chondrites system with simple branches that emerge almost perpendicularly from the main tunnel (Fu 1991, Uchman 1999). Tunnels are 0.5 - 0.7 mm wide. Only two orders of branchings were identified. Branches are straight and parallel to each other, and tunnel fill is lighter than the host rock (Fig. 5f). The specimens are preserved in full relief.

Ichnogenus Phycosiphon Fischer-Ooster, 1858

Phycosiphon comprises small spreite burrows with narrow U-shaped lobes. Each lobe includes a millimetric to centimetric scale spreite and a marginal string (Wetzel and Bromley 1994, Uchman 1995, Knaust 2017). The burrow system is mainly parallel to bedding, although some inclined and
vertical sections are also observed. This ichnogenus mostly occurs in silty or fine-grained sandy substrates (Knaust 2017). In the study section, Phycosiphon occurs in the fine tuffaceous sandstones within the levee deposits (Fig. 6).

**Phycosiphon incertum** Fischer-Ooster, 1858

Globally, this ichnospecies is the most common within this ichnogenus. The specimens comprise recurving U-lobes with spreite and occur mostly parallel to bedding (Fig. 6a-c). In
cross-section, they show two dark cores (0.4 - 0.8 mm wide) surrounded by light halos (0.3 - 0.09 mm wide), the latter connected by the light spreite (Fig. 6d). They are preserved in full relief.

**Ichnogenus *Trichichnus* Frey, 1970**

*Trichichnus* comprises straight to sinuous, sparsely branched or unbranched, hair-like cylindrical trace fossils that can be oriented at various angles to bedding (Uchman 1999). Burrows can be lined or unlined, and they are typically filled with sulphide minerals such as pyrite (Knaust 2017). *Trichichnus* has been reported from shallow to deep marine sediments, most commonly in fine-grained substrates (Frey 1970, Wetzel 1981, Werner and Wetzel 1982, Uchman 1998). In the studied section, *Trichichnus* occurs in mudrocks of the offshore-shelf and levee settings (Fig. 7).

**Trichichnus isp.**

Straight to sinuous, branched or unbranched cylindrical structure oriented mostly perpendicular to oblique to bedding (Fig. 7a-b). Burrows show a pyrite filling (Fig. 7c) and a halo slightly different in color from the host rock (Fig. 7). Diameter of the tunnels is constant, ranging between 0.1 and 0.3 mm (Fig. 7). Some specimens resemble *T. appendicus* Uchman 1999 (Fig. 7a-b) as they appear to have a main string with lateral and thinner branches. The specimens are preserved in full relief.

**DISCUSSION**

Some of the trace fossils recognized in the studied outcrop are stated to be related to settings experiencing oxygen deficiency. In particular, *Chondrites* is interpreted as produced by
Figure 7. *Trichichnus*: a) *Trichichnus* (Tr) in muddy offshore-shelf deposits; note downward ramification; b) *Trichichnus* (Tr) in offshore-shelf sandstones (MUCPi2854); c) Scanning electron microscope image of *Trichichnus* (Tr); note frambooidal pyrite within tunnel fill and the sediment reworked around the main burrow (MUCPi2855); d) *Trichichnus* (Tr) in muddy offshore-shelf deposits; note the frambooidal pyrite filling the core of the traces (binocular microscope photography) (MUCPi2856); e) Macroscopic image of *Trichichnus* (Tr) in a concretion formed in offshore-shelf deposits (MU-CPI2855); f) Cross section view of *Trichichnus* in fine tuffaceous sandstones of levee deposits.
infaunal deposit feeders or chemosymbiotic organisms and, hence, represents a good indicator for dysoxic environments when occurring alone or in poorly diverse ichnofossil assemblages (Bromley and Ekdale 1984, Savrda and Bottjer 1991, Knaust 2017). Some sipunculids, polychaetes, and bivalves produce geometrically similar structures today (Kotake 1991 and references therein). Similarly, Trichichnus has been interpreted as an indicator of fossil bioelectric microbial activity while anoxic-anoxic interface developed along the wall of the burrow formed within anoxic marine sediments (Kędzierski et al. 2015). This trace fossil is common in sediments with poorly oxygenated pore waters (McBride and Picard 1991, Uchman 1995, Kotlarczyk and Uchman 2012). It is classified as a chemichnion produced by organisms having a chemosymbiotic nutritional mode (Uchman 1999, Kędzierski et al. 2015). The third recognized ichnogenus is Phycosiphon that is interpreted as a deposit-feeding structure of vermiform, opportunistic organisms (Wetzel and Bromley 1994, Rodriguez-Tovar et al. 2014). Phycosiphon producers are related to settings with abundant nutritious material and sufficient oxygen in sediment (Wetzel and Uchman 2001, Wetzel 2010, Rodriguez-Tovar et al. 2014, Celis et al. 2018). It is common in lower shoreface to offshore (shelf) settings, slope deposits, and even deep-marine settings including marginal channel-levee and depositional-lobes facies (Wetzel and Balson 1992, Callow et al. 2013, Knaust 2017 and references therein).

Although the trace-fossil content of the studied succession shows low diversity and rather low abundance, it was possible to distinguish two different ichnocoassemblages: 1 - a Chondrites-Trichichnus suite that occurs in the offshore and shelf deposits, and 2 - a Chondrites-Trichichnus-Phycosiphon suite present in levee deposits in the lower part of the section (Fig. 8). The occurrence of organic-rich, slightly laminated mudrock is typical of rather low-oxygenated dysoaerobic to anaerobic conditions in the offshore-shelf settings, and at least temporarily subaerobic to aerobic conditions in the levee domain (but see also Wetzel and Uchman 1998). The presence of large pyrite frambooids (>10 µm) in the offshore and shelf deposits may be indicating their diagenetic origin in anoxic/dysoxic sediments (Wignall and Newton 1998, see also Rickard 2019). Therefore, these observations, in addition to the presence of Trichichnus and Chondrites, support the interpretation that some levels of Los Molles Formation in the Chacay Melehué section were deposited under dysoxic conditions (Uchman 1995, Wignall and Newton 1998, Knaust 2017).

In the studied deposits, most likely the first organisms colonizing the seafloor after improvement of oxygenation were the producers of the biodeformational structures (Uchman et al. 2008). The very shallow feeding strategy suggests that the seafloor was rich in benthic food, and/or that the sediment was very low in oxygen, precluding the development of very deep burrows (e.g., Edwards 1985, Uchman et al. 2008, Wetzel et al. 2011). The occurrence of biodeformational structures also implies a very soft to soupy substrate (see Lobza and Schieber 1999, Uchman et al. 2008). Colonization by the producers of Trichichnus and Chondrites occurred probably later, when the oxygen content at the sediment-water interface has increased and when the substrate has dewatered to be firm.

**Figure 8.** Schematic reconstructions of the two ichnocoassemblages recognized in this paper. a) The trace fossil suite recorded in the offshore-shelf deposits is characterized by *Trichichnus* and *Chondrites*; b) The trace fossil suite in the levee deposits consists of specimens assigned to *Phycosiphon*, *Trichichnus*, and *Chondrites*. Compare these diagrams with figure 7 in Kotlarczyk and Uchman (2012).
enough to favor the construction of these burrows. In this regard, some studies considered that *Trichichnus* producers seem to be more tolerant to dysaerobic conditions than *Chondrites* producers (McBride and Picard 1991, Uchman 1995, 1999) and, thus, the occurrence of *Chondrites* probably reflects slightly more oxygenated bottom water.

In order to undoubtedly state if *Trichichnus* was produced prior to *Chondrites* or if the construction of both trace fossils was simultaneous, clear crosscutting relationships are required. Unfortunately, the low abundance of the trace fossils prevented such observations. In contrast, in the levee deposits along channels formed by density-current activity, the occurrence of *Phycosiphon* reflects at least short periods of rather normal oxygen conditions, as the opportunistic *Phycosiphon*-producer did not maintain a permanent connection to the seafloor and therefore, needs oxygenated pore water (Wetzel and Balson 1992, Wetzel and Uchman 2001, Uchman et al. 2016). Density-currents originating in shallow, oxygenated while agitated water transferred sediment and (larvae of) organisms and supplied oxygenated water to the depositional area as for instance, suggested by Dzulynski and Slaczka (1958) and Föllmi and Grimm (1990).

Studies in other sections (e.g., Arroyo Lapa and Arroyo Serrucho) have also documented phases of lowered oxygenation in the Los Molles Formation, and they are suggested to be related to the Early Toarcian Oceanic Event (T-OAE, e.g., Al-Suwaidi et al. 2010, 2016). Widespread deposition of organic-rich shales commonly under anoxic/euxinic conditions and somewhat elevated seawater temperatures characterize this episode during that about 5% of the global diversity at the family level disappeared while there was a severe loss in shallow-marine mollusk taxa (see Bond and Wignall 2014 and references therein, Ros-Franch et al. 2019). Additionally, the T-OAE interval of the Los Molles Formation contains the bivalve *Posidonotis cancellata* that shows distinct adaptations for living in a low-oxygen habitat (Damborenea and Manceñido 2005, Ros-Franch et al. 2014, 2019) and, hence, it provides a better understanding of the dominant ecogetic conditions on the seafloor. The T-OAE is well documented in the Tethys-Atlantic realm (e.g., Jenkyns 2010), while for the ancient Pacific Ocean along the South America continental margin, the event is recorded from the south and north of the Neuquén Basin (Al-Suwaidi et al. 2016), and also from the Andean Basin in Chile (Fantasia et al. 2018). Therefore, it is a matter of further investigation to clarify if the intervals interpreted as having oxygen-deficient conditions found in the studied section of the Los Molles Formation are related to the T-OAE or not.

**CONCLUSIONS**

Ichnological analysis in the Los Molles Formation reveals the occurrence of ichnoassemblages exhibiting very low diversity and abundance. Particularly, two trace fossil assemblages have been recognized; (1) in offshore-shelf mudrock the *Chondrites-Trichichnus* suite is recurrently present, and (2) a *Chondrites-Trichichnus-Phycosiphon* suite occurs within levee deposits.

The dominance of *Chondrites*, *Trichichnus*, and framoidal pyrite, with sizes greater than 10 µm, in the muddy sediments within the studied section reflects the prevalence of oxygen-deficient dysaerobic to anaerobic conditions during deposition. The occurrence of *Phycosiphon* in the levees indicates a temporary, short-term increase in oxygenation, while density currents originating in shallow water transferred oxygen and sediment to the depositional area.

Further analyses are required in order to decipher if the studied oxygen-deficient facies coincide with the Toarcian Oceanic Anoxic Event or if they represent a local/regional phenomenon within the Neuquén Basin.

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