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PALEOENVIRONMENT AND AGE OF LOS MONOS FORMATION (DEVONIAN), TARIJA BASIN, ARGENTINA AND BOLIVIA

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ABSTRACT

The objective of this work is to discuss the paleoenvironment and age of the Los Monos Formation, in outcrop and subsurface, along a regional transect (west-east) in the southern sector of the Tarija basin. The lithofacies and ichnofacies of the Alarache, Angosto del Pescado and Balapuca outcrops and core-intervals of the Aguas Blancas xp-13, Ramos x-12, Tartagal x-1 and Tonono x-1 boreholes were analyzed. The definition of lithofacies and ichnofacies allowed us to interpret a shallow to outer shelf paleoenvironment (from the offshore-transition, offshore and shelf). Towards the top of the Tonono Formation, the equivalent of the Los Monos Formation in the Chaco-Salteño was defined as a brackish-waters marginal-marine paleoenvironment. The mineralogy of the mentioned sections plus the Vespucio x-1 borehole was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), thus the majority elements in clay minerals were also determined from EDAX. Authigenic and detrital clays from SEM-EDAX were recognized. Four clay mineral assemblages were defined (I+Ch; Ch+I; I+K; K+I), where I+K and K+I assemblages characterize the transgressive events within the basin. The palynofacies of the Balapuca, Alarache and Angosto del Pescado outcrops and samples from the Ramos xp-1002, Ramos xp-1011 and Ramos xp-1012 boreholes were defined, the dominance of terrestrial palynomorphs was identified with variable participation of marine palynomorphs, according to a shallow marine paleoenvironment with shoreline shifts. Two transgressive events were recognized during the late Eifelian-early Givetian and the late Givetian-early Frasnian, which are characterized by an increase in marine components and clay assemblages of I+K and K+I. The palynological associations point to a late Eifelian-early to middle Givetian age for the Los Monos Formation in the study area. The analysis of illite crystallinity and expansive layers in the mixed-layer IS indicated advanced diagenesis for the unit, from late mesodiagenesis (Tonono x-1 and Vespucio x-1) to telodiagenesis (Balapuca and Ramos), according to the final stage of oil generation window to gas generation window, respectively. Finally, based on the mineral composition with a predominance of quartz (>70% in average) and low content of clays (<20% in average), thermal maturity in oil and gas window, the important thickness in the subsurface (700-1000 meters) and significant lateral continuity (>100 km2), the unit has some of the attributes to be considered as a potential shale-type unconventional reservoir.

INTRODUCTION

The Los Monos Formation (Middle Devonian) is the main source rock of the Paleozoic area of the Tarija Basin, Argentina and Bolivia. This unit was named and described for the first time by Matter (1922) in the creek with the same name, it comprises black shales with very fine-grained sandstone intercalations. The formation constitutes a siliciclastic unit of great continuity (>100 km) and thickness (700-1000 meters) in the subsurface of the basin, in northern Argentina and southern Bolivia (Disalvo and Villar, 1999).

The previous stratigraphic and sedimentological studies of the Silurian-Devonian units propose basin models, sedimentary processes and genetic-stratigraphy models (Montemurro, 1994; Suárez and Díaz, 1996; Starck, 1996; Fernández Seveso *et al.*, 1998, 2000; Miranda *et al.*, 2003, among others). The most recent studies present lithofacies and biofacies developed in a shallow marine paleoenvironment (siliciclastic ramp), with some continental and littoral lithofacies; framed in genetic-stratigraphic sequences, as a consequence of eustatic variations within timelines that are defined by paleontology and palynology (Albariño *et al.*, 2002; Álvarez *et al.*, 2003).

The paleontological studies based on the distribution of benthic fauna and palynological taxa were carried out throughout the basin, but with little or no relation to facies analysis and sequential-stratigraphy (Suárez Soruco, 1988; López and López, 1975; Limachi *et al.*, 1996, among others). The studies of the last twenty years describe palynomorphs and invertebrates (trilobites and brachiopods) of the Eifelian-Frasnian period and their relationship with paleoenvironmental and paleoecological conditions within a stratigraphic-sequential scheme (Dalenz-Farjat, 2000; Grahn, 2002; Álvarez *et al.*, 2003; Melo, 2005; di Pasquo, 2005, 2007a, b; Noetinger, 2010; Noetinger and di Pasquo, 2011; Noetinger *et al.*, 2015; Noetinger, 2018; García Muro *et al.*, 2020).

The objective of this work is to discuss the paleoenvironment and age of the Los Monos Formation, in the outcrop and subsurface, in a regional transect (west to east) of the south part of the Tarija Basin. From a multi-methodological analysis were defined lithofacies, ichnofacies, palynofacies and clay mineral assemblages. The analysis of the clay assemblages allowed discussing the source areas, eustatic changes and paleoclimatic conditions. The analysis of the crystallinity of the illite and the quantification of expansive layers in the mixed-layer IS allowed to define the diagenetic degree of the unit and the potential for hydrocarbons generation. The study of the mineral composition of the unit, the determination of the thermal maturity and the analysis of the geochemical antecedents allowed us to discuss their implications for the exploration of unconventional reservoirs (shale gas and shale oil). Finally, the study of palynological assemblages allowed us to discuss the age of the Los Monos Formation in the study area.

GEOLOGICAL SETTINGS

The Siluro-Devonian sedimentary basin developed to the east of the Puna and the Eastern Cordillera comprises part of a large basin that extends into the territory of Bolivia and Paraguay. Its outcrops are present in the sub-Andean ranges and the Eastern Cordillera as well as in the Santa Bárbara System, and in the subsurface, it is present in the Chaco-Salteño in the province of Salta, Jujuy and Santiago del Estero (Fig. 1).

The Siluro-Devonian basin was located in the Western Gondwana and developed in paleolatitudes higher than 60°, under temperate-cold sea conditions (Albariño *et al.*, 2002; di Pasquo *et al.*, 2009; Noetinger *et al.*, 2018), with an estimated paleobathymetry < 200 m (Dalenz-Farjat *et al.*, 2019). The sedimentary fill is made up of several overlapping sedimentary basins that comprise most of the Phanerozoic. Starck (1995) defined four main sequences delimited by unconformities: Cambrian-Ordovician, Silurian-Jurassic, Cretaceous-Early

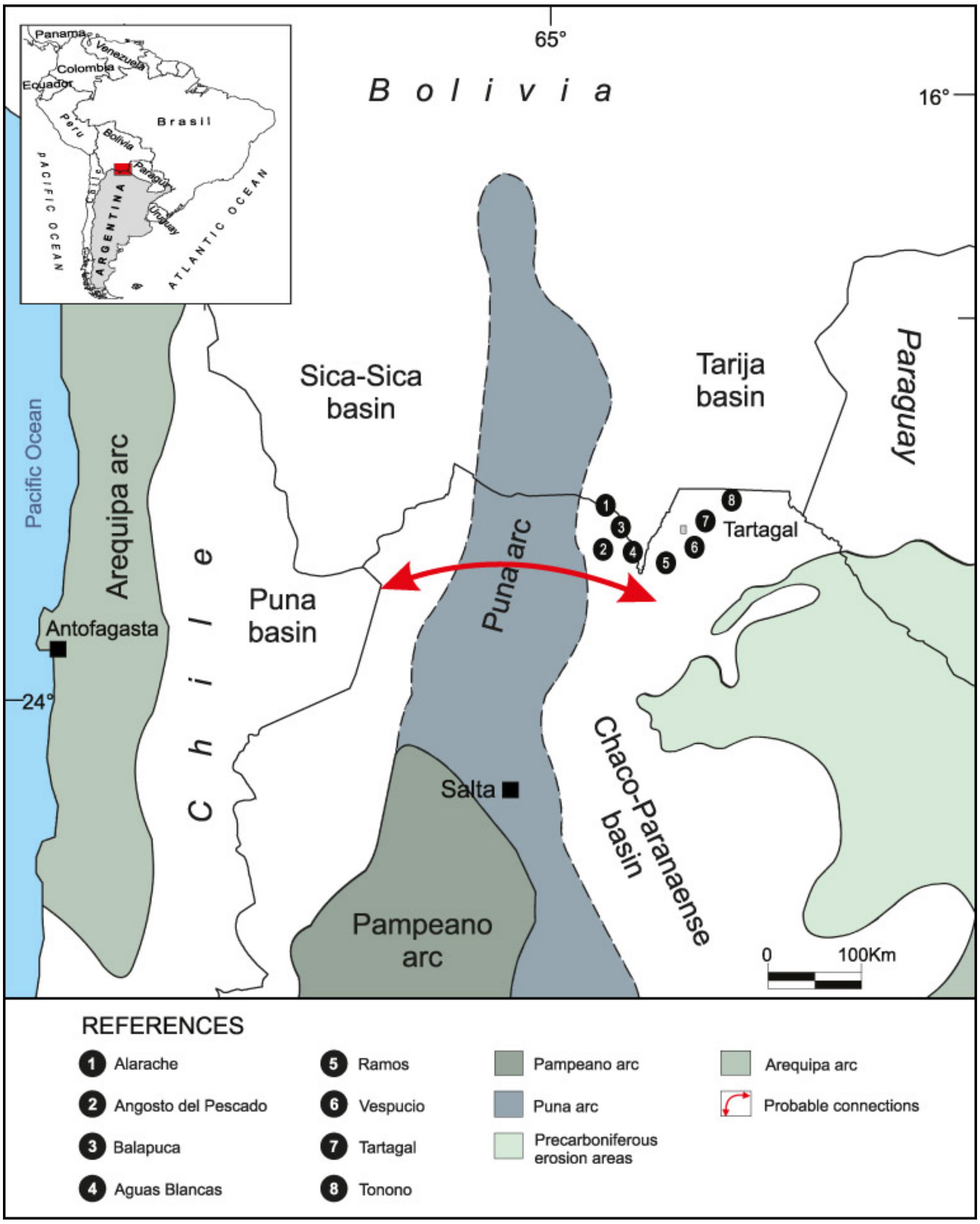


Figure 1. Location of study localities within the Tarija Basin.

Tertiary, and Early Tertiary-Recent. Each sequence represents different stages of the basin. During the Upper Cambrian-Lower Ordovician, a convergence or proto-subduction stage was activated (Sanchez and Salfity, 1999) and Famatinian magmatism began (Aceñolaza *et al*., 1999), the region comprises a back-arc basin passive margin, open to the west. Towards the Late Ordovician, a tectonic inversion occurred due to the Ocloyic orogeny, where the Arequipa-Antofalla craton collided with the Pampean terrain (Ramos and Coira, 2008). After the accretion of the terrain, intracratonic phase of the basin is registered and two intervals can be recognized, divided by an unconformity. The earliest interval comprises the Silurian and most of the Devonian periods, and the last interval is from the Carboniferous up to the Jurassic (Starck, 1995).

Although the present limits of the basin are erosive, the western basin border could have coincided with the eastern front of the Ocloyic orogen and Sierras Pampeanas (Puna and Pampeano arc), it has high relief and comprises main source-rocks of the largest volume of sediments deposited in the basin (Albariño *et al*., 2002; Dalenz-Farjat *et al*., 2002; Álvarez *et al*., 2003; Astini and Marengo, 2006; Aparicio González *et al*., 2020). The basement is made up of granitic, volcanic, and high-grade metamorphic rocks (gneiss and migmatites) (Ramos and Coira, 2008). While the Brazilian shield and the Las Breñas high could constituted the borders of the eastern and southeastern basin, respectively (Vistalli, 1999; Vistalli *et al*., 2005), it has low relief with a lower contribution of sediments. The Arequipa massif was largely sialic (Dalmayrac *et al*., 1980). The Puna plateau is composed of Upper Ordovician magmatic igneous rocks (Ramos and Coira, 2008). The Brazilian shield has a composition similar to the Arequipa massif (Dalmayrac *et al*., 1980).

STRATIGRAPHY

The sedimentary column in this region is represented by clastic sediments from the Lower Paleozoic to the Cenozoic, the oldest rocks in this area correspond to Precambrian to Silurian deposits (Escayola *et al*., 2011) that represent the substrate of the basin. Starck (1995) postulated a Phanerozoic tecto-stratigraphic scheme for northern Argentina and southern Bolivia, in which the Silurian-Jurassic period is divided into two intervals separated by a regional unconformity. Within the Silurian-Devonian interval, three coarsening-upward supersequences are defined, in ascending stratigraphic order are Cinco Picachos, Las Pavas and Aguaragüe (Fig. 2).

The Supersequence Cinco Picachos has in the base a bank of diamictites approximately 50 meters thick corresponding to the Zapla Formation (Upper Ordovician-Silurian) and is interpreted as a product of the Hirnantian glaciation (Díaz-Martínez and Grahn, 2007; Aceñolaza *et al*., 1999; Boso and Monaldi, 1987; Rubinstein, 2005; de la Puente and Rubinstein, 2013; Benedetto *et al*., 2015); above it is the Kirusillas Formation consisting of a sequence of monotonous shales and sandstone (Starck, 1995).

The Las Pavas Supersequence is separated from the previous one by a maximum flooding surface. This supersecuence has a thickness of approximately 900 meters in total, which are divided into coarsening and thickening-upward cycles. It is composed of the Icla Formation that corresponds to shales deposited in a distal platform paleoenvironment (Starck, 1995). Above is the Huamampampa Formation, which corresponds to sandstone deposited in a proximal platform paleoenvironment as well as continental-fluvial paleoenvironments (Ulrich, 1892; Aramayo Flores, 1989), these rocks are hydrocarbon reservoirs in some sectors of the basin.

The Aguaragüe Supersequence has thicknesses of around 1000 meters and is mainly formed by the Los Monos Formation. It comprises dark shales with thin sandstone intercalations, representing storm events, deposited on a distal platform. This unit constitutes the main source-rock of the petroleum system. Above is the Iquiri Formation that comprises sandstone with a coarsening-upward pattern deposited in a more proximal paleoenvironment, overlying the pelitic facies of the Los Monos Formation. This unit has recurrent storm characteristics (hummocky) (Bossi, 1983). In Argentina, these units have a good development in the subsurface, because pre-Carboniferous erosion eliminated a large part of the Devonian deposits that are now exposed on the surface (Starck, 1995).

The Devonian deposits are separated from the Upper Carboniferous stratigraphic units by an erosive surface, in the Sub-Andean ranges and the subsurface of the Bolivian Chaco and the northern Chaco-Salteño (Starck, 1995). The Upper Carboniferous of this basin is made up of the Macharetí and Mandiyutí Groups. In some sections of southern Bolivia, the Itacua or Saipurú formations (Famennian-Lower Carboniferous) (Suárez Soruco, 2000) are found above the Devonian levels described. The Carboniferous stratigraphic succession has been reinterpreted by Starck (1995) as composed of two supersequences separated by an unconformity, represented in Argentina by the Macharetí Groups (Tupambi, Itacuamí and Tarija formations) and Mandiyutí (Escarpment and San Telmo formations).

Cyclicity and eustatic curve

The sedimentation and cyclicity observed during the Devonian period were mainly subject to variations in sea level (eustatic control), in addition to the physiography of the basin margins, subsidence and climate (Albariño *et al*., 2002). The eustatic curve and the Palaeozoic cyclicity of the basin generally coincide with the eustatic curve presented by Johnson *et al*. (1985) for the Devonian sequences of Euroamerica (Albariño *et al*., 2002; Álvarez *et al*., 2003). In this way, following the criteria of the Genetic-Stratigraphy by Galloway (1989), within the Silurian-Devonian, three coarsening-upward supersequences were defined called Cinco Picachos, Las Pavas and Aguaragüe (Starck, 1995), previously described. Besides, during the Devonian, second-order regressive and transgressive sequences and

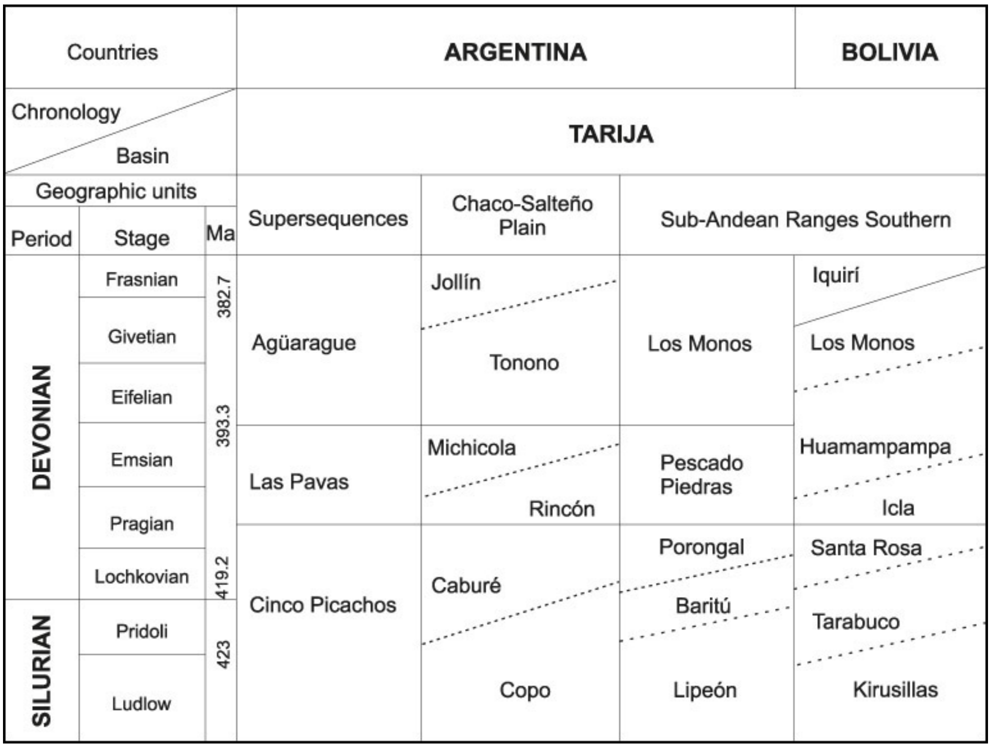


Figure 2. Stratigraphic chart of the Tarija Basin in the study area and its comparison with the units of Bolivia. Modified from Noetinger, 2015.

third-order sequences were recognized (Albariño *et al.*, 2002).

In general, prograding regressive events are observed, represented by forced and normal regressions such as Forced Regression system track (FR), Highstand system track (HST) and Lowstand system track (LST), where the latter is poorly preserved or not identified (Albariño *et al.*, 2002). Regressive processes are associated with most of the sandstone levels (hydrocarbon reservoirs) of upper Lochkovian, upper Pragian, middle to upper Emsian and lower-upper Givetian to Frasnian ages (Santa Rosa, Huamampampa and Iquiri formations, respectively). On the other hand, transgressive events and maximum flooding surfaces are observed, identified as Transgressive system track (TST) and synchronous lines respectively, with the transgressive onlap over the Highstand and Lowstand system track (Albariño *et al.*, 2002). The transgressive processes are associated with the main hydrocarbon generating rocks, during the Lower Lochkovian, Lower Emsian and Eifelian (Albariño *et al.*, 2002; Dalenz-Farjat *et al.*, 2002; Álvarez *et al.*, 2003).

The lower limit of the Emsian is defined by a maximum flooding surface (base SG VII, seismic “marker” 4), and then the development of a regressive sedimentary episode consisting of three genetic-sequences of third-order (SG VII, VIII, IX) is recognized, with a normal prograding pattern. Towards the end of the Emsian, a new third-order sequence (SG X) is recognized due to a relative sea-level fall (Forced or Normal Regression). The lower limit of the Eifelian is defined by a flooding surface (base SG XI and seismic marker 5), then four transgressive-regressive cycles are recognized (SG XI, XII, XIII, XIV), with a prograding pattern, corresponding to a normal regressive episode. The lower limit of the Givetian corresponds to a new cycle of relative sea-level fall and the development of two regressive-transgressive cycles (SG XV, XVI) (Forced Regression). Towards the end of the Givetian, scarce data permit to inferring a new transgressive stage (Albariño *et al.*, 2002).

MATERIALS AND METHODS

Lithofacial analysis

For the lithofacial analysis, the outcrops of the Los Monos Formation in the locality of Alarache, Angosto del Pescado and Balapuca were studied, overlying is the Tupambi Formation and at the base the Huamampampa Formation. In the subsurface, the following core intervals extracted from different sections the Los Monos Formation were studied: in the Aguas Blancas xp-13 borehole, core intervals from the middle-section of the 2810-2813 and 3056-3060 mbgs (meters below ground surface); in the Ramos x-12 borehole, core intervals of the basal-section of the 2713.4-2719 mbgs; in the Tartagal x-1 borehole, core intervals of the basal section of the 4030-4032 and 4052-4054 mbgs; in the Tonono x-1 borehole, core intervals of the upper section 3285-3289 mbgs and a middle part of the formation 3365-3368 mbgs and 3638-3640.5 mbgs. Besides, two core intervals extracted from the overlying unit (Jollín Formation) 3073-3077 mbgs and 3133-3134 mbgs and the underlying unit (Michicola Formation) 3945-3946.8 mbgs were studied (Fig. 3).

Six sedimentary facies were defined (facies 1 to 6) based on lithology, sedimentary structures, the content of trace fossils and the bioturbation index (Table 1). The estimation of the bioturbation index (BI) follows the scheme of Taylor and Goldring (1993). In this scheme, BI = 0 is characterized by not presenting bioturbation (0%) and BI = 6 (100%) is for fully bioturbed and reworked sediment, related to repeated overprinting of trace fossils.

X-ray diffraction (XRD)

The mineral composition of the Los Monos Formation was analyzed by X-ray diffractometry (XRD) in 126 samples. Balapuca outcrop samples (48), samples from the core intervals of the Aguas Blancas xp-13 borehole (7 samples) and Ramos x-12 (10 samples) and cutting samples from the Ramos xp-1012 borehole (6 samples), Vespucio x-1 borehole (26 samples) and Tonono x-1 borehole (29 samples). The sampling was throughout the entire formation and systematic in the 140-meter-thick Balapuca outcrop, in the 900-meter-thick Vespucio x-1 borehole and the 985-meter-thick Tonono x-1 borehole. Samples of the underlying formations such as the Huampampa and the Michicola and overlying units such as the Tupambi Formation and the Jollín Formation were also analyzed to establish a comparative compositional analysis between the different units.

Samples for XRD analysis were subjected to soft griding with a rubber mortar and repeatedly washed in distilled water until deflocculation occurred. The <2 mm fraction was separated by suspension and gravity decantation, and oriented mounts were prepared on glass slides. Clay mineralogy was determined from diffraction patterns obtained using samples that were air-dried, solvated with ethylene glycol, and heated to 550 °C for 2 hours (Brindley and Brown, 1980). The diffractograms were performed in an X PANalytical model X'Pert PRO diffractometer (CIG), using Cu/Ni radiation and 40 kV and 40 mA generation settings.

The weighting (semi-quantitative) of the minerals present in the whole rock was carried out from the intensity of the main peak for each mineral (Schultz, 1964; modified with own standards; Moore and Reynolds, 1997). The estimation of the mineralogical components has a methodological error ca. 10%. The crystallinity of clay minerals was deduced from the shape and sharpness of the XRD peaks (Brindley and Brown, 1980). The semi-quantitative estimations of the relative concentrations of clay minerals were based on the peak area method following the methodology from Biscaye (1965). The response of mineral species to sedimentation depends on the form of the particles (Pierce and Siegel, 1969); for that reason, each mineral proportion is not directly proportional to the defined areas. The relative percentages of each clay mineral were determined by applying empirical factors (Moore and Reynolds, 1997). The abundance of the different clay minerals in the <2 mm fraction is summarized in Tables 2-7.

In samples with illite (I) and interstratified illite/smectite (IS), the crystallinity index or Kubler index (KI) was measured from air-dried samples (Kubler, 1966). The KI values were calibrated according to the Crystallinity Index Standard (CIS) scale using the procedure and standards of Warr and Rice (1994). This index expresses the approximate overburden conditions to which the sediment was exposed. For illite, values greater than 0.42 are interpreted as diagenetic, between 0.42 and 0.25 as anchymetamorphism, and less than 0.25 are metamorphic. On the other hand, the Esquevin Index (EI) (Esquevin, 1969) was calculated, which measures the division between peak 002 and 001 of the illite in the natural sample, when the values are greater than 0.40 the samples are aluminous, and values less than 0.25 indicate ferromagnesian samples.

The IS interlayers identified, following the criteria of Moore and Reynolds (1997), were R1 (40-20% expandable layers of smectite) with reflection (001) close to 12-14 Å in samples solvated with ethylene-glycol. The relative abundance of illite

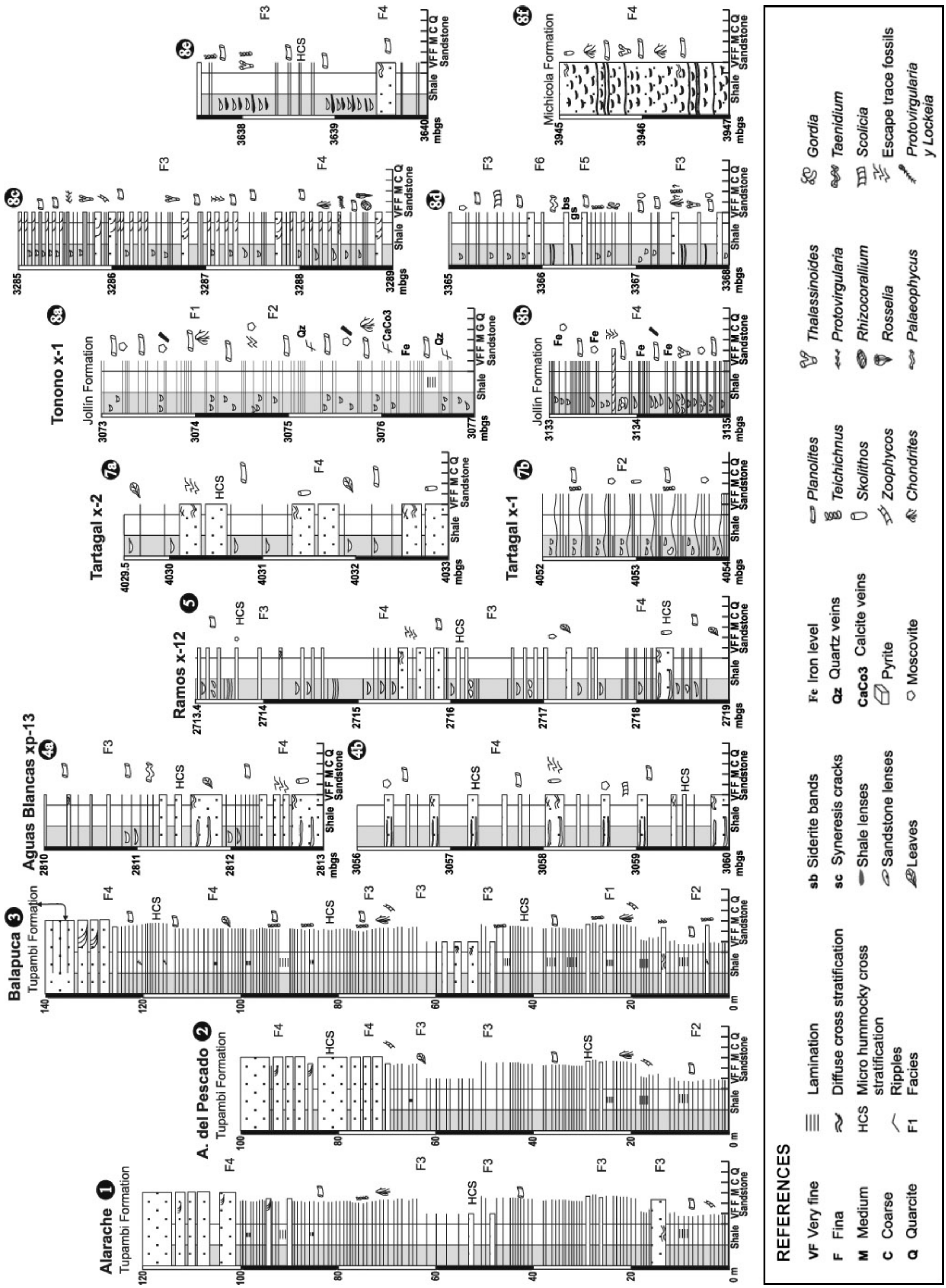


Figure 3. Sedimentary logs of the Los Monos Formation. Logs ubication in Fig. 1.

Facies	Lithology	Sedimentary structures	Bioturbation index	Traces fossils	Paleoenvironment
1	Black shale	Massive to locally parallel-lamination shale	0 a 1	Locally, *Asterosoma* isp. *Chondrites* isp. *Zoophycos* isp.	Shelf
2	Dark grey siltstone and very fine-grained sandstone	Siltstone interbedded with very fine-grained sandstone. The sandstone layers are continuous to discontinuous, also lenticulars. Locally with micro-hummocky. Gradational contact.	1-2	*Planolites* isp. *Teichichnus* isp. *Zoophycos* isp. *Chondrites* isp.	Lower Offshore
3	Sandy siltstone and sandstone with micro-hummocky cross-stratification	Interbedded grey, bioturbed siltstone, and light grey, very fine-grained sandstone. Higher bioturbation and sandstone beds. Locally with micro-hummocky and wave ripples towards the top. Gradational contact.	Variable: Silstones 3 and sandstone 0 a 1	*Planolites* isp. *Palaeophycus* isp. *Taenidium* isp. *Scolicia* isp. Escape trace fossils (*fugichnia*)	Upper Offshore
4	Very fine sandstone and bioturbed siltstone	Interbedded light grey, very fine-grained sandstone and light to dark grey, bioturbed siltstone. Sandstone beds have hummocky cross-stratification and very thin parallel-lamination	1 a 2	*Planolites* isp. *Skolithos* isp. *Ophiomorpha* isp. Escape trace fossils (fugichnia)	Offshore transition
5	Sandstone and finely interlaminated pelites	Very finely interlaminated light grey silty sandstone with dark grey shale. Locally, occur thinly dark laminae of organic debris, mud-drapes, syneresis cracks and siderite bands.	1 a 3	*Planolites* isp. *Palaeophycus* isp. *Teichichnus* isp. *Rosselia* isp. *Gordia* isp. *Treptichnus* isp.	Distal bay
6	Sandy siltstone	Massive	1-2	*Chondrites* isp.	Transgressive lag

Table 1. Description and interpretation of the sedimentary facies defined for the Los Monos Formation.

and smectite in the IS interlayers was determined by the parameter Δ°2θ (Moore and Reynolds, 1997). Based on the values obtained, the diagenetic degree of the unit was determined following the scheme of Fóscolos *et al.* (1976).

Scanning Electron Microscopy (SEM)

Fifty-three samples from the Los Monos Formation were analyzed by scanning electron microscopy (SEM) to study the mineralogical micromorphology of clay and non-clay minerals. The samples were air-dried to constant weight and then plated with gold (Au). Each sample was studied with different magnifications (12000, 15000 up to 25000x in some cases) to determine the majority and minority mineralogical components and to observe the microstructure. The samples were analyzed with an FEI Quanta 200 SEM microscope and an EDAX Phoenix 40 (acceleration voltage 20 Kw, spot size 3 to 4 mm, Faculty of Engineering, La Plata, Argentina).

Palynological analysis

Palynological studies were perfomed on outcrops and subsurface samples of the Los Monos Formation, in the Alarache, Balapuca and Angosto del Pescado sections and in the Ramos xp-1002, Ramos xp-1011 and Ramos xp-1012 boreholes (Perez Leytón, 2010 and Perez Leytón, 2014). The age determination is based on the Biostratigraphic Reference Scale for Bolivia proposed by Perez Leytón (2007) including spores, chitinozoans and acritarchs/prasinophyceae. Regarding spores, other regional zonations were also used, such as those proposed for the Amazon basin, Brazil, applicable to Western Gondwana

Sample	Whole rock						Clay fraction				
	Q	FK	Pl	Py	Clay	Formation	I	IS	Ch	K	Clay mineral assemblage
Ba 1	70	2	4	0	24	Tupambi	55	26	14	5	CMA I+IS
Ba 2	79	1	4	2	14		51	28	13	8	
Ba 3	75	2	4	3	16		51	22	24	3	
Ba 4	81	0	7	0	12	Los Monos	49	31	16	4	
Ba 5	84	0	8	0	8		34	42	19	5	CMA IS+I
Ba 6	82	0	7	0	11		52	18	24	6	CMA I+Ch
Ba 7	73	0	9	0	18		49	20	26	5	
Ba 8	65	0	5	0	30		54	21	21	4	
Ba 9	73	0	7	0	20		47	22	26	5	
Ba 10	82	0	8	0	10		30	21	16	33	CMA K+I
Ba 11	77	0	7	0	16		47	14	31	8	CMA I+Ch
Ba 12	73	0	8	0	19		47	23	26	4	
Ba 13	77	0	5	0	18		46	21	28	5	
Ba 14	83	0	10	0	7		43	13	34	10	
Ba 15	70	0	7	0	23		58	14	23	5	
Ba 16	66	0	6	0	28		62	16	19	3	
Ba 17	68	0	9	0	23		54	18	24	4	
Ba 18	65	0	7	0	28		51	22	22	5	
Ba 19	51	0	8	0	41		57	16	23	4	
Ba 20	85	0	5	0	10		13	18	27	42	CMA K+Ch
Ba 21	60	0	6	0	34		56	16	25	3	CMA I+Ch
Ba 22	67	0	7	0	26		48	23	24	5	
Ba 23	50	0	8	0	42		53	22	19	6	
Ba 24	63	0	5	0	32		54	18	23	5	
Ba 25	68	0	6	0	26		48	22	26	4	
Ba 26	73	0	11	0	16		47	24	24	5	
Ba 27	83	0	9	0	8		33	16	16	35	CMA K+I
Ba 28	72	0	9	0	19		51	23	21	5	CMA I+Ch
Ba 29	75	0	10	0	15		49	22	24	5	
Ba 30	66	0	12	2	20		58	18	18	6	
Ba 31	76	0	8	1	15		53	17	26	4	
Ba 32	75	0	8	0	17		54	18	25	3	
Ba 33	73	0	7	0	20		59	12	24	5	
Ba 34	66	0	6	0	28		62	13	23	2	
Ba 35	69	0	7	0	24		56	18	25	1	
Ba 36	63	0	8	0	29		47	24	18	11	CMA I+IS
Ba 37	72	0	6	0	22		40	18	25	17	CMA I+Ch
Ba 38	71	0	14	0	15		38	22	24	16	
Ba 39	74	0	10	0	16		44	14	31	11	
Ba 40	74	0	12	0	14		43	13	21	23	CMA I+K
Ba 41	82	0	7	0	11		18	8	36	38	CMA K+I
Ba 42	83	0	7	0	10		21	24	13	42	
Ba 43	83	0	11	0	6		13	32	12	43	
Ba 44	73	0	8	0	19		50	20	24	6	CMA I+Ch
Ba 45	66	0	10	0	24		43	22	24	11	
Ba 46	64	0	13	0	23		45	33	21	1	CMA I+IS
Ba 47	75	0	11	0	14		40	22	22	16	
Ba 48	79	0	9	0	12		55	18	23	4	CMA I+Ch

Table 2: Results of X-ray diffraction from the Los Monos Formation at Balapuca locality. Q: quartz; FK: potassium feldspar; Pl: plagioclase; Py: pyrite; I: illite; IS: illite-smectite mixed layer; Ch: chlorite; K: kaolinite; CMA: Clay mineral assemblage.

Depth (mbgs)	Whole rock						Clay fraction				
	Q	FK	Pl	Py	Clay	Formation	I	IS	Ch	K	Clay mineral assemblage
3771	69	0	8	0	23	Los Monos	54	3	43	0	CMA I+Ch
3801	64	0	4	2	30		50	5	45	0	
3831	72	0	5	3	20		48	2	22	28	CMA I+K
3861	73	0	4	0	23		42	5	21	32	
3891	78	0	5	0	17		47	3	20	30	
3952	74	0	3	0	23		49	5	18	28	
3984	83	0	5	0	12		33	8	24	35	CMA K+I
4020	86	0	6	0	8		31	10	26	33	
4056	78	0	5	0	17		44	18	11	27	CMA I+K
4092	71	0	4	0	25		45	20	13	22	
4214	74	0	5	0	21		45	22	15	18	CMA I+IS
4250	75	0	6	0	19		43	23	14	20	
4286	73	0	8	0	19		44	20	15	21	CMA I+K
4322	78	0	5	0	17		43	18	16	23	
4358	82	0	2	0	16		49	19	14	18	
4400	76	0	5	0	19		41	17	42	0	CMA Ch+I
4430	83	0	8	0	9		42	15	43	0	
4506	82	0	4	0	14		40	16	44	0	
4542	77	0	3	0	20		50	14	15	21	CMA I+K
4572	82	0	0	0	18		52	15	13	20	
4608	78	0	5	0	17		56	22	22	0	CMA I+Ch
4644	75	0	8	0	17		52	16	14	18	CMA I+K
4688	74	0	7	0	19		51	15	18	16	CMA I+Ch
4722	79	0	4	0	17		49	17	22	12	
4746	81	0	5	0	14		54	13	20	13	
4776	90	0	1	0	9		47	12	23	18	

Table 3. Results of X-ray diffraction from the Los Monos Formation at Vespucio x-1 borehole. References as in Table 2.

(Melo and Loboziak, 2003) and for northwestern Gondwana (Breuer and Steemans, 2013) including local elements or endemic. These biostratigraphic scales were defined by comparison with the two major reference zonations for the Devonian spores of Euroamerica and applicable to Western Gondwana of Richardson and McGregor (1986) and Streel *et al*. (1987). These two major zonations have independent age control since they are calibrated with associated marine faunas, such as conodonts, graptolites, foraminifera among others.

In the case of chitinozoans, the scale proposed by Perez Leytón (2007) has been defined and compared with global zonations (Paris, 1981; Paris *et al*., 2000) and with the Silurian and Devonian zonations of Western Gondwana (Grahn, 2005; Grahn, 2006). For the group of acritarchs/prasinophytes, the scale proposed by Perez Leytón (2007) was developed based on the synthesis of Molyneux *et al*. (1996) and an operational zonation developed by the author.

In addition, a palynofacies analysis was carried out distinguishing, according to Tyson (1995), algal facies, which consists of amorphous organic matter of algal origin and figurative elements of the acritarchs/prasinophytes group and compatible with type-I kerogen with high oleogenetic potential; a liptinic facies, represented by pollen, spores, cuticles, and compatible with the type-II kerogen with lower oleogenetic potential than the algal facies; a lignohumic facies, which includes the tissues of higher terrestrial plants, compatible with type-III kerogen, with low oleogenetic potential in

Depth (mbgs)	Whole rock						Clay fraction				
	Q	**FK**	**Pl**	**Py**	**Clay**	**Formation**	**I**	**IS**	**Ch**	**K**	**Clay mineral assemblage**
3098	67	5	3	0	25	Jollín	43	8	6	43	CMA K+I
3133	68	0	2	0	30		40	7	5	48	
3164	81	0	1	0	18	Tonono	36	9	6	49	
3194	78	0	5	1	16		41	10	5	44	
3236	78	0	4	0	18		42	8	7	43	
3266	76	0	6	0	18		42	9	6	43	
3290	82	0	7	2	9		39	11	5	45	
3314	83	0	5	0	12		43	13	6	38	CMA I+K
3352	77	0	4	0	19		50	18	9	23	
3386	75	5	2	3	15		48	20	10	22	
3422	73	0	3	0	24		46	21	8	25	
3458	72	0	7	2	19		44	22	10	24	
3482	69	0	5	0	26		45	24	23	8	CMA I+IS
3512	71	0	6	0	23		45	22	10	23	CMA I+K
3548	79	0	8	2	11		51	18	8	23	
3590	74	0	4	0	22		45	14	15	26	
3620	83	0	3	0	14		39	15	23	23	
3638	77	0	2	6	15		50	18	26	6	CMA I+Ch
3668	74	0	4	0	22		37	19	44	0	CMA Ch+I
3704	78	0	6	0	16		47	21	26	6	CMA I+Ch
3734	81	0	5	3	11		55	22	23	0	
3770	82	0	5	0	13		54	18	9	19	CMA I+K
3812	73	0	6	0	21		53	18	8	21	
3854	76	0	3	5	16		54	15	18	13	CMA I+Ch
3890	78	0	2	0	20		51	18	19	12	
3920	76	0	3	0	21	Michicola	48	21	18	13	CMA I+IS
3952	77	0	4	0	19		52	22	8	18	
3986	78	0	5	0	17		54	18	9	19	
4014	79	0	6	0	15		50	20	14	16	

Table 4. Results of X-ray diffraction from the Tonono Formation at Tonono x-1 borehole. References as in Table 2.

liquid hydrocarbons but high in gas and an inertinite facies, constituted by degraded organic matter, inert, with negligible oleogenetic potential.

LITHOFACIAL ANALYSIS

Six sedimentary facies have been defined based on lithology, sedimentary structures, the content of trace fossils and bioturbation index, in the outcrops and the core intervals studied of the Los Monos Formation in Argentina and Bolivia. These facies are Black shale facies (F1), Dark grey siltstone and very fine sandstone Facies (F2), Sandy siltstone and sandstone with micro-hummocky cross-stratification Facies (F3), Very fine sandstone facies and bioturbed siltstone Facies (F4) and Sandstone and finely interlaminated pelites Facies (F5) and Sandy siltstone Facies (F6) (Table 1).

Black shale Facies (F1)

This facies consists of black, massive (Fig. 4A) to locally parallel-laminated shale. Locally pyrite is present. Bioturbation is generally absent, but some levels revealed the presence of *Asterosoma* isp., *Chondrites* isp., and *Zoophycos* isp.

Depth (mbgs)	Whole rock					Clay fraction				
	Q	FK	Pl	Py	Clay	I	IS	Ch	K	Clay mineral assemblage
2810	68	1	12	0	19	63	17	18	2	CMA I+Ch
2830	77	0	6	2	15	65	16	19	0	
2850	83	2	3	3	9	36	12	51	1	CMA Ch+I
2870	72	0	5	0	23	33	10	57	0	
2890	71	3	4	0	22	64	12	22	2	CMA I+Ch
3056	78	0	8	0	14	52	16	32	0	
3066	72	2	10	0	16	55	3	41	1	

Table 5. Results of X-ray diffraction from the Los Monos Formation at Aguas Blancas xp-13 borehole. References as in Table 2.

Depth (mbgs)	Whole rock					Clay fraction				
	Q	FK	Pl	Py	Clay	I	IS	Ch	K	Clay mineral assemblage
2713	78	0	3	0	19	52	13	3	32	CMA I+K
2723	82	0	2	2	14	50	15	5	30	
2733	80	0	5	3	12	54	12	3	31	
2743	76	0	3	0	21	48	16	4	32	
2753	77	0	4	0	19	51	13	6	30	
2763	83	0	1	0	16	43	14	5	38	
2773	78	0	7	0	15	54	11	7	28	
2783	82	0	6	0	12	55	15	3	27	
2793	79	0	3	0	18	55	14	2	29	
2803	81	0	1	0	18	44	15	7	34	

Table 6. Results of X-ray diffraction from the Los Monos Formation at Ramos x-12 borehole. References as in Table 2.

Depth (mbgs)	Whole rock					Clay fraction				
	Q	FK	Pl	Py	Clay	I	IS	Ch	K	Clay mineral assemblage
2260	63	5	7	0	25	49	14	21	16	CMA I+Ch
2290	64	4	7	2	23	55	13	11	21	CMA I+K
2480	64	6	9	0	21	60	9	18	13	CMA I+Ch
2512	65	4	9	0	22	51	22	21	6	CMA I+IS
2534	65	5	10	0	20	41	32	14	13	
2614	64	4	11	2	19	57	18	16	9	

Table 7. Results of X-ray diffraction from the Los Monos Formation at Ramos xp-1012 borehole. References as in Table 2.

Interpretation: This facies records suspension-fallout deposition in a low-energy setting without the influence of waves and currents. The dark colour, the low bioturbation index and the scarcity of fauna suggest anoxic conditions. However, the presence of local bioturbation suggests brief periods of more favourable conditions on the sea floor. Furthermore, these fine-grained sediments may have been characterized by high water content, and their degree of consolidation probably affected biogenic-structure preservation, which is very low in soupy substrates (Ekdale, 1985).

Based on the described characteristics, this facies is interpreted as having been deposited in the shelf paleoenvironment below storm wave-base as indicated by the absence of oscillatory structures.

Dark grey siltstone and very fine-grained sandstone Facies (F2)

This facies consists of dark grey siltstone interbedded with very fine-grained sandstone (<0.5 cm thick) (Fig. 4B). The sandstone layers are continuous to discontinuous, also lenticular, locally with micro-hummocky cross-stratification. Deposits are generally sparse to moderately bioturbed. These deposits have a BI of 1 to 2 and are represented by *Planolites* isp., and *Teichichnus* isp. (Fig. 4B). *Chondrites* isp., and *Zoophycos* isp., are also observed. (Fig. 4C and 4D). The contact with underlying black shale (facies 1) is sharp but conformable and gradational with overlying sandy siltstone (facies 3).

Interpretation: The grey siltstone facies records suspension-fallout deposition in a low-energy environment, mainly in the absence of waves and currents. The very fine sandstone layers may have been emplaced by distal storms (episodic storms) where the discontinuous to lenticular shape could be related to bioturbation. Although the sedimentary processes involved during the deposition of this facies are similar to those in the black shale facies, the presence of sandstone levels and oxic conditions, revealed by bioturbation, suggests deposition in a lower offshore environment immediately above the storm wave-base.

Sandy siltstone and sandstone with micro-hummocky cross-stratification Facies (F3)

This facies consists of interbedded grey, bioturbed siltstone, and light grey, very fine-grained sandstone (<2 cm thick) with micro-hummocky cross-stratification. In some cases, wave ripples occur on top of micro-hummocky beds, also mud-drapes and ripple cross-lamination are observed (Fig. 5A). The BI is variable, in the siltstone the bioturbation index is generally 3, while in the sandstone it ranges between 0 and 1. The dominant ichnofauna in siltstone is *Planolites* isp., and *Palaeophycus* isp., in the sandy beds escape trace fossils are observed (*fugichnia*) (Fig. 5A). There are also traces fossil of *Taenidium* isp., and *Scolicia* isp. (Fig. 5B and 5C). Overall, the basal and top contact of this facies is gradational.

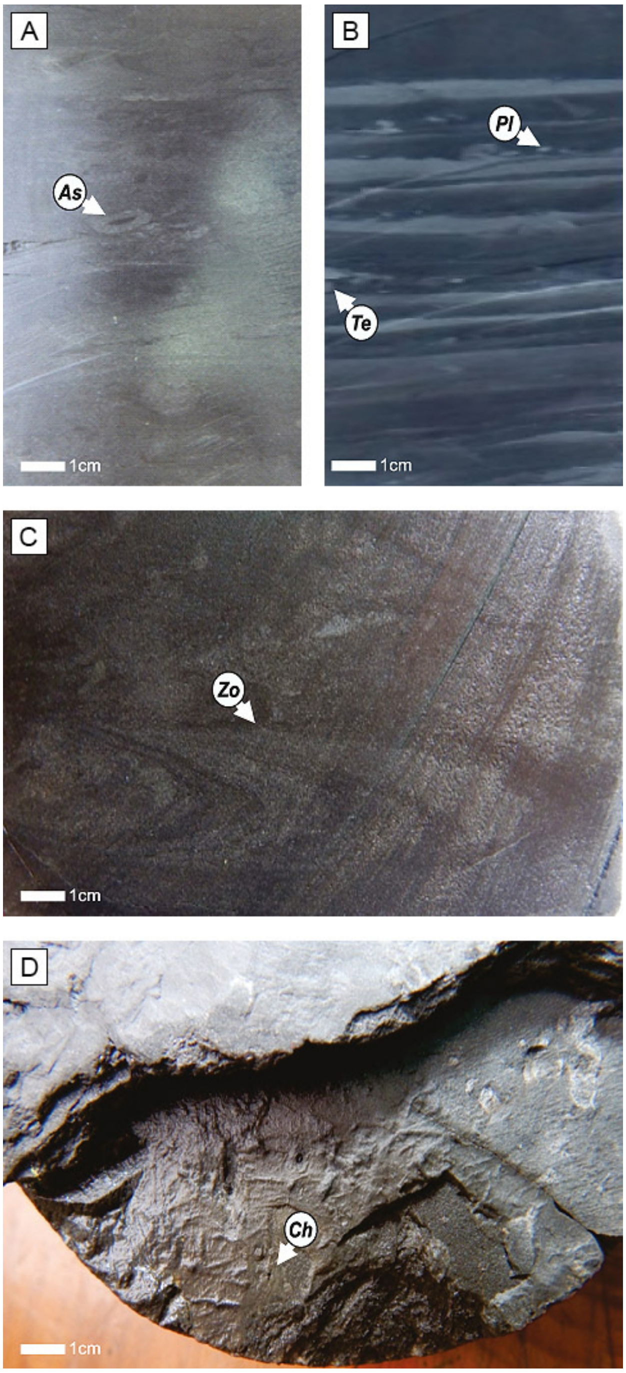


Figure 4. Core photographs showing the sedimentary structures and traces fossils of F1 and F2 facies defined in the Los Monos Formation. **a)** Facies 1, Aguas Blancas xp-13 borehole, 2810.5 mbgs; *Asterosoma* (As). **b)** Facies 2, Aguas Blancas xp-13 borehole, 2811 mbgs; *Planolites* (Pl), *Teichichnus* (Te). **c)** *Zoophycos* (Zo). **d)** *Chondrites* (Ch).

Interpretation: The bioturbed siltstone records quiet-water sediment fallout during fair-weather conditions, while the micro-hummocky, cross-stratified, very fine-grained sandstone beds were

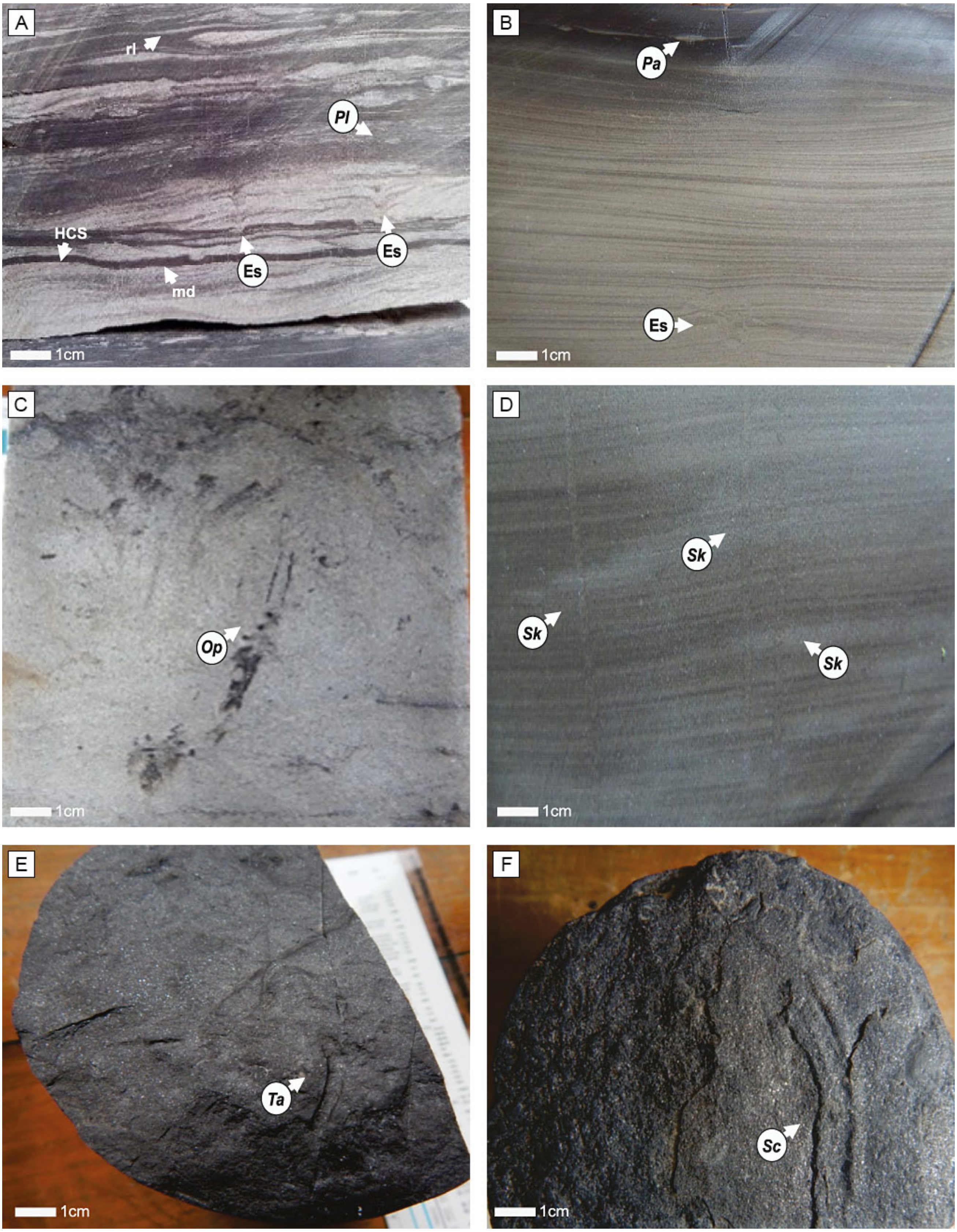


Figure 5. Core photographs showing the sedimentary structures and traces fossils of F3 and F4 facies defined in the Los Monos Formation. **a)** Facies 3, Ramos x-12 borehole, 2714.5 mbgs; ripples cross lamination (rl), micro hummocky cross lamination (HCS), mud drapes (md), escape trace fossils (Es) and *Planolites* (Pl). **b)** Facies 4, Aguas Blancas xp-13 borehole, 2813.5 mbgs; *Palaeophycus* (Pa). **c)** *Ophiomorpha* (Op). **d)** *Skolithos* (Sk). **e)** *Taenidium* (Ta). **f)** *Scolicia* (Sc).

generated by combined flows of oscillatory and unidirectional currents during storms events (Duke *et al.*, 1991). Wave ripples overlying the micro-hummocky zones indicate temporary reworking by waves during waning storms (Dott and Bourgeois, 1982). The ripple cross-lamination was formed when deposition took place during migration of current or wave ripples (Walker and James, 1992). The fair-weather deposits are dominated by a deposit-feeding ichnofauna. The presence of siltstone with higher bioturbation and higher participation of thicker sandstone (tempestites) compared to the F2 facies, suggests the deposition in an upper offshore paleoenvironment below fair-weather wave-base, but above storm wave-base.

Very fine-grained sandstone facies and bioturbed siltstone Facies (F4)

This facies consists of interbedded light grey, very fine-grained sandstone and light to dark grey, bioturbed siltstone. Sandstone beds have hummocky cross-stratification and very thin parallel-lamination (Fig. 5B). Traces of escape are observed, *Skolithos* isp., *Ophiomorpha* isp., and in the silt layers, *Planolites* isp. (Fig. 5B-D). At some levels, the presence of *Taenidium* isp., and *Scolicia* isp. (Fig. 5E and 5F). Locally, *Protovirgularia* isp., *Lockeia* isp., and *Thalassinoides* isp.

Interpretation: Very fine-grained sandstone with hummocky cross-stratification were generated by combined flows of oscillatory and unidirectional currents during storms. The preservation of sedimentary structures and the scarce to absent traces fossil suggests an environment of higher energy without activity by organisms. Only the presence of pioneer opportunistic organisms is observed. The predominance of tempestite sandstone suggests deposition in open-marine conditions, below fair-weather wave-base and above storm wave-base, in an offshore-transition zone.

Sandstone and finely interlaminated pelites Facies (F5)

This facies is composed of very finely interlaminated light grey silty sandstone with dark grey shale (Fig. 6A). The sandstone beds thickness varies from 1 to 5 cm, are continuous to discontinuous, in some cases lenticular. Locally, occur thinly dark laminae of organic debris, mud-drapes, syneresis cracks and siderite bands (identified by XRD). The BI is 1 to 3, the dominant ichnotaxa are *Planolites* isp., *Rosselia* isp., and *Teichichnus* isp. (Fig. 6A and 6B). *Gordia* isp., and *Treptichnus* isp. (Fig. 6C and 6D). It is restricted to the eastern portion of the study area (upper part of Tonono Formation, Tonono x-1 borehole), with a thickness ranging from 0.1 to 1 m.

Interpretation: The low ichnodiversity, mud-drapes, siderite bands, and regular interlamination of pelites and very fine-grained sandstone beds indicate fluctuations in energy conditions. The presence of syneresis cracks, which have been related to salinity fluctuations (Plummer and Gostin, 1981), supports this idea. This facies was deposited in a tidal-influenced brackish-water environment, most likely a distal bay relatively far from the river discharge area (MacEachern *et al.*, 2007). The sandstone layers with thin parallel lamination correspond to storm deposits within the bay. The sandy siltstone represents a transgressive lag produced due to high-energy ravinement in a basinwide transgression, during which time occurs the drowning of the bay and the shoreline moves towards the land, accompanied by a reduction sediment influx into the basin and erosion of the previously deposited sediments (Cattaneo and Steel, 2003).

Sandy siltstone Facies (F6)

This facies is composed of light grey, massive, sandy siltstone with granules (Fig. 6A). The BI is 1 to 2. The ichnofauna consists of *Chondrites* isp. The interval thickness of this facies is less than 50 cm. The contact with underlying brackish-water deposits is erosive and gradational with overlying offshore deposits. It is restricted to the eastern portion of the study area (upper part of Tonono Formation, Tonono x-1 borehole).

Interpretation: The sandy siltstone represents a transgressive lag produced due to high-energy ravinement in a basinwide transgression, during which time occurs the drowning of the bay and the shoreline moves towards the land, accompanied by a reduction sediment influx into the basin and erosion of the previously deposited sediments (Cattaneo and Steel, 2003).

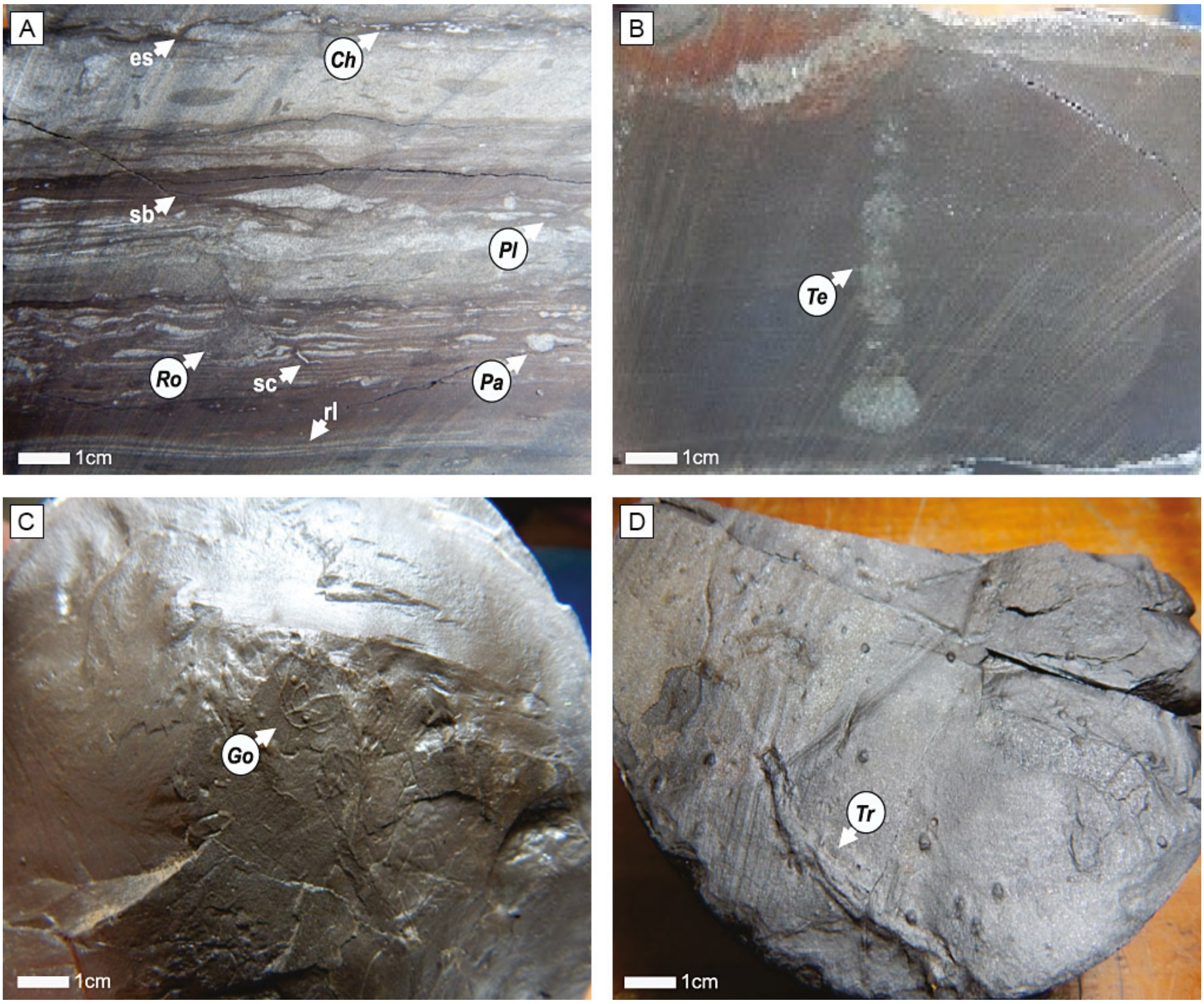


Figure 6. Core photographs showing the sedimentary structures and traces fossils of F5 defined in the Los Monos Formation. **a)** Facies 5, Tonono x-1 borehole, 3366.5 mbgs, to the top transgressive lag; *Planolites* (Pl), *Rosselia* (Ro) and *Palaeophycus* (Pa) with siderite bands (sb) and syneresis cracks (sc), ripples cross lamination (rl) and erosive surface to the top (es). **b)** *Teichichnus* (Te). **c)** *Gordia* (Go). **d)** *Treptichnus* (Tr).

Sedimentary Facies associations

Two facies associations are recognized for the Los Monos Formation, one association corresponds to a paleoenvironment with open-marine conditions, which are arranged along a depositional profile from the offshore transition to the shelf and another association corresponds to brackish-water marginal-marine conditions.

The open-marine succession comprises F1 that has been interpreted as suspension-fallout deposits in a shelf, below storm wave-base. The dark colour, rare local bioturbation, and sparse fauna suggest that anoxic to dysoxic conditions prevailed during deposition. The F2 transitionally overlie the shelf black shale. The presence of interbedded siltstone and sandstone, lighter colours and bioturbation, indicate an increase in oxygen level, probably due to sporadic storms events above the storm wave-base or by sediment progradation overtopping the basin sill. The presence of discontinuous or lenticularly sandstone beds is attributed to biogenic reworking. The degree of bioturbation is moderate to low. The lower offshore siltstone gradually passes into F3 of the upper offshore. Bioturbation degree is higher and the sandstone beds are thicker. The upper offshore deposits are gradually overlain by F4 of the offshore transition. Bioturbation is scarce to absent, showing a higher energy environment. The sand content gradually increases upward. All contacts between each of the open-marine facies are gradational.

Except for the black shale, the open-marine succession, including the lower and upper offshore and the offshore-transition deposits, are characterized by a moderate to low BI (1 to 3) and a "distal" *Cruziana* ichnofacies can be assigned to these deposits. The dominant elements are *Planolites* isp., and *Palaeophycus* isp., while subordinate elements are *Teichichnus* isp. and *Rosselia* isp. Occasionally, *Chondrites* isp., and *Zoophycos* isp., are observed near the top of storm micro-HCS deposits from lower offshore and offshore-transition, which indicates post-storm colonization by opportunistic organisms (Frey and Ring, 1992). The trace fossils are generally produced by selective deposit-feeding, which is the dominant strategy for elements of "distal" *Cruziana* ichnofacies (Buatois *et al*., 2013). Locally, rare *Protovirgularia* isp., and *Lockeia* isp., accompanied by *Thalassinoides* isp., *Scolicia* isp., and *Taenidium* isp., are present. These could represent levels with a diverse *Cruziana* ichnofacies generally with more trophic types (Buatois *et al*., 2013).

According to MacEachern and Pemberton (1992), a "distal" or "outer" *Cruziana* assemblage is characteristic of lower offshore deposits, while a diverse *Cruziana* is more common in upper offshore and lower shoreface deposits. In contrast, in the Los Monos Formation, the "distal" *Cruziana* seems to have spread over large areas of the depositional profile, from the lower offshore to the offshore-transition deposits.

In the upper section of the Tonono Formation, in the Tonono x-1 borehole, intervals deposited under brackish-water marginal-marine conditions are recognized, within the distal zone of an open-bay (F5). There are traces fossils of *Planolites* isp., *Palaeophycus* isp., as well as *Rosselia* isp. and *Teichichnus* isp. These deposits are characterized by a low to moderate BI, a relatively low ichnodiversity, representing the depauperate *Cruziana* ichnofacies (Buatois *et al*., 2005; MacEachern *et al*., 2007). At some levels are observed the presence of *Gordia* isp., and *Treptichnus* isp. Locally, the restricted presence of *Chondrites* isp. and *Zoophycos* isp., are present. Besides, syneresis cracks and siderite bands are recognized that could indicate salinity fluctuation (Burst, 1965; MacEachern and Pemberton, 1994). In the same locality, F6 is observed, which represents a transgressive lag, formed locally the drowning of the bay. Where F6 is present, the contact with the underlying brackish-water marginal-marine environment is erosional and gradational with overlying offshore deposits.

CLAY MINERAL ASSEMBLAGES

The Los Monos Formation is composed of quartz as the prevalent mineral (between 50% and 90%; 74% in average); followed by clay in varied abundance (10-40%; 18% in average), while plagioclase (5-10%; 6% in average) and potassium-feldspars (always subordinate to the previous ones) are less frequents. Calcite, pyrite and traces of dolomite, siderite and clinoptilolite can appear in very low concentrations (<5%). The clay-fraction (<2um) is characterized on average by illite (47%), with subordinate and variable percentages of mixed-layer of IS (17%), chlorite (20%) and kaolinite (16%).

In the Los Monos Formation four clay mineral assemblages are characterized based on the presence, type and relative amount of the clay minerals. These assemblages are present in all of the analysed sections. A synthesis of the mineralogical characteristics and stratigraphic location of each assemblage is exposed in Table 2-7, and representative X-ray diffraction patterns of the <2 um fraction are illustrated in Fig. 7.

The illite+chlorite assemblage (I+Ch; 62 samples; Fig. 7A): is characterized by the presence of illite in more than 38%, varying from 38 to 65% in average 51% and accompanied by chlorite (14-45%; 24% in average) and in less proportion the mixed-layer illite-smectite (3-33%; 18% in average) and kaolinite (0-20%; 7% in average).

The chlorite+illite assemblage (Ch+I; 6 samples; Fig. 7B) shows the highest chlorite contents (42-57%; 47% in average) accompanied by variable illite contents (36-41%; 38% in average), IS (12-19%; 15% in average) and kaolinite is almost absent with the exception for a sample with 1%.

The illite+kaolinite assemblage (I+K; Fig. 7C): differs of I+Ch assemblages by the higher proportion of kaolinite (18-38%; 26% in average), recognized in 35 samples which also have illite (39-55%; 48% in average) and similar proportions of chlorite (2-23%) and IS (2-22%).

The kaolinite+illite assemblage (K+I; 15 samples; Fig. 7D): differs of I+K assemblages by a higher proportion of kaolinite (33-49%; 41% in average)

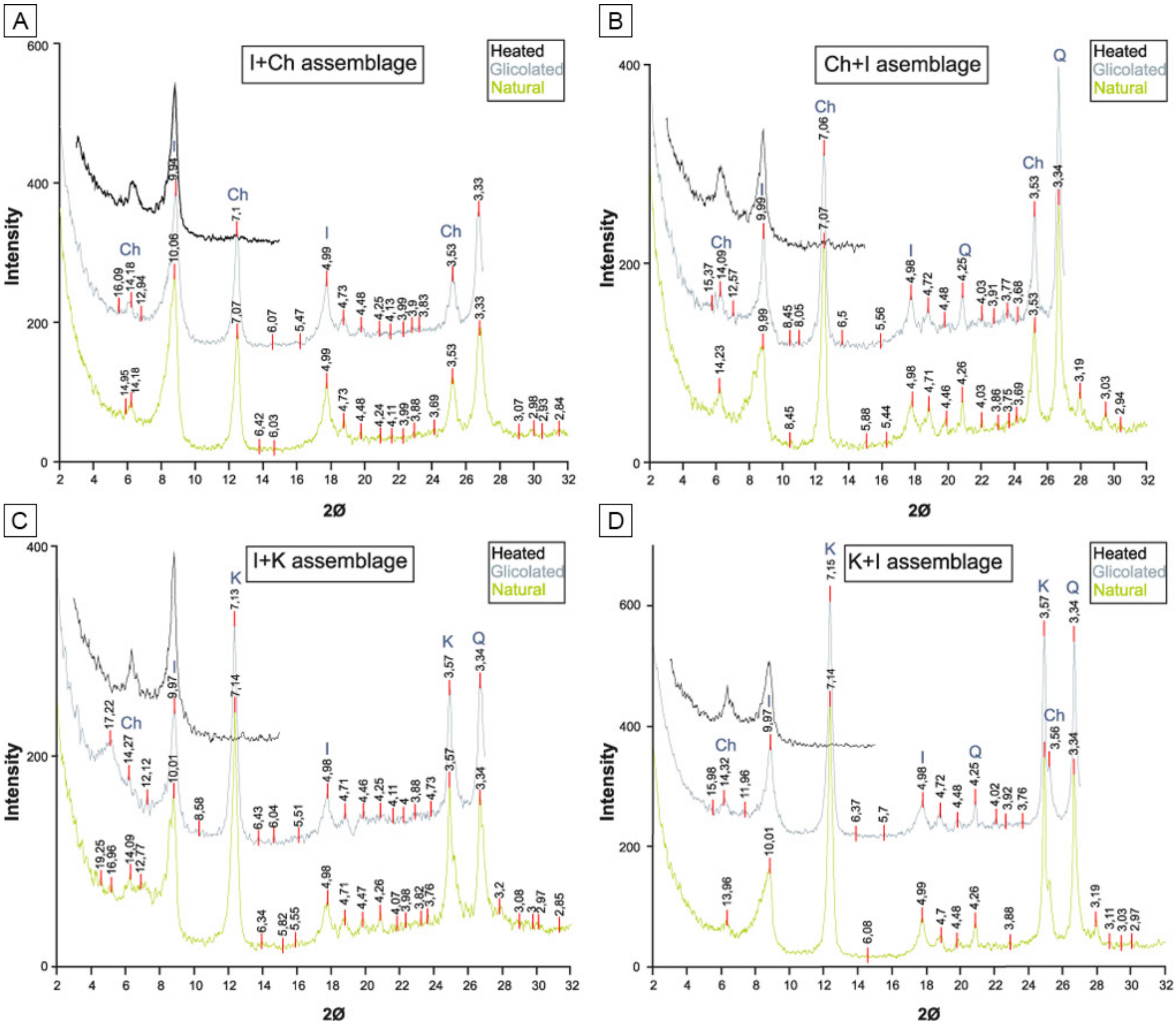


Figure 7. X-ray diffractograms of the clay assemblages from Los Monos Formation. **a)** Illite+Chlorite assemblage (I+Ch). **b)** Chlorite+Illite assemblage (Ch+I). **c)** Illite+Kaolinite assemblage (I+K). **d)** Kaolinite+Illite assemblage (K+I).

compared with illite (13-43%; 32% in average) and similar proportions of chlorite (5-36%; 14% in average) and IS (7-32%; 13% in average).

Clay minerals are species sensitive to diagenetic changes (de Segonzac, 1970) and some of the most used criteria in defining the postdepositional processes intensity are based on the analysis of the crystallinity of the illite and percentage of expansive layers on the mixed-layer I/S. The participation of illite in the mixed-layer IS structure increases as the degree of burial diagenesis increases (Fóscolos *et al*., 1976).

Based on the measurement of the smectite proportion in mixed-layer IS between 20 to 40%, suggest that Los Monos Formation reached advanced diagenesis, from a late-mesodiagenesis stage (Tonono x-1 and Vespucio x-1) to telodiagenesis (Balapuca and Ramos), respectively. These results coincide with gas generation window and final stage of oil generation window, according to Fóscolos *et al*. (1976).

Distribution of clay mineral assemblages of Los Monos Formation

The illite+chlorite assemblage (I+Ch) is present in all of the analyzed sections, it predominates in the Balapuca locality (82% of the 45 analyzed samples), in less proportion in the Vespucio x-1 borehole (34% of the 26 analyzed samples) and less common in the Tonono x-1 borehole (26% of the 25 analyzed samples). Although few samples were analyzed in the Aguas Blancas xp-13 borehole, almost all the samples have this assemblage (71% of the 7 analyzed samples), as in the Ramos xp-1012 borehole (90 % of the 5 analyzed samples). This assemblage is highly variable in the vertical distribution, a decrease is observed towards the base in the Balapuca section and towards the top of the Vespucio x-1 and Tonono x-1 boreholes with an increase in the kaolinite+illite assemblage.

The kaolinite+illite assemblage (K+I) is present in some of the analyzed sections, it predominates in the Tonono x-1 borehole (30% of the 23 analyzed samples), in less proportion in the Vespucio x-1 borehole (8 % of the 26 analyzed samples) and less common in the Balapuca section (13% of the 45 analyzed samples). This assemblage is absent in the Aguas Blancas xp-13, Ramos x-12 and Ramos xp-1012 boreholes. This assemblage is variable in the vertical distribution, an increase is observed towards the base in the Balapuca locality and the top of the Vespucio x-1 and Tonono x-1 boreholes in detriment of the illite+chlorite assemblage. In addition, this assemblage is present in thin beds along the sections.

The illite+kaolinite assemblage (I+K) predominates in the Tonono x-1 borehole (48% of the 23 analyzed samples) and in the Vespucio x-1 borehole (48% of the 26 analyzed samples) and almost absent in the Balapuca section (2% of the 45 analyzed samples). This assemblage is present in all the samples from Ramos x-12 borehole, in less proportion in the Ramos xp-1012 borehole (16% of the 6 analyzed samples) and absent in the Aguas Blancas x-13 borehole. This assemblage has a vertical distribution similar than kaolinite+illite assemblage.

The chlorite+illite assemblage (Ch+I) is poorly represented in the sections. It is present in the Vespucio x-1 borehole (11% of the 26 analyzed samples), in the Aguas Blancas xp-13 borehole (29% of the 7 analyzed samples) and 1 sample in the Tonono x-1 borehole (4% of the 23 analyzed samples).

Therefore, in the west-east regional section is observed that the content of illite and chlorite (I+Ch assemblage) increases towards the west of the basin (Balapuca section), while the kaolinite content (K+I and I+K assemblage) has an inverse behaviour. Vertically, the distribution of clay assemblage is highly variable, an increase in kaolinite (K+I assemblage) is observed towards the base of Balapuca and the top of the Vespucio x-1 and Tonono x-1 boreholes, in detriment of illite and chlorite (I+Ch assemblage).

Finally, the clay mineral assemblage was analyzed in the Jollín and Michicola Formations, over and underlying units of the Tonono Formation in Tonono x-1 borehole, respectively. The Jollín Formation presents the assemblage of kaolinite+illite (K+I), while the Michicola Formation presents the assemblage of illite+chlorite (I+Ch).

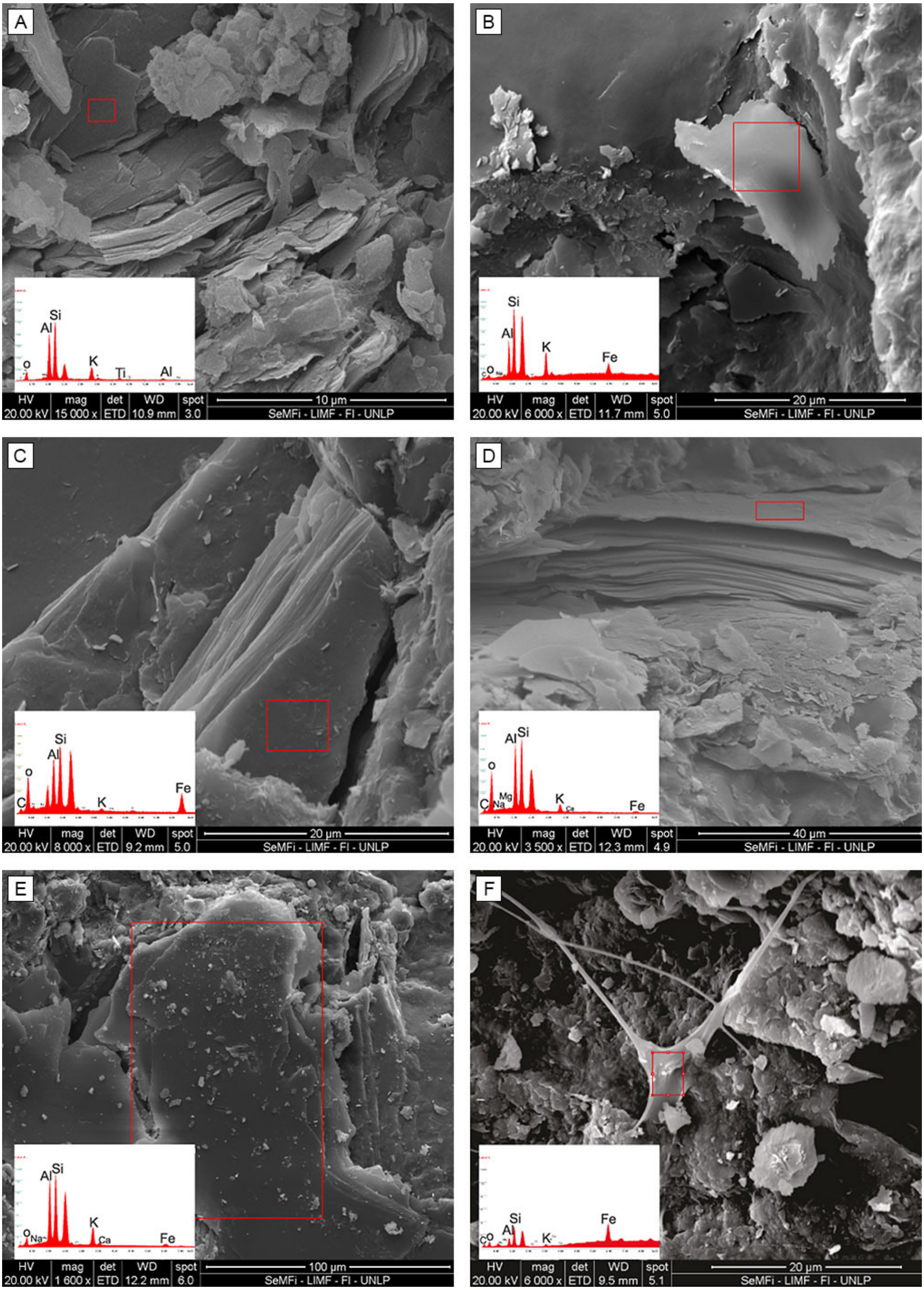
XRD and SEM characterization of clay minerals

Clay mineral micromorphology recognized by SEM analysis shows two types of clays, clays are non-oriented, detrital, with irregular borders and with basal sections (001) lower than 20 **μm (illites) and authi**genic clays, oriented with stacked sheets and some with border dissolution with sizes varying from lower than 10 μm to 100 μm (IS and chlorites), microporosity is observed (Fig. 8). EDAX analyzes of clays of illitic composition (illite and IS; Fig. 8A, B, D and E) show a dominance of Si, Al and K with lower proportions of Fe, Mg and Na and occasionally Ca and Ti. Chlorite is identified in crystals of approximately 20 μm, in which the contents of Fe are higher (Fig. 8C).

Additionally, SEM analyzes reveal that IS clays show thin flakes as the main micromorphology which are ordered according to the 001 faces. The flakes show equidimensional subhedral forms with defined borders in crystals with less than 100 μm. EDAX analyzes show Si and Al as the majority cations, followed by K, Mg and Fe (Fig. 8C). These results are consistent with XRD analyzes.

Organic matter was also identified by SEM (Fig. 8F) and shows intergrown with illite and IS with characteristic morphologies of elongated fibres. In this case, EDAX analyzes show peaks of C of low-intensity accompanied by other peaks from the clays of the rock (Al, Si, K, etc.).

The SEM-EDAX analyzes allow to identify that clays observed in the study have a detrital and authigenic origin, illite shows morphologies and dispositions that may indicate they were transported (Fig. 8B). On the other hand, XRD analysis allows recognizing the illite crystallinity (KI) which are


A
Si
Al
O
K
Ti
Al
HV | mag | det | WD | spot | 10 µm
20.00 kV | 15 000 x | ETD | 10.9 mm | 3.0 | SeMFi - LIMF - FI - UNLP
B
Si
Al
K
Fe
O
HV | mag | det | WD | spot | 20 µm
20.00 kV | 6 000 x | ETD | 11.7 mm | 5.0 | SeMFi - LIMF - FI - UNLP
C
Si
Al
O
C
K
Fe
HV | mag | det | WD | spot | 20 µm
20.00 kV | 8 000 x | ETD | 9.2 mm | 5.0 | SeMFi - LIMF - FI - UNLP
D
Al
Si
O
Mg
C
Na
K
Fe
HV | mag | det | WD | spot | 40 µm
20.00 kV | 3 500 x | ETD | 12.3 mm | 4.9 | SeMFi - LIMF - FI - UNLP
E
Al
Si
O
Na
K
Ca
Fe
HV | mag | det | WD | spot | 100 µm
20.00 kV | 1 600 x | ETD | 12.2 mm | 6.0 | SeMFi - LIMF - FI - UNLP
F
Si
Al
CO
K
Fe
HV | mag | det | WD | spot | 20 µm
20.00 kV | 6 000 x | ETD | 9.5 mm | 5.1 | SeMFi - LIMF - FI - UNLP

>0.4 related to the diagenetic origin and suggest the presence of polytype 1M. If the Esquevin index is considered, most of the samples are located in the field of aluminous illites.

On the other hand, the position of the main peaks of chlorite is in agreement with iron-rich chlorite type and polytypes observed are similar to those of low temperature during diagenesis (Fig. 8B). On the other hand, chlorite is observed filling pores with moderate crystallinity growth (Fig. 8C). Thus, IS is also observed in staggered arrangements according to a predominant orientation of the IS flakes in the pores (Fig. 8A, D and E). In these cases, it suggested that Ch, as IS, had an authigenic origin during burial diagenesis although the existence of detrital chlorite may not be discarded.

PALYNOFACIES

Alarache and Balapuca

The palynomorphs recorded in the Los Monos Formation, of late Eifelian to early Givetian age (Devonian) (Alarache) and late Eifelian to early-middle Givetian age (Balapuca), are predominantly terrestrial, with very few marine components, represented by organic-walled phytoplankton and indeterminate chitinozoans fragments. In general, its preservation is fair to poor.

The palynofacies analysis shows the predominance of lignohumic or inertinite components through the section, indicating a clear terrestrial contribution in low preservation conditions. The lignohumic facies reaches up to 70%, the inertinite up to 45%, while the liptinic generally constitutes 10% and can reach 15%.

Angosto del Pescado

In the samples from Huamampampa Formation, of late Eifelian-earliest Givetian age, the palynomorphs are well diversified and their preservation is moderate to poor. The analysis of the palynofacies shows the predominance of the lignohumic facies (up to 50%) followed by the algal facies (up to 40%). The liptinic facies may reach 15%, similar to the inertinite.

In the samples corresponding to the Los Monos Formation, of early-middle Givetian age, the palynomorphs present a moderate to poor preservation. A marked predominance of the lignohumic facies (75%) is observed, with the liptinic (15%), and inertinite (10%) subordinate.

Ramos area

In the Ramos area, the Ramos xp-1012, Ramos x-1002 and Ramos x-1011 boreholes were analyzed. In the Ramos xp-1012 borehole, in transition over the Los Monos Formation, the lower part of the Iquiri Formation (1050-1120 mbgs), of late Givetian-earliest Frasnian age is observed. The marine participation is important, the phytoplankton is diverse and dominate palynological associations. Palynomorphs show fair to good preservation. The lignohumic facies constitutes 40-50%, the algal facies 20-30%, inertinite 20-30% and the liptinic 5%.

In the same Ramos xp-1012 borehole, a side-track (Ramos 1012-ST1) was made that comprises the upper part of the Los Monos Formation (4975-5035 mbgs), early to middle Givetian in age. The palynomorphs are diverse and well preserved. The lignohumic facies predominate 50-60%, followed by inertinite 20-30%, liptinic 10-15% and algal 5-10%.

In the Ramos x-1002 borehole, in the upper part of the Los Monos Formation (2704 to 2780 mbgs), of early to middle Givetian age, the palynofacies are distributed in lignohumic 60-70%, liptinic 10-20%, algal facies 5-15% and inertinite 10%. Downwards (2780 to 3106 mbgs), in the early-middle Givetian levels, the lignohumic facies predominates 50-65%, followed by inertinite 15-35%, liptinic 10-20% and algal 1-5%. In the lower part of the Los Monos Formation (3156 to 3206 mbgs), of possible late Eifelian- early Givetian age, few poorly preserved palynomorphs are observed. The inertinite

Figure 8. SEM microphotographs and EDAX results. **a)** IS mixed layers with stacked sheets. **b)** illites, photos show high fragmented clays of illite with variable size, irregular borders and without a preferential order. **c)** Authigenic chlorites appear as stacked sheets with border dissolution. **d)** Authigenic IS mixed layers with stacked sheets and clay microporosity. **e)** Authigenic IS mixed layers with stacked sheets and border dissolution. **f)** elongated fibres of organic composition over a detrital clay mixture. The red area indicates the area measured by EDAX analysis of major elements.

facies predominates 70-85%, the lignohumic one constitutes the remaining percentage: 15 -30%.

Immediately below, in the upper part of the Huamampampa Formation (3206 to 3230 mbgs), of probable late Eifelian- early Givetian age and the interval of 3230 to 3280 mbgs, of possible Eifelian age, the facies are mainly distributed in lignohumic 45% and inertinite 50%. The preservation of the palynomorphs is moderate to poor in all the sections studied.

In the Ramos x-1011 borehole, the upper part of the Los Monos Formation (1080 to 1330 mbgs), of early-middle Givetian age, the preservation of the palynomorphs is moderate to poor and the predominant facies is the lignohumic 65-75%, followed by liptinic 20-30% and algal and inertinite in the same proportion 0-10%.

In the middle levels (1400 to 2520 mbgs), of early to middle Givetian age, the preservation of palynomorphs is moderate to poor and the predominant facies is lignohumic 70-80%, followed by inertinite 10-20% and liptinic 5-15%

BIOSTRATIGRAPHY

Alarache

Two assemblages are distinguished, a younger one among whose most relevant spores are *Geminospora lemurata* Balme emend. Playford, *Geminospora punctata* Owens, *Rhabdosporites parvulus* Richardson, *Verrucosisporites scurrus* (Naumova) McGregor and Camfield, *Cymbosporites catillus* Allen, *Archaeozonotriletes variabilis* Naumova emend. Allen, *Grandispora douglastownense* McGregor, *Biharisporites parviornatus* Richardson, *Verruciretusispora ornata* Menendez and Pöthe de Baldis emend. Perez Leytón and *Convolutispora disparilis* Allen. These spores correspond to AD Lem Association (Perez Leytón, 2007), of early Givetian age. The spore assemblage is correlated with the Interval Zone *Geminospora lemurata-Chelinospora* ex gr. *ligurata* (LLi), of early Givetian age formerly established for Brazil and applicable to western Gondwana (South America) (Melo and Loboziak, 2003); the lower part of the *lemurata-magnificus* Assemblage Zone of Euramerica (Richardson and McGregor, 1986), the Lem Interval Zone, within the upper part of the Oppel *acanthomammillatus-devonicus* (AD) Zone of western Europe (Streel *et al*, 1987) and the *Geminospora lemurata* Interval Zone, from the *Geminospora lemurata* – *Rhabdosporites langii* Assemblage Zone of northwestern Gondwana (Breuer and Steemans, 2013) (Fig. 9).

The oldest assemblage contains *Geminospora lemurata* “early form” Marshall, *Geminospora punctata* Owens, *Grandispora douglastownense* McGregor and *Acinosporites* cf. *acanthomammillatus* Richardson. This corresponds to the *Geminospora lemurata* “early form” Local Association (Perez Leytón, 2007), restricted to the Eifelian-Givetian limit. It is correlated with the Oppel AD Zone of western Europe, pre-Lem (pre lemurata), assigned to the late Eifelian-early Givetian (Streel *et al*., 1987) and the *Grandispora permulta* Interval Zone (Per), of western Gondwana (Fig. 9).

Angosto del Pescado

In its lower part, the Huamampampa Formation could be present. It contains *Acinosporites acanthomammillatus* Richardson and other spores compatible with the Pre Lem AD Association (Perez Leytón, 2007) assigned to the late Eifelian-earliest Givetian. The spore assemblage is correlated with the Oppel AD Zone of Western Europe, pre-Lem (pre lemurata), assigned to the late Eifelian-early Givetian (Streel *et al*., 1987), the *Grandispora permulta* Interval Zone (Per), of Western Gondwana, although it does not present its characteristic species. Among the chitinozoans, it is worth to remark the presence of *Alpenachitina eisenacki* Dunn & Miller, of Eifelian-earliest Givetian age, eponymous species of the *eisenacki* Association Perez Leytón (2007). It correlates with the *Alpenachitina eisenacki* Interval Zone, defined for Western Gondwana, which extends from the late early Eifelian to the early Givetian (Grahn, 2005) (Fig. 9).

At the middle levels, corresponding to the Los Monos Formation, the presence of *Geminospora lemurata Verruciretusispora ornata*, *Grandispora gabesensis* and *Grandispora douglastownense*, is compatible with the Association AD Lem of Perez Leytón (2007), early Givetian in age. This association correlates with the spore zones of Euramerica, Western Europe and western Gondwana mentioned above. The chitinozoans *Ramochitina boliviensis* Grahn, *Ancyrochitina biconstricta* (Lange) and *Ancyrochitina escalaensis* Perez Leytón *nomen nudum*, the two latter eponymous species of Local

Association Perez Leytón (2007) confirm the age, suggesting a gradual transition towards the middle Givetian (Fig. 9).

In the upper part of the section, the presence of *Geminospora lemurata*, *Chelinospora ligurata*, *Verrucosisporites premnus* Richardson, *Verrucosisporites scurrus*, *Grandispora mammillata*, *Raistrickia aratra* Allen, is congruent with the upper part of the Association AD Lem of Perez Leytón (2007), early to middle Givetian in age. This spore assemblage is correlated with the aforementioned Euramerican, Western Europe and Western Gondwana spore zones (Fig. 9).

Balapuca

Among the most relevant species are *Geminospora lemurata* Balme emend. Playford, *Geminospora punctata* Owens, *Rhabdosporites parvulus* Richardson, *Verrucosisporites scurrus* (Naumova) McGregor and Camfield, *Cymbosporites catillus* Allen, *Acinosporites macrospinosus* Richardson, *Archaeozonotriletes variabilis* Naumova emend. Allen, *Grandispora* cf. *mammillata* Owens, *Grandispora douglastownense* McGregor, *Biharisporites parviornatus* Richardson and *Verruciretusispora ornata* Menendez and Pöthe de Baldis emend. Perez Leytón. These spores are present in the upper part of the AD Lem Association of Perez Leytón (2007), of early to middle Givetian age. The assemblage of spores is correlated with the *Geminospora lemurata*-*Chelinospora* ex gr. *ligurata* (Lli) Interval Zone, from Western Gondwana (Melo and Loboziak, 2003) and with the spore zones of Euramerica, Western Europe and northwestern Gondwana mentioned above. The chitinozoans present correspond to the *escalaensis* Local Association (Perez Leytón, 2007), of middle Givetian age (Fig. 9).

The lower levels contain spores such as *Geminospora lemurata* “early form” Marshall, *Geminospora punctata* Owens and *Samarisporites eximius* (Allen) Loboziak and Streel, which correspond to the *Geminospora lemurata* “early form” Local Association (Perez Leytón, 2007), assigned to the Eifelian-Givetian boundary (Fig. 9).

Ramos

In the Ramos area, the Ramos xp-1012, Ramos x-1002 and Ramos x-1011 boreholes were analyzed. In the Ramos xp-1012 borehole, transitionally overlying the Los Monos Formation, the lower part of the Iquiri Formation is observed (1050-1120 mbgs). It contains *Samarisporites triangulatus* Allen, *Cymbosporites catillus* Allen, *Cymbosporites cyathus* Allen and other concomitant species, which confirm the correspondence with the Associations TA-TCo of Perez Leytón (2007), late Givetian- earliest Frasnian in age. This association is correlated with the *Samarisporites triangulatus* (Trg), Interval Zone from the late early Givetian-earliest Frasnian, of western Gondwana (Melo and Lobozoiak, 2003). *Samarisporites triangulatus*, is the eponymous species of the *optivus-triangulatus* Zone, of the late Givetian-early Frasnian of Euramerica (Richardson and McGregor, 1986), the *S. triangulatus*- *A. ancyrea* (TA) Oppel Zone, of the middle Givetian from Western Europe (Streel *et al*., 1987) and the *triangulatus-catillus* Assemblage Zone, *triangulatus* subzone, of the middle Givetian of northwestern Gondwana (Breuer and Steemans, 2013) (Fig. 9).

The marine participation is important, the phytoplankton is diverse and dominate palynological assemblages. The species *Leifusa bisubulata* Brito and Quadros, *Maranhites brasiliensis* Brito, *Maranhites stockmansii* Martin emend. Martin, *Umbellasphaeridium deflandrei* Moreau-Benoît ex Jardiné *et al*., *Duvernaysphaera radiata* Brito and other concomitant species, correspond to the *bisubulata* and “Zone C not Defined” associations of Perez Leytón (2007) confirming the Givetian – earliest Frasnian age (Fig. 9).

In the same Ramos xp-1012 borehole, a sidetrack was made (Ramos 1012-ST1), that comprises the upper part of the Los Monos Formation (4975-5035 mbgs). The presence of *Geminospora lemurata*, *Cymbosporites cyathus*, *Cymbosporites catillus*, *Rhabdosporites parvulus*, *Verrucosisporites scurrus*, *Verrucosisporites premnus* and *Raistrickia aratra* matches with the upper part of the Association AD Lem de Perez Leytón (2007), of early to middle Givetian age, correlatable with the Interval Zone Lli, assigned to the early Givetian (Fig. 9).

In the Ramos x-1002 borehole, in the upper part of the Los Monos Formation (2704 to 2780 mbgs), *Geminospora lemurata*, *Verrucosisporites scurrus*, *Verrucosisporites premnus*, *Raistrickia aratra*, *Cymbosporites catillus*, *Archaeozonotriletes variabilis* and *Rhabdosporites parvulus* constitute the spore assemblage. This assemblage corresponds

Species	**Alarache**	**A. Pescado**	**Balapuca**	**R. xp-1012**	**R. x-1002**	**R. xp-1011**	**1**	**2**	**3**	**4**
Cymbosporites catillus				X			**TA-Tco** (late Givetian- earliest Frasnian)	Iquiri	To3	Trg
Cymbosporites cyathus				X						
Samarisporites triangulatus				X						
Duvernaysphaera radiata				X			***L. bisubulata*** **Association C not defined** (late Givetian- earliest Frasnian)			
Leifusa bisubulata				X						
Maranhites brasiliensis				X						
Maranhites stockmansii				X						
Umbellasphaeridium deflandrei				X						
Acinosporites macrospinosus			X				**AD Lem** upper part (early-middle Givetian)	Los Monos	To2	Lli
Archaeozonotriletes variabilis			X							
Biharisporites parviornatus			X							
Cymbosporites catillus			X							
Geminospora lemurata			X							
Geminospora punctata			X							
Grandispora douglastownense			X							
Grandispora cf. *mammillata*			X							
Rhabdosporites parvulus			X							
Verruciretusispora ornata			X							
Verrucosisporites scurrus			X							
Ancyrochitina cf. *escaleraensis*			X				**A. escaleraensis** (middle Givetian)			
Chelinospora ligurata						X	**AD Lem** upper part (early-middle Givetian)			
Geminospora lemurata						X				
Grandispora mammillata						X				
Verrucosisporites scurrus						X				
Arkonites bilixus						X	**Association C not defined** (middle-late? Givetian)			
Maranhites brasiliensis						X				
Chelinospora ligurata		X					**AD Lem** (early-middle Givetian)			
Geminospora lemurata		X								
Grandispora douglastownense		X								
Grandispora gabesensis		X								
Grandispora mammillata		X								
Verruciretusispora ornata		X								
Raistrickia aratra		X								
Verrucosisporites premnus		X								
Verrucosisporites scurrus		X								
Ancyrochitina escaleraensis		X					***A. escaleraensis*** (early-middle Givetian) ***A. biconstricta***			
Ancyrochitina biconstricta		X								
Ramochitina boliviensis		X								
Cymbosporites catillus				X	X		**AD Lem** (early-middle Givetian)			
Cymbosporites cyathus				X						
Geminospora lemurata				X	X					
Raistrickia aratra				X	X					
Rhabdosporites parvulus				X	X					
Verrucosisporites premnus				X	X					
Verrucosisporites scurrus				X	X					
Archaeozonotriletes variabilis					X					

continuation...

Species	Alarache	A. Pescado	Balapuca	R. xp-1012	R. x-1002	R. xp-1011	1	2	3	4
Ancyrochitina biconstricta					X		***A. biconstricta*** (early-middle Givetian)	Los Monos	To2	Lli
Ramochitina ramosi					X					
Acinosporites lindlarensis						X	**AD Lem** (early-middle Givetian)			
Acinosporites macrospinosus						X				
Geminospora lemurata						X				
Verruciretusispora ornata						X				
Verrucosisporites scurrus						X				
Ancyrochitina biconstricta						X	***A. biconstricta*** (early-middle Givetian)			
Ancyrochitina langei						X	(early-middle Givetian)			
Ramochitina ramosi						X				
Ramochitina sp. cf. *stiphrospinata*						X				
Cymbosporites catillus	X						**AD Lem** (early Givetian)			
Archaeozonotriletes variabilis	X									
Biharisporites parviornatus	X									
Convolutispora disparilis	X									
Geminospora lemurata	X									
Geminospora punctata	X									
Grandispora douglastownense	X									
Rhabdosporites parvulus	X									
Verruciretusispora ornata	X									
Verrucosisporites scurrus	X									
Geminospora lemurata “early form”	X		X				***Geminospora lemurata* “early form”** (late Eifelian-early Givetian)		To1	Per
Geminospora punctata	X		X							
Grandispora douglastownense	X									
Acinosporites cf. *acanthomammillatus*	X									
Samarisporites eximius			X							
Ramochitina candelariaensis					X		***R. candelariaensis*** (late Eifelian-early Givetian)			
Acinosporites acanthomammillatus		X					**AD pre Lem** (late Eifelian-early Givetian) ***A. eisenacki***	Huamampampa	To1	Per
Alpenachitina eisenacki		X								
Geminospora cf. *lemurata*					X		(late Eifelian-early Givetian?)			
Alpenachitina esenacki					X					
Acinosporites acanthommamillatus					X		(Eifelian?)			
Grandispora verrucosa					X					

Figure 9. Stratigraphic distribution of terrestrial and marine palynomorphs from the studied localities. From west to east (left to right). Bioestratigraphy: 1- Bolivia (Perez Leytón, 2007); 2- stratigraphic units herein analysed; 3- associations of Noetinger (2010); 4- spore biozones from western Gondwana (Melo and Loboziak, 2003).

to the upper part of the Association AD Lem de Perez Leytón (2007), early to middle Givetian in age, correlatable with the Lli Interval Zone, from the early Givetian (Fig. 9). Immediately below (2780 to 3106 mbgs), the spores correspond to the AD Lem Association of the early Givetian, correlatable with the LLi Interval Zone, of the same age. Marine palynomorphs are scarce, with the relevant presence of the chitinozoans *Ancyrochitina biconstricta* (Lange) and *Ramochitina ramosi* Sommer and Van Boekel, which support the Givetian age (Fig. 9).

In the lower part of the Los Monos Formation (3156 to 3206 mbgs), there are few palynomorphs, poorly preserved, which do not allow a precise dating. The presence of the chitinozoan *Ramochitina candelariaensis* Perez Leytón *nomen nudum* (Perez Leytón, 2007), the eponymous species of the *candelariaensis* Local Association proposed by this author, which is usually found associated with *Alpenachitina eisenacki* Dunn and Miller and *Ancyrochitina postdesmea* Grahn, would suggest a late Eifelian - early Givetian age. Immediately below, in the upper part of the Huamampampa Formation (3206 to 3230 mbgs), the presence of *Geminospora* cf. *lemurata* and *Alpenachitina esenacki* suggest a probable late Eifelian-early Givetian age. The interval below, 3230 to 3280 mbgs, is doubtfully assigned to the Eifelian due to the presence of *Acinosporites acanthommamillatus* Richardson and *Grandispora verrucosa* (Richardson) McGregor (Fig. 9).

In the Ramos x-1011 borehole, the upper part of the Los Monos Formation (1080 to 1330 mbgs) corresponds to the upper part of the AD Lem Association of early to middle Givetian age, correlatable with the Lli Interval Zone, early Givetian in age, due to the presence of the spores *Geminospora lemurata*, *Chelinospora ligurata*, *Grandispora mammillata* and *Verrucosisporites scurrus*. Among the marine phytoplankton, *Arkonites bilixus*, *Maranhites brasiliensis* and other concomitant species of the Association C not Defined of Perez Leytón (2007), support a middle Givetian age. Among chitinozoans, the presence of *Ancyrochitina biconstricta*, the eponymous species of the *biconstricta* Local Association confirms this age (Fig. 9).

The middle levels (1400 to 2520 mbgs) correspond to the Association AD Lem, of early to middle Givetian age, correlatable with the Lli Interval Zone, of early Givetian age, based on the presence of the spores *Geminospora lemurata*, *Verrucosisporites scurrus*, *Verruciretusispora ornata*, *Acinosporites lindlarensis* and *Acinosporites macrospinosus*. The chitinozoans *Ancyrochitina langei* Sommer and Van Boekel, *Ramochitina ramosi*, *Ramochitina* sp. cf. *stiphrospinata* support this age (Fig. 9).

DISCUSSION

Facies associations

Based on sedimentological and ichnological characteristics, the Los Monos Formation is interpreted as deposited in shallow to outer shelf paleoenvironment, on a siliciclastic shelf with alternating deposits of fair and storm weather conditions, as suggested by previous interpretations (Arispe and Díaz-Martínez, 1995; Starck, 1995; Vistalli, 1999; Albariño *et al*., 2002; Dalenz-Farjat *et al*., 2002; Álvarez *et al*., 2003).

In a core section of the upper-middle part of the Tonono Formation in the Tonono x-1 borehole (3366.5 mbgs) is observed a low abundance of traces fossil, low ichnodiversity, a reduction in the size of the traces and sedimentary structures of salinity fluctuation (siderite bands and syneresis cracks), indicating a brackish- water marginal-marine paleoenvironment, possibly an open-bay.

Deposits of offshore-transition to lower offshore were described “distal” Cruziana ichnofacies, even in well-oxygenating deposits, where a diverse *Cruziana* ichnofacies could be expected. On the other hand, deposits of brackish-water marginal-marine (open-bay) were described the “depauperate” *Cruziana* ichnofacies, although both deposits have a similar degree of bioturbation and ichnodiversity, as previously suggested by MacEachern *et al*. (2007).

Low degree of bioturbation and low ichnodiversity of the well-oxygenation deposits could be related to the decline of the Malvinokafric fauna due to the Kačák extinction event of the late Eifelian (Isaacson, 2007; Bosetti *et al*., 2010). During this event, the Malvinokafric fauna was reduced from 65 genera to 8 genera, with a high abundance of individual taxa and a reduced size of the surviving taxa (Bosetti *et al*., 2010).

It is also interesting to note that paleoenvironmental conditions could have been stressed, possibly by eustatic changes (relative rise and fall sea level) and/or climatic (fair and storm weather conditions)

(Albariño *et al.*, 2002; Dalenz-Farjat *et al.*, 2002; Álvarez *et al.*, 2003). Another less possible reason could be tectonic changes that occurred during sedimentation (Díaz-Martínez *et al.*, 1996).

Clay mineral assemblages

The mineralogical analysis of the whole rock of the Los Monos Formation shows significant amounts of quartz, accompanied by a low amount of plagioclase and a low to absent proportion of potassium feldspars, which suggests that the granite rocks of the granitic basement (Puna Arc) were an important source-rock. Clay-fraction contains (XRD) quartz, feldspars and clay minerals (illite, illite/smectite, chlorite and kaolinite). The argillominerals present are polygenetic; some of the species could be products of chemical and/or physical weathering of the basement and subsequent detrital mobilization towards the basin. This could be the case of kaolinite for the alteration of the feldspars, volcanic lithics (Chamley, 1997) and weathering of micaceous siltstone (Zeballos *et al.*, 2016). Chemical weathering of pre-existing clay minerals, probably illite and minor proportion chlorite, could also have led to the formation of kaolinite.

The presence of kaolinite within marine deposits could be an indicator of transgressive events (Chamley, 1997; Holanda *et al.*, 2019; Aparicio González *et al.*, 2020). In the present study, a good correlation is observed between the increase in kaolinite (K+I and I+K assemblages) and the transgressive events of the second and third-order eustatic model defined by Albariño *et al.* (2002) (Fig. 10). In the Vespucio x-1 borehole, it is observed that the K+I and I+K clay assemblages coincide with the transgressive system tracks (TST) while I+Ch and Ch+I assemblages coincide with the highstand system tracks (HST) (Fig. 10). On the other hand, in the Tonono x-1 borehole, the presence of the K+I and I+K assemblages is observed towards the top of the unit, where a transgressive event of late Givetian-earliest Frasnian is recognized (Albariño *et al.*, 2002; Noetinger, 2010) (Fig. 10). In the Balapuca section, the presence of these assemblages is observed towards the base of the unit, where a transgressive event of late Eifelian-early Givetian is also recognized (Albariño *et al.*, 2002) (Fig. 10). Furthermore, thinner levels of the kaolinite assemblages could coincide with transgressive events of a lower order (third-order genetic-sequences) (Albariño *et al.*, 2002) (Fig. 10).

From a paleoclimatic point of view, kaolinite is under near-surface/meteoric conditions and at a regional scale is correlated to warm and humid paleoclimatic conditions (Do Campo *et al.*, 2018). The paleoclimate described for this portion of the basin located at paleolatitudes greater than 60 ° is temperate-cold during the Devonian (Scotesse *et al.*, 1999; di Pasquo *et al.*, 2009), but the presence of kaolinite could indicate the alternation of warm and humid conditions. The kaolinite was previously described in Lower and Middle Devonian rocks of the Villa Villa Formation and Sica Sica Formation, in the Bolivia Altiplano (La Paz; Zeballos *et al.*, 2016) in Devonian Mississippian deposits of the Toregua Formation, north of Bolivia (Koltonik *et al.*, 2019) and Paraná Basin (Cordobés and Cerrezuelo Formations, Uruguay; Uriz *et al.*, 2016).

Regarding the illite (I+Ch assemblages), the presence of the illite 1M polytype and the recognition of diagenetic mixed-layer I/S, as well as its increase towards the base of the studied section, could confirm the existence of processes of neoformation by the diagenetic transformation from smectite to illite, a fact frequently documented in various sedimentary successions (Aoyagi and Kazama, 1980; Spalletti and Iñiguez, 1981). Given the above, it is deduced that illite/smectite and at least part of the illite have been the product of diagenetic transformation (Fóscolos *et al.*, 1976; Hower *et al.*, 1976). The detrital origin of the illite could be related to the physical weathering of the metamorphic and granite rocks of the basement.

Regarding chlorite (Ch+I assemblages), although diagenetic chlorites are observed, these could also have a detrital origin. The diagenetic origin could be linked to the formation of mesogenetic chlorite after the release of Fe, Mg and Si during the passage from smectite to illite. The presence of the mixed-layer Ch/S suggests that some chlorite could be neoformed by mesodiagenetic modification of smectite rich in Fe and Mg.

Based on direct organic geochemistry information from vitrinite reflectance and pyrolysis rock eval of Los Monos Formation (Disalvo and Villar, 1999), the maturation values indicate a lower diagenetic degree, within the oil generation window, for the boreholes studied. These differences between inorganic thermal maturity indicator (Sm% in mixed-layer IS) and organic thermal maturity indicators (Ro and

Pyrolysis Rock-Eval) could be related to retardation phenomena of the vitrinite reflectance due to the overpressure of the unit during maturation (Veizaga-Saavedra *et al.*, in preparation).

Palynofacies

In the western sector of the basin (basin edge), in the Alarache and Balapuca sections, the sedimentary successions of the late Eifelian-early-middle Givetian show a dominance of terrestrial palynomorphs. The same is observed in the sequences from the early-middle Givetian of the Ramos area (Ramos x-1012 and Ramos x-1011) and sequences from the late Eifelian to early-middle Givetian from the Ramos x-1002 borehole (Fig. 10). The dominance of terrestrial palynomorphs in the late Eifelian-early Giveitan interval is observed in other sedimentary records from the western sector of the basin (Sierra de Zenta, Balapuca; di Pasquo, 2007a; Noetinger and di Pasquo, 2010). However, in the locality of Balapuca, a transgressive event is described towards the base of the Los Monos Formation, dated as late Eifelian-early Givetian (Albariño *et al.*, 2002; Álvarez *et al.*, 2003; Vistalli *et al.*, 2005). Towards the south of Balapuca, in the Angosto del Pescado section, a higher proportion and diversity of marine palynomorphs is observed in the late Eifelian-earliest Givetian sequences (40% of algal facies) (Fig. 10). Other authors recognize the same trend (Noetinger *et al.*, 2018).

Further east (centre of the basin), in the Santa Victoria x-1 borehole, an increase of marine palynomorphs is noticed towards the late Eifelian-early Givetian (Noetinger, 2015), similar to what is observed in the Pimenteira Formation of the Parnaíba basin (Soares *et al.*, 1978) and the shales of the top of the São Domingos Formation in the Paraná basin (Grahn *et al.*, 2013). The increase of marine palynomorphs towards the late Eifeilian-early Givetian is observed in Bolivia by Troth *et al.* (2011). These authors recognized an epibole (peak of abundance) of *Evittia sommerii* related to a transgressive event at the base of the Los Monos Formation (upper Eifelian-lower Givetian) and correlated it to the Kačák transgressive event (Bosetti *et al.*, 2010). In the Tacobo TCB X-1001 borehole, located in the Sub-Andean region of Bolivia, an important predominance of marine palynomorphs (70%) is observed at the base of the Los Monos Formation, assigned to the Eifelian? - Early Givetian? (García Muro *et al.*, 2020).

Towards the Givetian-earliest Frasnian, in the Ramos x-1012 borehole, an increase of marine participation is observed (30% algal facies), the same occurs in the San Antonio x-1 borehole and Tonono x-1 borehole (Noetinger, 2010; Noetinger and di Pasquo, 2011). This coincides with the second-order eustatic model that represents a transgressive and highstand systems tracks for the Middle and Upper Devonian of Bolivia and northwestern Argentina (Fernández-Seveso *et al.*, 1998; Albariño *et al.*, 2002; Álvarez *et al.*, 2003; Miranda *et al.*, 2003). A coeval maximum flooding surface was also recognized in the neighbouring Paraná and Parnaiba basins (Breuer and Grahn, 2011).

The palynofacies described in the Los Monos Formation throughout the studied sections are heterogeneous, with the dominance of terrestrial palynomorphs, as observed by numerous authors (di Pasquo *et al.*, 2009; Noetinger *et al.*, 2010; Noetinger, 2015, among others). Both marine and terrestrial elements point to a shallow marine paleoenvironment, with shoreline shifts. Two transgressive events were recognized in different localities of Argentina, Bolivia and Brazil corresponding to the late Eifelian-early Givetian and the late Givetian-early Frasnian (Fig. 10). The latter contradicts the single transgressive event from the East, interpreted by Noetinger (2015).

Also, it is interesting to note that in the Tonono x-1 borehole, a good correlation is observed between the palynomorphs marine index (PMI) (Noetinger, 2010) and the lithofacies described, where the lowest PMI coincides with an increase in the sandstone beds (facies F4) while the highest PMI values coincide with a predominance of fine material (facies F2 and F1) (Fig. 10).

Finally, the palynomorphs recorded from the base of the Los Monos Formation (late Eifelian-early Givetian) are scarce and low diverse, in coincidence with the characteristics mentioned by Bosetti *et al.* (2010) during the extinction (Kačák event) and post-extinction (“Lilliput effect”) events. Abundance and diversity of palynomorphs are restored after the post-extinction event, during the early Givetian (Bosetti *et al.*, 2010). Finally, from the analysis of the eustatic changes based on palynofacies, stressed environment conditions can be inferred for the Middle-Upper Devonian, which is in agreement with

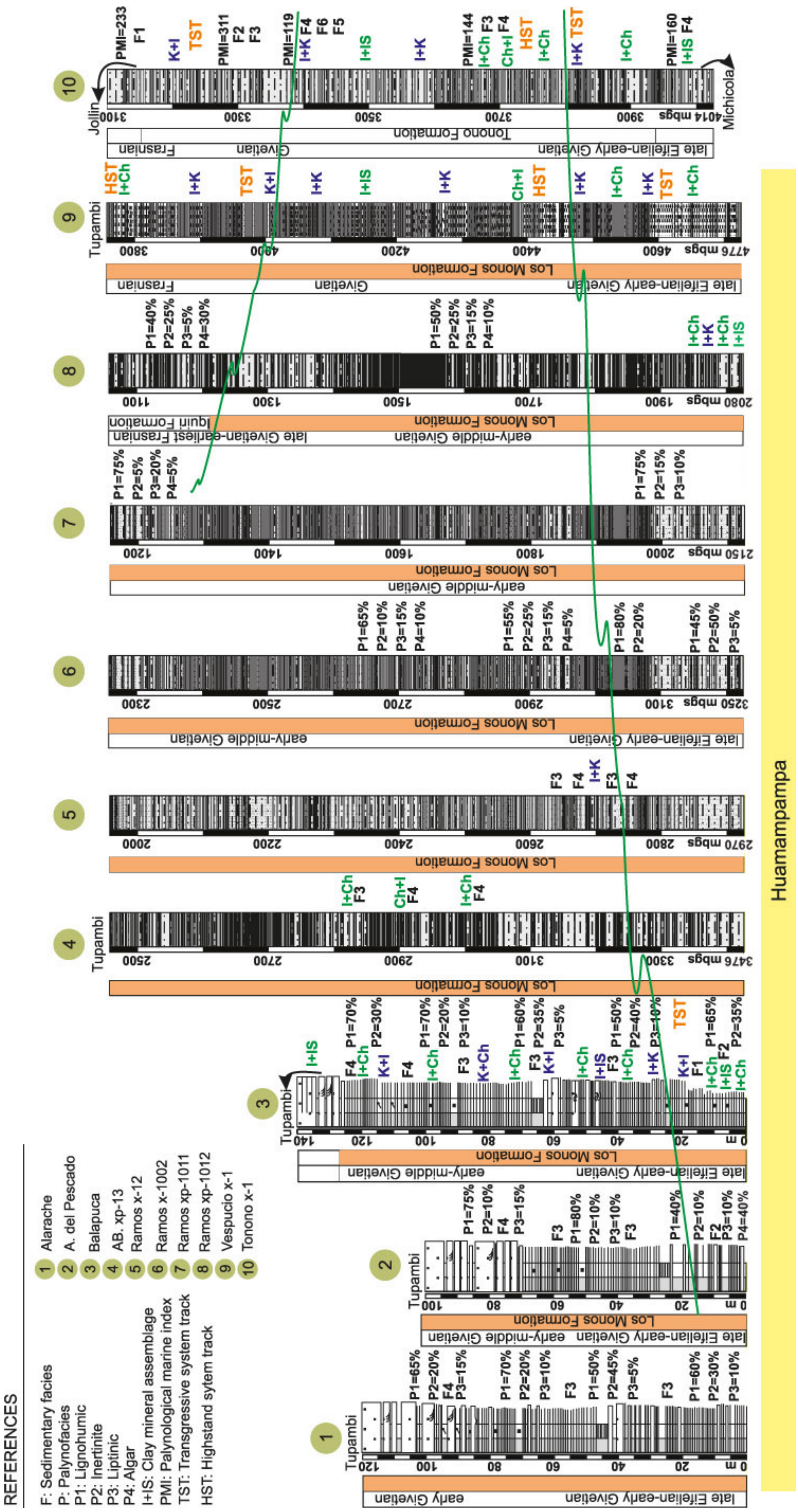


Figure 10. Integration of sedimentary facies, palynofacies and clay mineral assemblages in relation with variations in the relative sea level of the Los Monos Formation. The PMI of the Tonono x-1 borehole are taken from Noetinger (2010) and the stratigraphic-sequential scheme was modified from Albariño *et al*. (2002).

the low abundance and diversity of traces fossil.

Biostratigraphy of Los Monos Formation

The age of the Los Monos Formation in the study area is late Eifelian-early middle Givetian (Fig. 9). The presence of the Iquiri Formation of late Givetian-early Frasnian in the Ramos x-1012 borehole is interpreted based on its lithological characteristics (sandstone predominance) and the age of the palynological assemblages, correlated with those of the Jollín Formation towards the east in the Tonono x-1 borehole (Fig. 9). The most recent contributions propose different ages for the Los Monos Formation. Grahn (2002) suggested an early to middle Givetian age for the lower part of this unit, reaching the early Frasnian at its top in southern Bolivia. On the other hand, Troth *et al*., (2011) indicated an older age for this formation, from the early to late Eifelian, in the southern sub-Andean of Bolivia. di Pasquo *et al*. (2015), interpreted a late Eifelian-early Frasnian age for the Los Monos Formation in the Sub-Andean of Bolivia and Argentina. García Muro *et al*. (2020) propose, for this stratigraphic unit in the Tacobo TCB X-1001 borehole in the sub-Andean of Bolivia, an age that extends from the Eifelian? - Early Givetian to the Middle Givetian, although the samples analyzed could not reach the upper levels of the formation. The discrepancies in the ages interpreted by different authors may be due to the diachronism of the formation across the basin, probably related to the physiography of the basin (Albariño *et al*., 2002).

Based on the Eifelian to early Frasnian ages interpreted for the Los Monos Formation, in this work and previous contributions, from localities such as Balapuca, Angosto del Pescado, Ramos and Tonono x-1, both in western and eastern sectors of the basin, a pre-Carboniferous erosion that removed middle Frasnian to Famennian deposits could be inferred. Finally, the ages of the transgressive events were constrained based on clay mineral assemblages and palynological and palynofacies results of Noetinger (2010), which were correlated with the transgressive events in the Vespucio x-1 borehole (Fig. 10). A probable late Eifelian to earliest Frasnian age was assigned to the Los Monos Formation in the Vespucio x-1 borehole, based on the correlation of the transgressive events with those of the Tonono x-1 borehole (Noetinger, 2010) and the age suggested for the formation in the Quebrada de Galarza borehole (Ottone, 1996), very close to the Vespucio x-1 borehole.

Implications for hydrocarbon exploration

Unconventional hydrocarbon reservoirs such as shale-gas and shale-oil are constituted by rocks with a high content of organic matter (TOC> 2%), thermal maturity in the oil/gas window, fragile (quartz content> 40% and clay content <40%) and capable of producing commercially significant amounts of hydrocarbons with extensive fracture (Jarvie *et al*., 2007; Britt and Schoeffler, 2009; Binnion, 2012). Barnett Shale is a classic example of a shale-type reservoir, giving the best production from areas with 45% quartz and only 27% clays (Bowker, 2007), although the content of clays, quartz, and carbonates is highly variable and these differences result in variable fracture gradients (Bowker, 2007).

The Los Monos Formation is composed mainly of quartz (>70% on average) and a low proportion of clays (<20% on average). Comparatively, the Los Monos Formation has a higher content of quartz than the Barnett Shale and other important North American shale-type reservoirs (Barnett, Marcellus, Woodford, Haynesville, and Doig), so the rocks of the Los Monos Formation could have a clear fragile behaviour according to the classification of Pérez and Marfurt (2014) (Veizaga-Saavedra *et al*., in preparation). Despite its low organic matter content of 1% in average and its moderate to poor quality (original pyrolysis S2 <400 mgHC/gTOC in average) (Disalvo and Villar, 1999) significant volumes of hydrocarbons are dispersed within the shales. This is evidenced by overpressure and manifestations during drilling (Dilsavo and Villar, 1998; Cruz *et al*., 2001; Vistalli *et al*., 2005). The poor generation quality of the shales could be compensated by the significant subsurface thickness (700-1000 m) and the wide areal distribution (Disalvo and Villar, 1999).

Finally, based on the regional characteristics of Los Monos Formation such as thermal maturity in oil/gas window, considerable thickness of 1 km, lateral extension >100 km, overpressured >0.62 psi/ft and mineral composition, it shows some of the necessary attributes to be considered an unconventional reservoir (shale). Additionally, petrophysical and geomechanical properties would contribute to determinate the real potential as shale source play.

CONCLUSIONS

The lithofacial and ichnofacial analysis allowed defining a shallow to outer shelf paleoenvironment for the Los Monos Formation from the shelf to the offshore transition with the recognition of the distal *Cruziana* ichnofacies; a marginal-marine paleoenvironment with recognition of the depauperate *Cruziana* ichnofacies towards the top of the Tonono Formation, in the Tonono x-1 borehole, east of the study area. The trace fossils in all the described paleoenvironments are scarce and low diverse, possibly due to Kačák extinction event and stressful conditions by eustatic and/or climatic changes and less likely tectonic.

Based on palynofacial analysis, it was possible to identify a dominance of terrestrial palynomorphs in all localities, indicating a shallow marine paleoenvironment with changes in the shoreline. In addition, an increase in the proportion and diversity of marine palynomorphs is observed towards the late Eifelian-early Givetian in Angosto del Pescado and towards the late Givetian-earliest Frasnian in the Ramos x-1012 borehole, identifying two transgressive events, widely recognized in other locations from Argentina, Bolivia and Brazil.

Whole-rock XRD analyzes of the Los Monos Formation in the study area indicate a mineralogical composition dominated by quartz and clays, with small amounts of plagioclase and potassium feldspars. The fine sediments were grouped into four clay assemblages (I+Ch, I+K, Ch+I, K+I), where the marine sediments are composed of the association I+Ch and Ch+I while the associations I+K and K+I characterize the transgressive levels, in coincidence with an increase in marine palynomorphs. It is observed that illite and chlorite increase towards the west (basin edge) and kaolinite increase towards the east (basin centre).

Based on the local palynostratigraphic scale and its correlation with established palinozones for the region and other continents, a late Eifelian-early to middle Givetian age age is assigned for most of the unit, in all sections and boreholes analyzed. This age is approximately the same as that previously interpreted for this unit.

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REFERENCES

Aceñolaza, F.G., Buatois, L.A., Mángano, M.G., Esteban, S.B., Tortello, M.F. and Aceñolaza, G.F. (1999). Cámbrico y Ordovícico del noroeste argentino. In *Geología Argentina. Instituto de Geología y Recursos Minerales, Anales* 29: 169-187.

Albariño, L., Dalenz-Farjat, A., Álvarez, L., Hernández R. and Pérez-Leytón, M. (2002). *Las Secuencias Sedimentarias del Devónico en el Subandino Sur y el Chaco. Bolivia y Argentina.* In V Congreso de Exploración y Desarrollo de Hidrocarburos, 687-748.

Álvarez, L.A., Dalenz-Farjat, A., Hernández, R.M. and Albariño, L. (2003). Integración de facies y biofacies en un análisis secuencial en plataformas clásticas devónicas del sur de Bolivia y noroeste argentino. *Latin American Journal of Sedimentology and Basin Analysis*, *10*(2): 103-121.

Aoyagi, K., and Kazama, T. (1980). Transformational changes of clay minerals, zeolites and silica minerals during diagenesis. *Sedimentology* 27: 179-188.

Aparicio González, P.A., Uriz, N., Arnol, J., Dopico, C.M., Cayo, E.L., Cingolani, C., Impiccini, A. and Basei, M.A.S. (2020). Sedimentary provenance analysis of the ordovician to devonian siliciclastic units of the Subandean Ranges and Santa Barbara System, northwestern Argentina. *Journal of South American Earth Sciences*, p.102629.

Aramayo Flores, F. (1989). El cinturón plegado y sobrecorrido del norte argentino. *Boletín de Informaciones Petroleras, Tercera Época 17*: 2-16.

Arispe, O. and Díaz-Martínez, E. (1996). *Facies y ambientes sedimentarios del Silúrico y Devónico inferior de Bolivia.* Simpósio Sul Americano do Siluro-Devoniano, Ponta Grossa, Brazil. Anais, 247-261.

Astini, R.A. and Marengo, L.F. (2006). Paleoambientes y estratigrafía secuencial de depósitos marinos marginales del Ordovícico de la sierra de Zapla (Sierras Subandinas, noroeste argentino) y su relación con la Cuenca Andina Central. *Revista geológica de Chile* 33: 247-276.

Benedetto, J.L., Halpern, K., de la Puente, S.G. and Monaldi, C.R. (2015). An in situ shelly fauna from the lower Paleozoic Zapla diamictite of northwestern Argentina: Implications for the age of glacial events across Gondwana. *Journal of South American Earth Sciences* 64: 166-182.

Binnion, M. (2012). How the technical differences between shale gas and conventional gas projects lead to a new business model being required to be successful. *Marine and Petroleum Geology* **31**: 3-7.

Biscaye, P.E. (1965). Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geological Society of America Bulletin 76*: 803-832.

Bosetti, E.P., Grahn, Y., Horodyski, R.S., Mauller, P.M., Breuer P. and Zabini, C. (2011). An earliest Givetian "Lilliput Effect" in the Paraná Basin, and the collapse of the Malvinokaffric shelly fauna. *Paläontologische zeitschrift* 85: 49-65.

Boso, M. and Monaldi, C.R. (1987). Estratigrafía y sedimentología de los depósitos silúricos ferriferos del norte argentino. *Tercer informe parcial (inédito). CONICET, Buenos Aires*.

Bossi G. (1983). *Tempestitas en la Formación Iquiri en la Angostura del rio Piraí (Departamento de Santa Cruz-Bolivia).* Unión Internacional de Ciencias Geológicas, Programa Internacional de Correlación Geológica. Proyecto 193 "Silúrico y Devónico de América Latina", II Reunión Internacional, Sucre, Bolivia.

Bowker, K.A. (2007). Barnett shale gas production, Fort Worth Basin: Issues and discussion. *AAPG bulletin* **91**: 523-533.

Breuer, P. and Grahn, Y. (2011). Middle Devonian spore stratigraphy in the eastern outcrop belt of the Parnaíba Basin, northeastern Brazil. *Revista Española de Micropaleontología* **43**: 19.

Breuer, P. and Steemans, P. (2013). Devonian Miospores from Northwestern Gondwana. *Special Papers Palaeontology* 89: 1-163.

Brindley, G.W. and Brown, G. (1980). Quantitative X-ray mineral analysis of clays. *Crystal structures of clay minerals and their X-ray identification 5*: 411-438.

Britt, L.K. and Schoeffler, J. (2009). The geomechanics of a shale play: what makes a shale prospective? In *SPE eastern regional meeting. Society of Petroleum Engineers*, 1-9.

Buatois, L.A., Gingras, M.K., MacEachern, J., **Mángano,** M.G., Zonneveld, J.P., Pemberton S.G. and Martin, A. (2005). Colonization of brackish-water systems through time: evidence from the trace-fossil record. *Palaios* 20: 321-347.

Buatois, L.A., Angulo, S. and Mangano, M.G. (2013). Onshore expansion of benthic communities after the Late Devonian mass extinction. *Lethaia* 46: 251-261.

Burst, J.F., (1965). Subaqueously formed shrinkage cracks in clay. *Journal of Sedimentary Research* 35: 348-353.

Cattaneo, A. and Steel, R.J. (2003). Transgressive deposits: a review of their variability. *Earth-Science Reviews*, 62: 187-228.

Chamley, H. (1997). Clay mineral sedimentation in the ocean. In H. Paquet and N. Clauer (Eds), *Soils and sediments*. Springer, Berlin, Heidelberg, 269-302.

Cruz, C.E., Albariño, L., Sylwan, C.A. and Villar, H.J. (2001). Source Rocks and Hydrocarbons South of the Santa Cruz Elbow, Bolivia and Northwestern Argentina. *AAPG Annual Meeting* 2001.

Dalenz-Farjat, A. (2000). *Taxonomía, Paleoecología y Paleogeografía de Moluscos Bivalvos del Siluro-Devónico del Altiplano, Cordillera Oriental, Interandino y Subandino de Bolivia* (Doctoral dissertation, Tesis Doctoral, Universidad Nacional de Córdoba.351 pp. (Inédito).

Dalenz-Farjat, A., Álvarez, L.A., Hernández, R.M. and Albariño, L.M. (2002). *Cuenca Siluro-Devónica del sur de Bolivia y del noroeste argentino: algunas interpretaciones. V Congreso de Exploración y Desarrollo de Hidrocarburos,* 222-248.

Dalenz-Farjat, A., Riglos M.S. and Ortiz, J.L. (2019). Silurian and Devonian Autobranchia Grammysiidae Bivalves from Bolivia. *Ameghiniana* 56: 402-421.

Dalmayrac, B., Laubacher, G., Marocco, R., Martínez C. and Tomasi, P. (1980). La chaine hercynienne d'amerique du sud structure et evolution d'un orogene intracratonique. *Geologische Rundschau* 69: 1-21.

De la Puente, G.S. and Rubinstein, C.V. (2013). Ordovician chitinozoans and marine phytoplankton of the Central Andean Basin, northwestern Argentina: a biostratigraphic and paleobiogeographic approach. *Review of Palaeobotany and Palynology* 198: 14-26.

Di Pasquo, M.M. (2005). *Resultados palinológicos preliminares de estratos del Devónico y Carbonífero en el perfil de Balapuca, sur de Bolivia.* XVI Congreso Geológico Argentino, 293-298.

Di Pasquo, M.M. (2007a). Asociaciones palinológicas en las formaciones Los Monos (Devónico) e Itacua (Carbonífero Inferior) en Balapuca (cuenca Tarija), sur de Bolivia. Parte 1. Formación Los Monos. *Revista geológica de Chile* 34: 97-137.

Di Pasquo, M.M. (2007b). Asociaciones palinológicas en las formaciones Los Monos (Devónico) e Itacua (Carbonífero Inferior) en Balapuca (Cuenca Tarija), sur de Bolivia: Parte 2. Asociaciones de la Formación Itacuae interpretación estratigráfica y cronología de las formaciones Los Monos e Itacua. *Revista geológica de Chile* 34: 163-198.

Di Pasquo, M.M., Amenábar, C.R. and Noetinger, S. (2009). Middle Devonian microfloras and megafloras from western Argentina and southern Bolivia: their importance in the palaeobiogeographical and palaeoclimatic evolution of western Gondwana. *Geological Society, London, Special Publications* 314: 193-213.

Di Pasquo, M.M., Noetinger, S., Isaacson, P., Grader, G., Starck, D. Morel, E. and Folnagy, H.A. (2015). Mid-Late Devonian assemblages of herbaceous lycophytes from northern Argentina and Bolivia: Age assessment with palynomorphs and invertebrates and paleobiogeographic importance. *Journal of South American Earth Sciences* 63: 70-83.

Díaz-Martínez E., Limachi, R., Goitia, V.H., Sarmiento, D., Arispe, O. and Montesinos, R. (1996). *Relación entre Tectónica y Sedimentación en la Cuenca de Antepaís del Paleozoico medio de los Andes centrales de Bolivia (14 a 22°S).* XII Congreso Geológico Bolivia: 97-102.

Díaz-Martínez, E. and Grahn, Y. (2007). Early Silurian glaciation along the western margin of Gondwana (Peru, Bolivia and northern Argentina): Palaeogeographic and geodynamic setting. *Palaeogeography, Palaeoclimatology, Palaeoecology* 245: 62-81.

Disalvo A. and Villar, H.J. (1999). *Los sistemas petrolíferos del área oriental de la cuenca Paleozoica Noroeste, Argentina.* IV Congreso de Exploración y Desarrollo de Hidrocarburos, IAPG, *Actas Trabajos Técnicos*, Mar del Plata.

Do Campo, M., Bauluz, B., Del Papa, C., White, T., Yuste, A. and Mayayo, M.J. (2018). Evidence of cyclic climatic changes recorded in clay mineral assemblages from a continental Paleocene-Eocene sequence, northwestern Argentina. *Sedimentary Geology* 368: 44-57.

Dott Jr, R. H. and Bourgeois, J. (1982). *Hummocky* stratification: significance of its variable bedding sequences. *Geological Society of America Bulletin* 93: 663-680.

Duke, W.L., Arnott, R.W.C. and Cheel, R.J. (1991). Shelf sandstone and hummocky cross-stratification: new insights on a stormy debate. *Geology* 19: 625-628.

De Segonzac, G.D. (1970). The transformation of clay minerals during diagenesis and low‐grade metamorphism: a review. *Sedimentology* 15: 281-346.

Ekdale, A.A. (1985). Paleoecology of the marine endobenthos. *Palaeogeography, Palaeoclimatology, Palaeoecology 50*: 63-81.

Escayola, M.P., van Staal, C.R. and Davis, W.J. (2011). The age and tectonic setting of the Puncoviscana Formation in northwestern Argentina: An accretionary complex related to Early Cambrian closure of the Puncoviscana Ocean and accretion of the Arequipa-Antofalla block. *Journal of South American Earth Sciences* 32: 438-459.

Esquevin, J. (1969). Influence de la composition chimique des illites sur leur cristallinité. *Bull. Centre Rech. Pau-SNPA* 3: 147-153.

Fernández-Seveso, F., Vistalli, M.C. and Viñes, R.F. (1998). *The Silurian–Devonian Chaco Basin: a review for reservoir correlation in Argentina and Bolivia.* Extended Abstracts Volume: AAPG International Conference and Exhibition: 452-453.

Fernández-Seveso, F., Vistalli, M.C. and Viñes, R.F. (2000). Correlación de reservorios en la cuenca silúrica-devónica del Chaco: Una revisión integrada previa a la adquisición de bloques exploratorios en Bolivia. *Boletín de Informaciones Petroleras: Tercera Época* 17.61: 152-166.

Frey, R.W. and Ring, R.G. (1992). Marine event beds and recolonization surfaces as revealed by trace fossil analysis. *Geological Magazine* 129: 325-335.

Galloway, W.E. (1989). Genetic stratigraphic sequences in basin analysis I: architecture and genesis of flooding-surface bounded depositional units. *AAPG bulletin* 73: 125-142.

García Muro, V.J., Rubinstein, C.V., Camina, S.C, Vergani, G. and Pereira, M. (2020). Palynology and organic geochemistry of an Early to Middle Devonian succession from TCB X-1001–Tacobo borehole, sub-Andean basin, southern Bolivia. *Journal of South American Earth Sciences,* https://doi.org/10.1016/j.jsames.2020.102912.

Grahn, Y. (2002). Upper Silurian and Devonian Chitinozoa from central and southern Bolivia, central Andes. *Journal of South American Earth Sciences* 15: 315-326.

Grahn, Y. (2005). Devonian chitinozoan biozones of Western Gondwana. *Acta Geologica Polonica* 55: 211-227.

Grahn, Y. (2006). Ordovician and Silurian chitinozoan biozones of Western Gondwana. *Geol*ogical *Magazine* 143: 509-529.

Grahn, Y., Mauller, P.M., Bergamaschi, S. andBosetti, E.P. (2013). Palynology and sequence stratigraphy of three Devonian rock units in the Apucarana Sub-basin (Paraná Basin, south Brazil): additional data and correlation. *Review of Palaeobotany and Palynology* 198: 27-44.

Holanda, W., dos Santos, A.C., Bertolino, L.C., Bergamaschi, S., Rodrigues, R., da Costa D.F. and Jones, C.M. (2019). Paleoenvironmental, paleoclimatic and stratigraphic implications of the mineralogical content of the Irati Formation, Paraná Basin, Brazil. *Journal of South American Earth Sciences* 94: 102243.

Hower, J., Eslinger, E.V., Hower, M.E. and Perry, E.A. (1976). Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geological Society of America Bulletin* 87: 725-737.

Isaacson, P.E. (2007). Mid-Paleozoic biogeography of the central Andes: endemic faunas, immigrants, and paleogeography. In: Díaz-Martínez, E., Rábano, I. (Eds.), *4th European Meeting on the Palaeontology and Stratigraphy of Latin America: Cuadernos Del Museo Geominero*: 213-218.

Jarvie, D.M., Hill, R.J., Ruble, T.E. and Pollastro, R.M. (2007). Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. *AAPG bulletin* 91: 475-499.

Johnson, J.G., Klapper, G. and Sandberg, C.A. (1985). Devonian eustatic fluctuations in Euramerica. *Geological Society of America Bulletin* 96: 567-587.

Kołtonik, K., Isaacson, P., Pisarzowska, A., Paszkowski, M., Augustsson, C., Szczerba, M., Slama, J., Budzyń, B., Stachacz, M. and Krawczyński, W. (2019). Provenance of upper Paleozoic siliciclastics rocks from two high-latitude glacially influenced intervals in Bolivia. *Journal of South American Earth Sciences* 92 : 12-31.

Kubler, B. (1966). La cristallinité de l'illite et les zones tout à fait supérieures du métamorphisme. *Colloq.* **étages** *tectoniques, Nêuchatel*: 105-122.

Limachi, R., Goitia, V.H., Sarmiento, D., Arispe, O., Montecinos, R., Díaz-Martínez, E., Dalenz-Farjat, A., Liachenco, N., Pérez-Leytón, M. and Aguilera, E. (1996). *Estratigrafía, geoquímica, correlaciones, ambientes sedimentarios y bioestratigrafía del Silúrico-Devónico de Bolivia*. XII Congreso Geológico de Bolivia. Tarija, Bolivia. Memorias: 183-197.

MacEachern, J.A. and Pemberton, S. G. (1992). *Ichnological aspects of Cretaceous shoreface successions and shoreface variability in the Western Interior Seaway of North America.* In: S.G.

Pemberton (ed.), Applications of ichnology to petroleum exploration. Society of Economic Paleontologists and Mineralogists, Core Workshop 17: 57-84.

MacEachern, J. A. and Pemberton, S.G. (1994). *Ichnological aspects of incised-valley fill systems from the Viking Formation of the Western Canada Sedimentary Basin, Alberta, Canada.* In: R. Dalrymple, R. Boyd and B.A. Zaitlin (eds.), Incised valley systems - Origin and sedimentary sequences. Society of Economic Paleontologists and Mineralogists Special Publication 51: 129-157

MacEachern, J.A., Pemberton, S.G., Gingras, M.K. and Bann, K.L. (2007). *The ichnofacies paradigm: a fifty-year retrospective*. In Miller III, W., (Ed). Trace fossils, Elsevier: 52-77.

Melo, J.H.G. (2005). Palynostratigraphy of some Paleozoic rock units of Bolivia: additional results. *IV Congreso de Exploración y Desarrollo de Hidrocarburos*, Mar del Plata. Trabajos técnicos (CD-Rom), IAPG/AAGGP, Buenos Aires (2005), p. 20.

Melo, J.H.G and Loboziak, S. (2003). Devonian–Early Carboniferous miospore biostratigraphy of the Amazon Basin, Northern Brazil. *Review of Palaeobotany and Palynology* 124: 131-202.

Miranda, A.P., Cruz, C.S., Melo, J.H. and Oller, J. (2003). *Sequence Stratigraphy of the Late Silurian-Devonian Subandean Basin in Southern Bolivia and Northern Argentina.* In VIII Simposio Bolivariano-Exploracion Petrolera en las Cuencas Subandinas. European Association of Geoscientists & Engineers: cp-33.

Molyneux, S.G., Le Hérissé, A. and Wicander, R. (1996). Chapter 16, Paleozoic Phytoplancton, in: Jansonius, J. and D.C. Mc Gregor (Eds.) Palynology: principles and applications. *American Association of Stratigraphic Palynologists Foundation*, 2: 493-529.

Montemurro, G. (1994). *Estratigrafía y ambiente sedimentario del Silúrico y Devónico en la cuenca del Chaco Boliviano*. XI Congreso Boliviano de Geología: 151-160.

Moore, D. M. and Reynolds Jr, R.C. (1997). X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, Oxford.

Noetinger, S. (2010). Middle-upper devonian palynoflora from the

Tonono x-1 borehole, salta province, northwestern Argentina. *Ameghiniana* 47(2): 165-184.

Noetinger, M.S. and Di Pasquo Lartigue, M. (2010). Palynomorphs from Abra Límite, Zenta Range, Eastern Cordillera, Northwestern Argentina. *Revista Brasileira de Paleontologia*, 13(1): 13-20.

Noetinger, S. and di Pasquo, M.M. (2011). Devonian palynological assemblages from the San Antonio x-1 borehole, Tarija Basin, northwestern Argentina. *Geologica Acta: an international earth science journal*: 199-216.

Noetinger, S. (2015). Spore diversity trends in the Middle Devonian of the Chaco-Salteño Plain, northwestern Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology* 417: 151-163.

Noetinger, S., di Pasquo, M. and Starck, D. (2018). Middle-Upper Devonian palynofloras from Argentina, systematic and correlation. *Review of Palaeobotany and Palynology* 257: 95-116.

Ottone, E.G. (1996). Devonian palynomorphs from the Los Monos formation, Tarija basin, Argentina. *Palynology 20*: 105-155.

Paris, F. (1981). Les chitinozoaires dans le Paléozöique du sud-ouest de l'Europe (cadre géologique – étude systématique – biostratigraphie). *Mémoire Société Géologique Minéralogique Bretagne* 26: 1-496.

Paris, F., Winchester-Seeto, T., Boumendjel, K. and Grahn, Y. (2000). Toward a global biozonation of Devonian chitinozoans. *Courier Forschungsinstitut Senckemberg* 220: 39-55.

Perez-Leytón, M.A. (2007). *Analyse des assemblages de palynomorphes du Silurien supérieur et du Dévonien de Bolivie: proposition de mise en place d'une échelle biostratigraphique de reference.* Tesis de Doctorado Universidades de Brest y Lieja (Inédita), 1-319.

Perez-Leytón, M.A. (2010). Informe Palinológico Final de los pozos Ramos: PLUE. ST.R-XP 1012, R-XP 1012 ST1, R-XP 1012 ST2, PLUE.ST.R-XP 1002, PLUE.ST.RXP 1010, PLUE.ST.XP 1011, R-X11; Perfiles de Alarache, Arasayal, Balapuca, Lipeo, Iruya, Angosto del Pescado, Alisal, y un perfil sin datos de nombre ni ubicación, Yacimiento Ramos, Argentina. Reporte Interno Pluspetrol.

Perez-Leytón, M.A. (2014). Informe Palinológico Final de muestras de superficie de los perfiles de Alarache y Balapuca. Reporte Interno Pluspetrol.

Pérez Altamar, R. and Marfurt, K. (2014). Mineralogy-based brittleness prediction from surface seismic data: Application to the Barnett Shale. *Interpretation* 2 : T1-T17.

Pierce, J.W. and Siegel, F.R. (1969). Quantification in clay mineral studies of sediments and sedimentary rocks. *Journal of Sedimentary Research* 39: 187-193.

Plummer, P.S. and Gostin, V.A. (1981). Shrinkage cracks; desiccation or synaeresis? *Journal of Sedimentary Research* 51: 1147-1156.

Ramos, V.A. and Coira, B. (2008). *Evolución tectónica preandina de la provincia de Jujuy y áreas aledañas.* XVIII Congreso Geológico Argentino: 401-415.

Richardson, J.B. and McGregor, D.C. (1986). Silurian and Devonian spore zones of the Old Red Sandstone continent and adjacent regions. *Bulletin of the Geological Survey of Canada* 384: 1-79.

Rubinstein, C.V. (2005). Ordovician to Lower Silurian palynomorphs from the Sierras Subandinas (Subandean ranges), northwestern Argentina: a preliminary report. *Carnets de Géologie — Notebooks on Geology*, Memoir 2005/02, Abstract 09: 51–56

Sánchez, M.C. and Salfity, J.A. (1999). La cuenca cámbrica del Grupo Mesón en el Noroeste Argentino: desarrollo estratigráfico y paleogeográfico. *Acta geológica hispánica*: 123-139.

Schultz, L.G. (1964). Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. *United States Geological Survey Professional Paper*, 391-C.

Scotese, C.R., Boucot, A.J. and McKerrow, W.S. (1999). Gondwanan palaeogeography and paleooclimatology. *Journal of African Earth Sciences* 28: 99-114.

Spalletti, L.A. and Rodriguez, A.M.I. (1981). Significado geológico de los argilominerales y zeolitas de sedimentitas volcanísticas terciarias (Formación Ñirihuau), Provincia de Río Negro. *Revista de la Asociación Geológica Argentina*, 36(4): 358-371.

Starck, D. (1995). *Silurian - Jurassic Stratigraphy and Basin Evolution of Northwestern Argentina.* In A.J. Tankard, R. Suárez-Soruco and H.J. Welsink (Eds.), Petroleum Basins of South America. American Association of Petroleum Geologists, Memoir 62:251-267.

Starck, D. (1996). *Facies Continentales en el Siluro-Devónico de la Cuenca del Noroeste. Provincia de Salta, Argentina.* Memorias del XII Congreso Geológico Bolivia, Tarija: 231-238.

Streel, M., Higgs, K., Loboziak, S., Riegel, W. and Steemans, P. (1987). Spore stratigraphy and correlation with faunas and floras in the type marine Devonian of the Ardenno-Rhenish regions. *Review of Palaeobotany and Palynology* 50: 211-229.

Suárez Soruco, R. (1988). *Estudio bioestratigráfico del ciclo Cordillerano de Bolivia*, Academia Nacional de Ciencias de Bolivia, Cochabamba, 142pp.

Suárez Soruco, R. (2000). Compendio de geología de Bolivia. *Revista Técnica Yacimientos Petrolíferos Fiscales Bolivianos* 18: 1-213.

Suárez-Soruco, R. and Díaz-Martínez, E. (1996). Léxico Estratigráfico de Bolivia. *Revista Técnica de Yacimientos Petrolíferos Fiscales Bolivianos* 17: 3-227.

Tyson, R.V. (1995). Abundance of organic matter in sediments: TOC, hydrodynamic equivalence, dilution and flux effects. In: Tyson, R.V. (Ed.) *Sedimentary organic matter.* Springer, Dordrecht: 81-118.

Taylor, A.M. and Goldring, R. (1993). Description and analysis of bioturbation and ichnofabric. *Journal of the Geological Society* 150: 141-148.

Troth, I., Marshall, J.E., Racey, A. and Becker, R.T. (2011). Devonian sea-level change in Bolivia: A high palaeolatitude biostratigraphical calibration of the global sea-level curve. *Palaeogeography, Palaeoclimatology, Palaeoecology* 304: 3-20.

Ulrich, A. (1892). Palaeozoische Versteinerungen aus Bolivien. In Steinmann, G. (Ed.), Beiträge zur Geologie und Paläontologie von Südamerika. Schweizerbart, Stuttgart 8, 1–116

Uriz, N.J., Cingolani, C.A., Basei, M.A.S., Blanco, G., Abre, P., Portillo, N.S. and Siccardi, A. (2016). Provenance and paleogeography of the Devonian Durazno Group, southern Paraná Basin in Uruguay. *Journal of South American Earth Sciences* 66: 248-267.

Vistalli, M.C., (1999). *Cuenca siluro-devónica*. In: González Bonorino, G., Omarini, R. and Viramonte, J. (Eds.), Relatorio 14º Congreso Geológico Argentino: 168-184. Salta.

Vistalli, M. C., Hernández, R., Disalvo, A., Starck, D. and Sylwan, C. (2005). *Cuencas paleozoicas del noroeste argentino*. In Frontera Exploratoria de la Argentina. VI Congreso de

Exploración y Desarrollo de Hidrocarburos: 41-61.

Walker, R.G. and James, N.P. (1992). *Facies Models. Response to Sea Level Change*, Geological Association of Canada, Stittsville, Ontario, 409 pp.

Warr, L. N. and Rice, A.H.N. (1994). Interlaboratory standardization and calibration of day mineral crystallinity and crystallite size data. *Journal of metamorphic Geology* 12: 141-152.

Zeballos, A., Weihed, P. Blanco, M. and Machaca, V. (2016). Geological, mineralogical and chemical characterization of Devonian kaolinite-bearing sediments for further applications in the ceramic (tiles) industry in La Paz, Bolivia. *Environmental Earth Sciences* 75: 546-561.