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Lower Cretaceous anoxic conditions IN the Austral basin, south-western Gondwana, Patagonia Argentina

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ABSTRACT

The reconstruction of palaeo-oxygenation levels in marine deposits from the Cretaceous has obtained a huge interest all around the world in recent years. This fascinating topic is here pointed out for the first time in the Austral Basin using the information provided by the black shales of the Río Mayer Formation, Patagonia, Argentina. The combination of sedimentology, ichnology and geochemistry (TOC, Ce anomaly and MnO content) allow the identification of three major intervals respecting the oxygen content. During the Berriasian and early Valanginian anoxic conditions prevail in the outer shelf. After that, between the late Valanginian and Hauterivian dysoxic palaeoenvironments were developed. Finally, a more oxygenated palaeoenvironment occurred since Aptian associated with a progradation of a proximal deltaic system. The identification of anoxic conditions is of much interest for the hydrocarbon research in this stratigraphical unit, which represents the most significant source rock of the Austral Basin.

1. Introduction

During the Cretaceous the Earth experienced many changes (the opening and closing of oceans, widespread and enormous volcanism, dramatic climatic variations) that generated extremely different environmental responses and the most important one concerns the oxidation state of the oceans (Wagreich et al., 2011); these moments were called episodes of environmental changes (EECs) by Föllmi (2012). There are six EECs in the early Cretaceous, each one with one particular isotopic signature, including both positive and negative δC13 excursions (Arthur et al., 1988), and sometimes they are related to the generation of dark, laminated and organic-rich mud rock (LOM, *sensu* Föllmi, 2012). Overall, most of the available studies were carried out on Tethyan or Atlantic Tethys deposits and then correlated with other deposits worldwide. In this way, the study of different oxygen levels in the Cretaceous oceans contributes to a better understanding of the palaeoenvironmenal changes. In the Mesozoic sedimentary record, especially between the Upper Jurassic and the Lower Cretaceous, numerous dark-coloured (organic-rich) rocks were deposited, which suggests widespread anoxia (Wignall, 1994; Pancost et al., 2004; Melinte-Dobrinescu and Roban, 2011; Roban and Melinte-Dobrinescu, 2012). In general terms, black shales are dark-coloured fine-grained organic carbon rich sediment with TOC contents ranging from 1 to 15% (Stow et al., 1996, 2001).

Trace fossils have been used for the reconstruction of palaeo-oxygenation curves in many sedimentary basins in different areas worldwide (Rhoads and Morse, 1971; Savrda and Bottjer, 1986, 1987; Ekdale and Mason, 1988; Buatois and Mángano, 1992; Allison et al., 1995; Savrda, 1995; Doyle et al., 2005; Rodríguez-Tovar et al., 2009). The primary statement is that the rise of oxygen content generates an increase in the ichnodiversity as a result of more diverse epi and endobenthonic communities. Another consequence of better oxygen levels is the larger sizes of the fossil traces, specially the diameter of their galleries. Usually, the determination of a relative palaeo-oxygenation curve in the sedimentary record is not only based on trace fossils, but relies on other sources of evidence as well. In general, for shale deposits, the rock colour, the sedimentary structures and the presence/absence of pyrite should be taken into account. Another aspect to be considered in outer shelf shales is the occurrence of sandstone levels, indicative of the arrival of turbidity currents that could bring dissolved oxygen from the costal zones.

Apart from the features and factors mentioned, which can all be obtained from field observations, other sources of information can be used to estimate relative oxygenation of the palaeoenvironment. One of them is the total organic carbon (TOC) content, which is strongly affected by the fluctuation of the oxygen levels. Apart from this, there are two other geochemical indicators in this respect: one

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is the Ce anomaly, having negative values under reducing conditions (*i.e.* Shields and Stille, 2001); and another is the MnO content, with increasing percentage while the oxygen concentration rises (Jarvis et al., 2001).

The main objective of this contribution is to analyse changes in the relative palaeo-oxygenation conditions during the early Cretaceous of the Austral Basin, SW Gondwana, using in particular the information provided for the black shales of the Río Mayer Formation.

2. Geological background

2.1. The Austral Basin

The Austral Basin is located in southern Patagonia and developed during the Jurassic, connected to a phase of extension in the Pacific margin of Gondwana (Fig. 1). The initiation of this basin was linked to an extensional phase during the late Jurassic with the accumulation of a thick volcaniclastic syn-rift sequence assigned to El Quemado Complex (Biddle et al., 1986; Féraud et al., 1999; Pankhurst et al., 2000; Arbe, 2002). Overlying this complex, shallow marine deposits of the Springhill Formation were accumulated between the Tithonian and Hauterivian in response to an initial transgressive event from the south (Kraemer and Riccardi, 1997; Ottone and Aguirre-Urreta, 1999; Richiano, 2012). The climax of the transgression in the Berriasian led to the accumulation of black shales of the Río Mayer Formation, marking the first episode of offshore sedimentation during the Mesozoic in the Austral Basin and the onset of sag conditions. Towards the end of the thermal subsidence (early Aptian-Albian), a large passive-margin delta system, the Piedra Clavada Formation, developed in the northern and eastern sectors of the basin (Arbe, 2002). Finally, the regional change from an extensional to a compressional phase

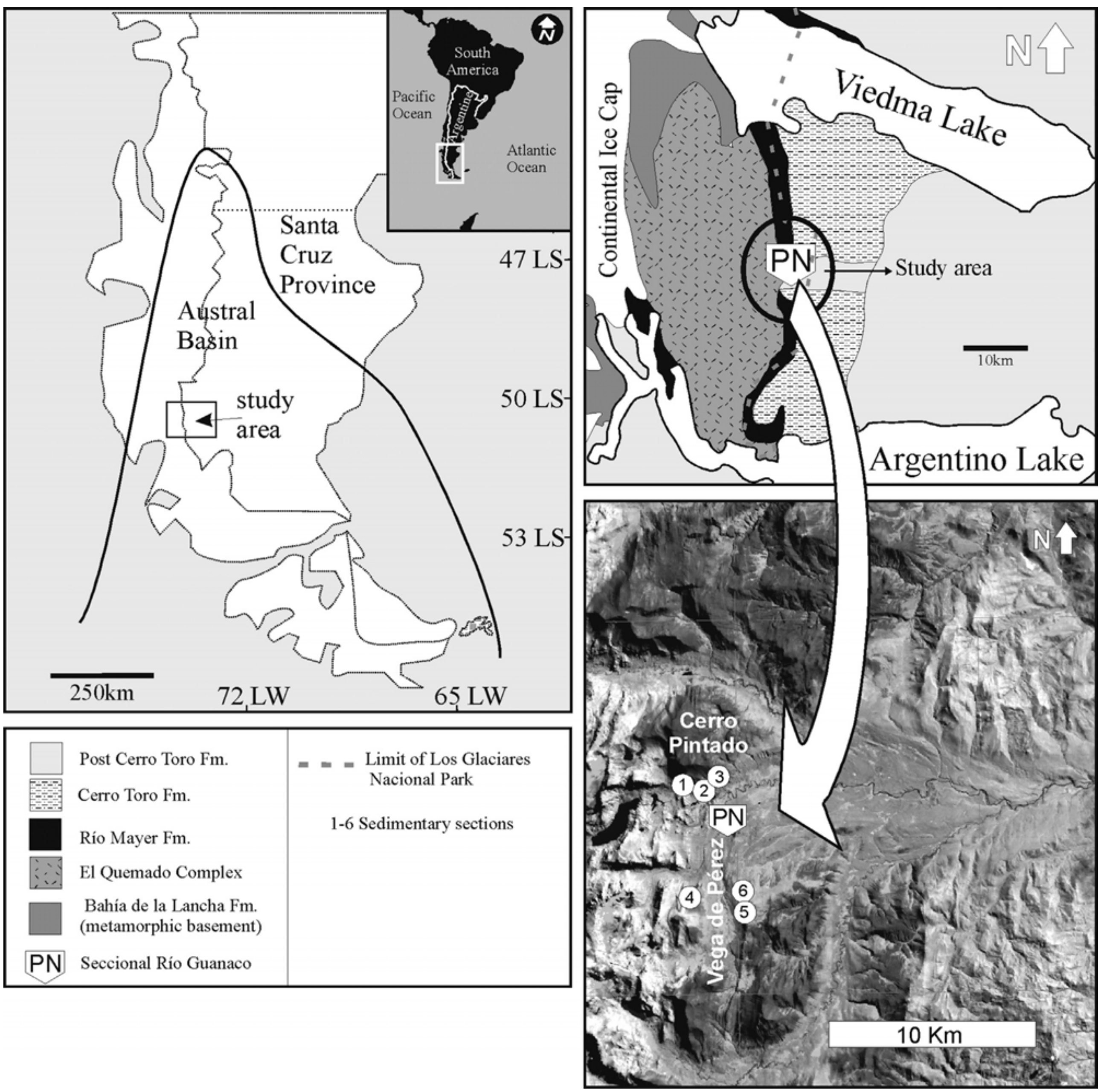

Fig. 1. Austral Basin location in South America and geological sketch of the study area with the position of the sedimentary logs.

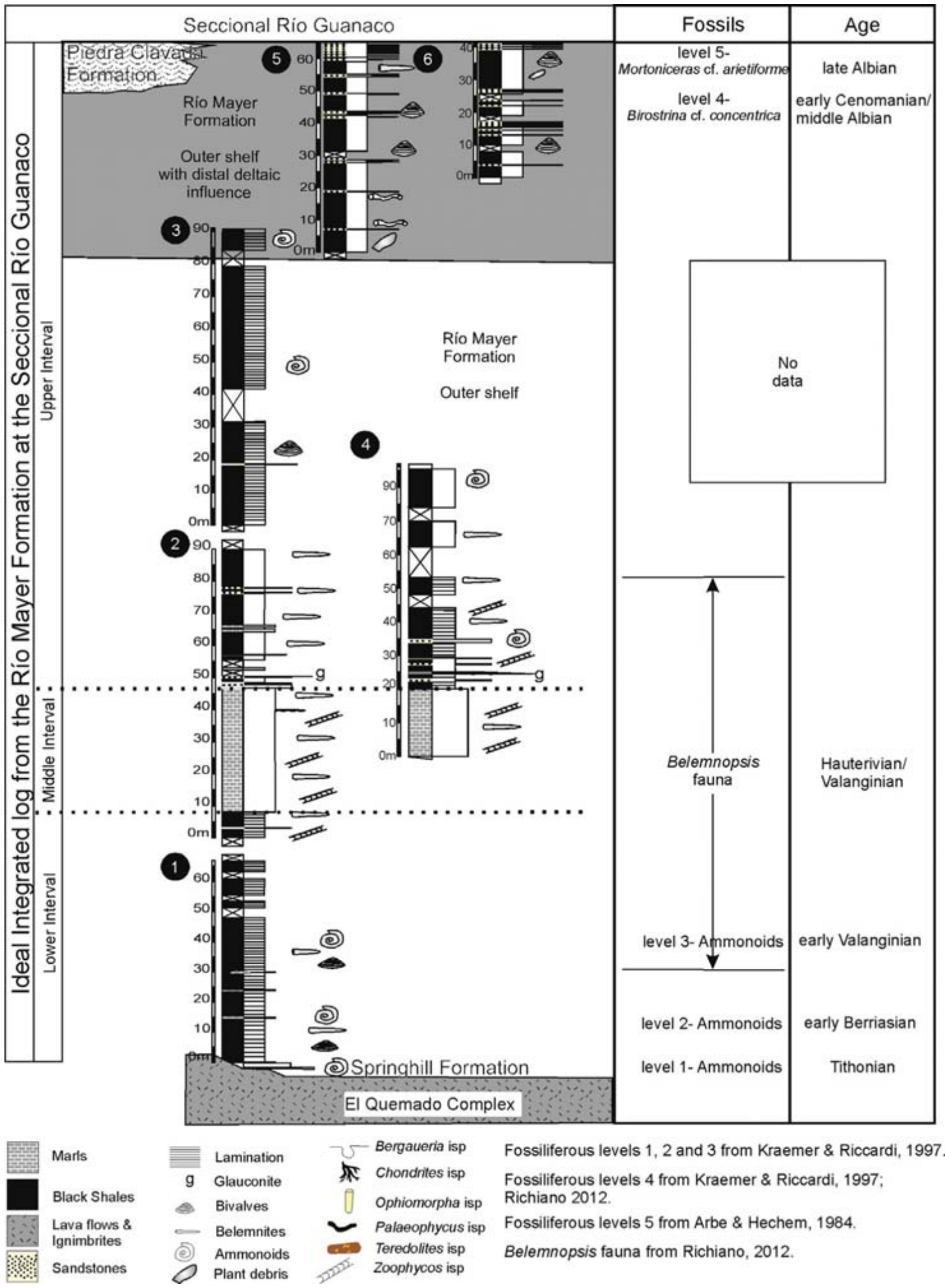

Fig. 2. Sedimentary sections of the Lower Cretaceous Río Mayer Formation recovered at the Seccional Río Guanaco locality. Fossils and ages identified in the unit.

took place in the mid-Cretaceous, as a result of the convergence of an arc and/or a craton, thus causing the obduction of the ophiolites — which constituted the sea floor of the Rocas Verdes Marginal Basin — over the cratonic continental margin (Dalziel et al., 1974). The compression associated with the early stages of the orogeny caused the development of a retroarc fold-and-thrust belt along the Patagonian–Fueguian Andes (Ramos et al., 1982; Biddle et al., 1986; Wilson, 1991; Fildani et al., 2003; Fildani and Hessler, 2005). This compression process extended from the Upper Cretaceous to the Neogene (Ramos et al., 1982; Biddle et al., 1986; Wilson, 1991; Spalletti and Franzese, 2007; Fosdick et al., 2011).

2.2. The Río Mayer Formation in the area of study

Previous studies in the Río Mayer Formation showed that this unit was deposited between Berriasian and Albian times (Arbe and Hechem, 1984; Kraemer and Riccardi, 1997; Richiano, 2012; Richiano et al., 2012). The wide content of fossil material was analysed by many researchers, especially the ammonoids fauna (*i.e.* Leanza, 1970; Riccardi, 1971, 1988; Aguirre-Urreta, 1985, 1986; Aguirre-Urreta and Klinger, 1986; Aguirre-Urreta and Riccardi, 1988a,b; Riccardi et al., 1987; Kraemer and Riccardi, 1997; Aguirre-Urreta, 2002) and recently the trace fossils (Richiano and Poiré, 2010; Richiano et al., 2012, 2013).

The study area is located between the Argentino and Viedma lakes in the Santa Cruz Province at the Seccional Río Guanaco (S 49° 57′ 11″; W 72° 04′ 56″) of Los Glaciares National Park (Fig. 1). Outcrop analyses allow the division of the 250 m thick studied succession into three informal intervals (Fig. 2; Richiano, 2010, 2012; Richiano et al., 2012). These intervals are grouped into two major palaeoenvironments based on facies analyses (Table 1).

The lower interval is ca. 100 m thick and is mainly composed of laminated black shales with both tabular and concretional marl levels (Fig. 3a–d). Trace fossils are not recorded in this section, but ammonites and belemnites are abundant (Fig. 3e–f). This section is interpreted as having accumulated in a distal shelf setting. Two fossiliferous levels (2 and 3, Fig. 2) were recorded by Kraemer and Riccardi (1997) assigned to this section; they indicate early Berrasian and early Valanginian ages.

The middle interval is 40 m thick and is composed of intensely bioturbated black marls and shales (Fig. 4a and b). This section is characterized by a well preserved *Zoophycos* ichnofacies consisting of *Bergaueria*, *Chondrites* and *Zoophycos* ichnogenera (Fig. 4c–f) (Richiano and Poiré, 2010; Richiano et al., 2013). Body fossils are common, especially belemnites (Fig. 4g–i). These fossils represent a *Belemnopsis* fauna that corresponds to a Valanginian-Hauterivian age (Aguirre Urreta, 2002; Richiano, 2012).

The upper interval is characterized by massive black shales with intercalations of very fine- to fine-grained sandstones and less frequent conglomerates (Fig. 5a–d). The coarser sedimentary rocks were interpreted as deposited by both debris flows and distal low-density-turbidity currents (Richiano, 2010, 2012; Richiano et al., 2012). *Zoophycos* ichnofacies and *Ophiomorpha* rudis ichnosubfacies occur associated with moulds of petrified wood containing *Teredolites* isp. (Fig. 5e–i) (Richiano and Poiré, 2010; Richiano et al., 2013). Two fossiliferous levels have been recorded from the top of this section suggesting an Albian-Cenomanian age (Fig. 2). During the late Aptian to early Cenomanian, the Piedra Clavada Formation (=Kachaike Fm.) was developed ca. 120 km northwards at San Martín Lake (Passalia, 2007; Archangelsky et al., 2008, 2009; Perez Loinaze, 2012). The massive deltaic system that constitutes this unit generates frequent distal low-density-turbidity currents at the Río Guanaco locality (Fig.6). This situation is reflected by the frequent intercalation of sandstones and wood fragments in the uppermost part of the Río Mayer Formation (Richiano, 2010, 2012; Richiano et al., 2012).

3. Material and methods

In this work, three methodological approaches were followed: 1) sedimentary data obtained from field observations; 2) ichnological studies; and 3) geochemical analyses. For the first two approaches, six sedimentary sections have been studied, with special emphasis on sedimentology and on the analysis of trace fossils from the Río Mayer Formation at the Seccional Río Guanaco locality (Figs. 1 and 2). Concerning the trace fossils, a bed-by-bed characterization was taken from the field.

Furthermore, in the Río Mayer Formation, different types of geochemical analyses were performed at the Río Guanaco sections (Fig. 6, Table 2). First, 29 TOC values were taken with a range of 5 m from the outcrop profile. A variation curve was generated. The analyses were performed using Leco equipment by Geolab Sur S.A. (Buenos Aires, Argentina). Then, 17 samples of black shales were analysed for major and minor elements as well as for traces and rare earth elements. The methodology applied was ICP-MS, developed by the ALS Laboratory Group. Ce anomalies were used to estimate reducing or oxidizing conditions in the palaeoenvironments (Wright et al., 1987; Bertram et al., 1992; Jarvis et al., 1994; Yang et al., 1999; Mazumdar et al., 1999; Shields and Stille, 2001). This concept is based on the oxidation state of Ce, as this element behaves with +3 and +4 valences, depending on the environmental conditions in which it is located. Ce anomaly was calculated employing the formula suggested by Elderfield and Graves (1982), using the normalized values (chondrite) of Ce, La and Nd. This is expressed by:

$$\text{Ce Anomaly} = \text{Ce/Ce}^* = (3\text{CeN}/2\text{LaN} + \text{NdN})$$

Shields and Stille (2001) suggested that Ce anomaly values above 1.05 are positive anomalies (they correspond to oxidizing palaeoenvironments), while values below 0.95 are negative anomalies (e.g. reducing palaeoenvironments). Values between 0.95 and 1.05 are considered as normal values. In addition, it is widely known that the content of Mn in fine marine deposits is connected to the oxygenation of the environment (Jarvis et al., 2001; Calvert and Pedersen, 1996). Mn+2 remains dissolved when marine water is deficient in oxygen (Jarvis et al., 2001), while this element participates in the composition of carbonates in conditions of greater oxygenation (Calvert and Pedersen, 1996).

The reconstruction of the relative palaeo-oxygenation curve has been based on the geochemical aspects (TOC, Ce anomaly and MnO content). Apart from this topic, the properties of the sedimentary rocks and the ichnology allow us to better define and characterize the three main oxygen intervals.

4. Results

4.1. Sedimentology and distribution of trace fossils

In the Seccional Río Guanaco locality, the Río Mayer Formation shows a very well preserved *Zoophycos* ichnofacies, which is present at two intervals (Richiano et al., 2013). The entire middle interval has the best exposure of this ichnofacies, showing the

Table 1
Facies analyses, sedimentological processes, fossil content and interpreted palaeoenvironments for the Río Mayer Formation at Seccional Río Guanaco locality (modified from Richiano et al., 2012).

Facies	Process		Fossils	Palaeoenvironments
Massive mudstones (Fm)-Laminated mudstones (Fl)- Mudstones with nodules(Fn)-Massive marls (Mm)- Bioturbated marls (Mb)	Hemipelagic deposition		Marine (ammonites; belemnites; bivalves)	MARINE Outer Platform
Glauconitic sandstones (Sg)	Autigenic deposition			
Massive sandstones (Sm)-Laminated sandstones (Sl)-Sandstones with parallel stratification (Sp)	Turbiditic flows	Episodic Sedimentation		
Massive conglomerates with intraclasts (Cmi)	Debris flows			
Massive mudstones (Fm)	Hemipelagic deposition		Marine & continental (ammonites; bivalves; tree fragments)	MARINE Outer Platform influenced by deltaic activity
Massive sandstone (Sm)- Laminated sandstones (Sl)	Turbiditic flows	Episodic Sedimentation		

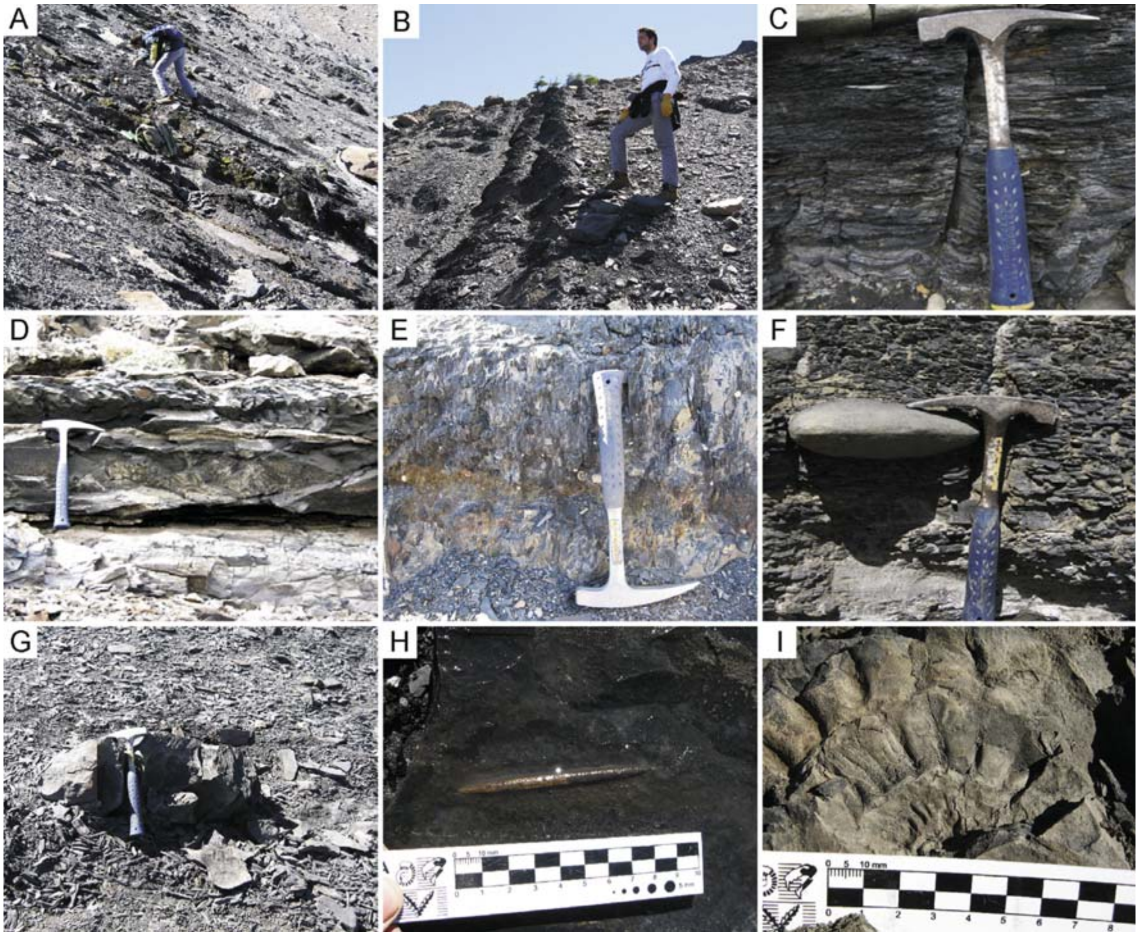

Fig. 3. General aspects of the lower interval of the Río Mayer Formation at Seccional Río Guanaco locality. A-B, general view; C, detail of the laminated black shales; D, massive shale; E, marl level; F-G, concretional levels; H–I, general fosiliferous content.

ichnogenera *Zoophycos*, *Chondrites* and *Bergaueria*. The main characteristic of this interval is a high bioturbation degree in the marls and the small diameter of the galleries (less than 1 cm).

The second sector with trace fossils is located near the top of the upper interval, presenting a less well-developed *Zoophycos* ichnofacies, associated with *Ophiomorpha rudis* ichnosubfacies and *Teredolites* isp (Richiano et al., 2013). At this interval, the galleries of *Ophiomorpha* show the largest size in the unit with an average of 2 cm in diameter.

4.2. Total organic carbon (TOC), Ce anomaly and % MnO

In the Río Mayer Formation, three well identified intervals regarding TOC values appear (Fig. 7). First, the whole lower interval of the unit (samples 1 to 16, Table 2) concentrates the highest values of TOC, with a maximum of 2.81%. In the second interval, in almost the entire middle section between the samples 17 and 24, the TOC values are lower than 0.31%. Finally, the upper interval of the Río Mayer Formation presents, at the beginning, TOC values from 0.6 to 1.8%, but then the rest of the unit contains less than 0.1% of TOC in the analysed samples (Fig. 7).

Taking into account the Ce anomaly (Fig. 7), it is slightly negative in the lower section (0.925–0.724), in connection to reducing palaeoenvironments (Zimmermann et al., 2011). By contrast, in the middle and upper sections, the Ce anomaly is slightly positive (1.09–1.32), which marks oxidizing depositional conditions in the palaeoenvironment (Zimmermann et al., 2011).

Correspondingly, the MnO content shows a similar distribution to the Ce anomaly (Fig. 7). The lower section of the Río Mayer Formation displays the lowest values of this oxide, generally with less than 0.01%. On the other hand, an increase is detected from the middle to the upper sections, with values ranging from 0.14 to 0.5%.

5. Discussion and final remarks

The Río Mayer Formation contains exceptional – and some of the best exposed – records of black shales in SW Gondwana from the early Cretaceous. For this reason, the study of the variability of oxygen content in this unit can be used as an environmental archive for this part of the Cretaceous world, and as a tool for correlations with other ocean basins (among others, Wignall, 1994; Pancost et al., 2004; Doyle et al., 2005; Rodríguez-Tovar et al., 2009; Melinte-Dobrinescu and Roban, 2011; Roban and Melinte-Dobrinescu, 2012). For such purpose, a relative palaeo-oxygenation curve has been reconstructed using different sources of information (Fig. 7), such as the properties of rocks (colour and lamination for shales, presence/absence of sandstones), ichnology (diversity and size of the trace fossils) and geochemistry (TOC, Ce anomaly and MnO content).

From the relative palaeo-oxygenation curve, three distinct intervals in the Río Mayer Formation have been recognized. The Lower Berriasian to Lower Valanginian deposits (lower interval) developed over a period of very low oxygen content, dissolved in the outer shelf bottom deposits, which gave them a distinctive

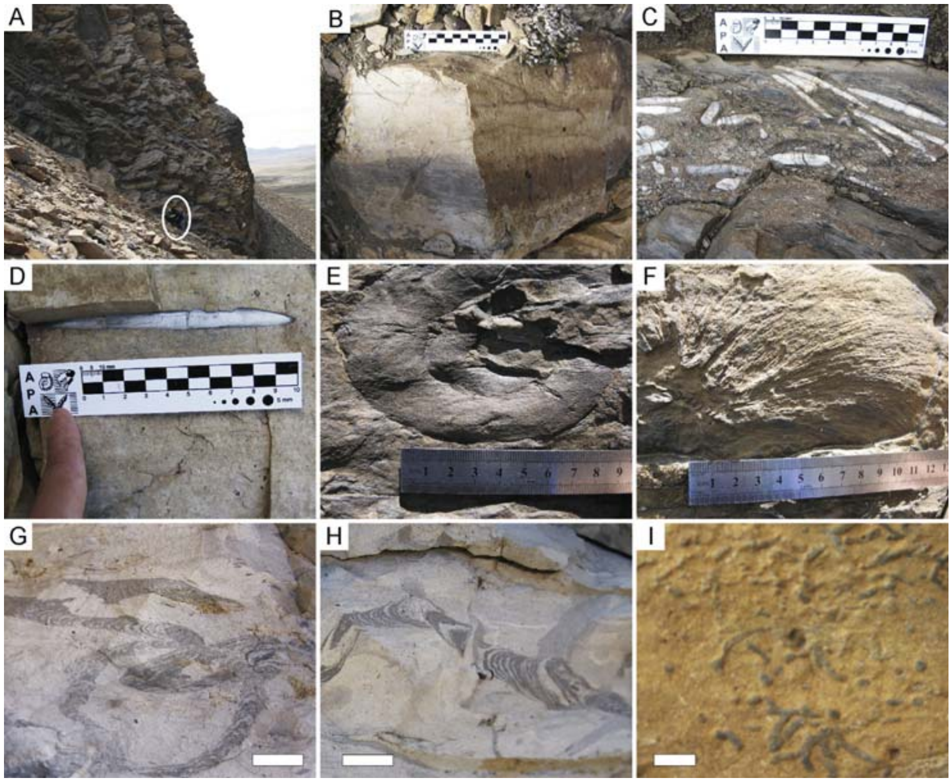

Fig. 4. General aspects of the middle interval of the Río Mayer Formation at Seccional Río Guanaco locality. A, general view (person for scale); B, detail of one bioturbated marl level; C-E, general body fossils assemblage; F—H, *Zoophycos* isp.; I, *Chondrites* isp.

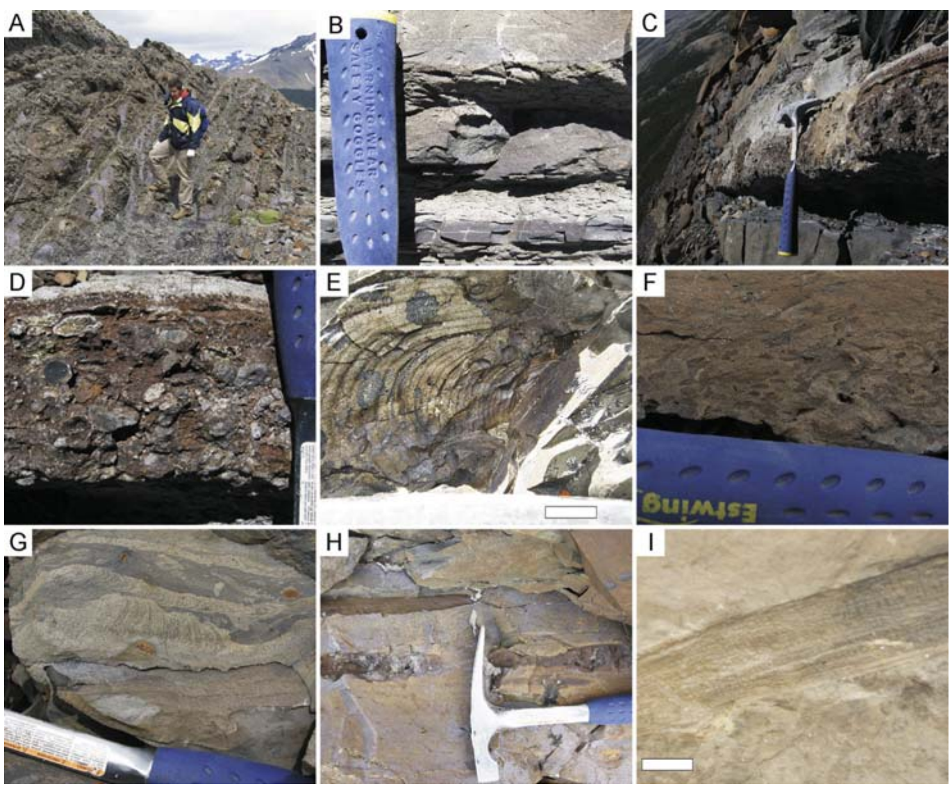

Fig. 5. General aspects of the upper interval of the Río Mayer Formation at Seccional Río Guanaco locality. A, general view (person for scale); B, detail of fine-grained sandstone levels interbedded with the massive shales; C-D, massive conglomerate; E, common body fossils assemblage (bivalve); F, *Chondrites* isp.; G, *Zoophycos* isp.; H, *Ophiomorpha* isp.; I, impression of wood fragment.

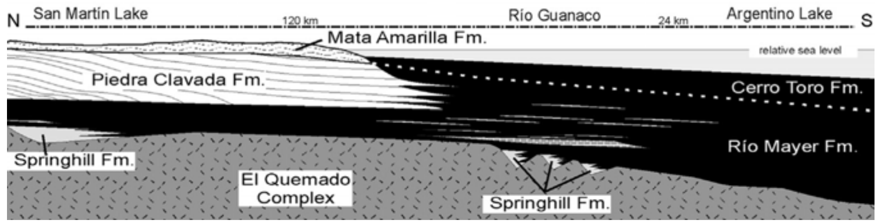

Fig. 6. General scheme of the Río Mayer Formation during Lower Cretaceous between the San Martín and Argentino lakes and its relation with others units from the Austral Basin. The upper limit of the Río Mayer Formation at the study area correlates with a marine transgression that marks the beginning of the Cerro Toro Formation. Modified form Richiano et al., 2012.

black colour, well-preserved lamination, high organic matter and the absence of trace fossils.

The middle interval (Valanginian-Hauterivian) has better oxygenation conditions than the lower interval. This feature allowed the development of a significant *Zoophycos* ichnofacies, which caused a high bioturbation degree in the interval. Even when the oxygen content is greater than it was previously available, this ichnofacies is typically generated in an oxygen-deficient environment, but not in an anoxic one. For this reason, the deposits are still of a dark grey colour, but present very low TOC values.

The upper interval of the unit has a dual behaviour; the lower part is less oxygenated than the upper part. Towards the end of this interval, the maximum level of oxygen —largely influenced by the contribution of turbidity flows from shallow areas— was recorded. This situation has caused poor organic matter preservation. In general, the rocks are dark green mudstones with a higher ichnodiversity and trace fossils of a larger size, in comparison to the rest of the unit. Despite the increased oxygenation, it is clear that the mean values remain moderate.

In summary, the Río Mayer Formation developed in response to a regional transgression (Ramos and Aguirre-Urreta, 1994) following the late Jurassic rifting and half-graben development. In the study area, this unit has three well differentiated sections from a palaeo-oxygenation point of view, which partially match the sedimentologic division of the unit. First, anoxic conditions prevail in the lower interval of the Río Mayer Formation as a response to a main transgression which took place in the Berriasian. These anoxic conditions during the Berriasian-early Valanginian times in SW Gondwana produced well laminated black shales without bioturbation. As the main transgression continued, the middle interval deposited during the ca. late Valanginian-Hauterivian, when the terrigenous sediment input to the basin was minimum and allowed the marls to deposit. In this context, the presence of a very well preserved *Zoophycos* ichnofacies and the rare occurrence of fine-grained sandstones suggest that the environment was at least dysoxic. Then, towards the top of the unit, the deltaic Piedra Clavada Formation (Aptian-early Cenomanian) developed, advancing from the northern edge of the basin. This situation generated better oxygenation conditions in the upper part of the unit, which produced a greater ichnodiversity and very low TOC values from the Aptian to the Cenomanian.

The early Cretaceous (early Neocomian) anoxic palaeoenvironments were potentially connected to the Gondwana break-up and the formation of restricted deep-marine basins, as suggested by Macdonald et al. (2003). However, these authors have not considered the Río Mayer Formation in their model of evolution and generation of the potential source rocks in SW Gondwana. The development of these low-oxygen conditions could be related to the rapid transgression that occurred between the Tithonian and the Berriasian at this part of the world (Aguirre-Urreta and Ramos, 1981). Two conceptual models have been cited as the cause of

Table 2
Data sets used for the reconstruction of the relative palaeo-oxygenation curve of the Río Mayer Formation at Seccional Río Guanaco locality. Additional information about samples is provided by Richiano et al., 2012.

	Sample	TOC %	Ce/Ce*	MnO%
Upper Interval	43		1.11	0.28
	42	0.09		
	41		1.19	0.28
	40	0.09		
	39	0.09		
	38		1.24	0.36
	37		1.23	0.5
	36		1.23	0.44
	35	0.09	1.25	0.46
	34	1.48		
	33		1.1	0.14
	32	0.6		
	31	1.81		
	30		1.2	0.18
	29	0.62		
	28		1.01	0.35
Middle Interval	27		1.32	0.21
	26	0.58		
	25		1.23	0.22
	24	0.09		
	23	0.17		
	22	0.09		
	21	0.07		
	20	0.09		
	19	0.13		
	18	0.17		
	17	0.31		
Lower Interval	16	1.49	0.724	0.01
	15	1.59		
	14	2.44		
	13	2.09	0.829	0.01
	12	1.88		
	11		0.9	0.01
	10	1.65		
	9		0.866	0.02
	8	1.56		
	7		0.925	0.01
	6	1.43		
	5	2.81		
	4	1.52		
	3	1.59		
	2		1,032	0.02
	1	0.07		

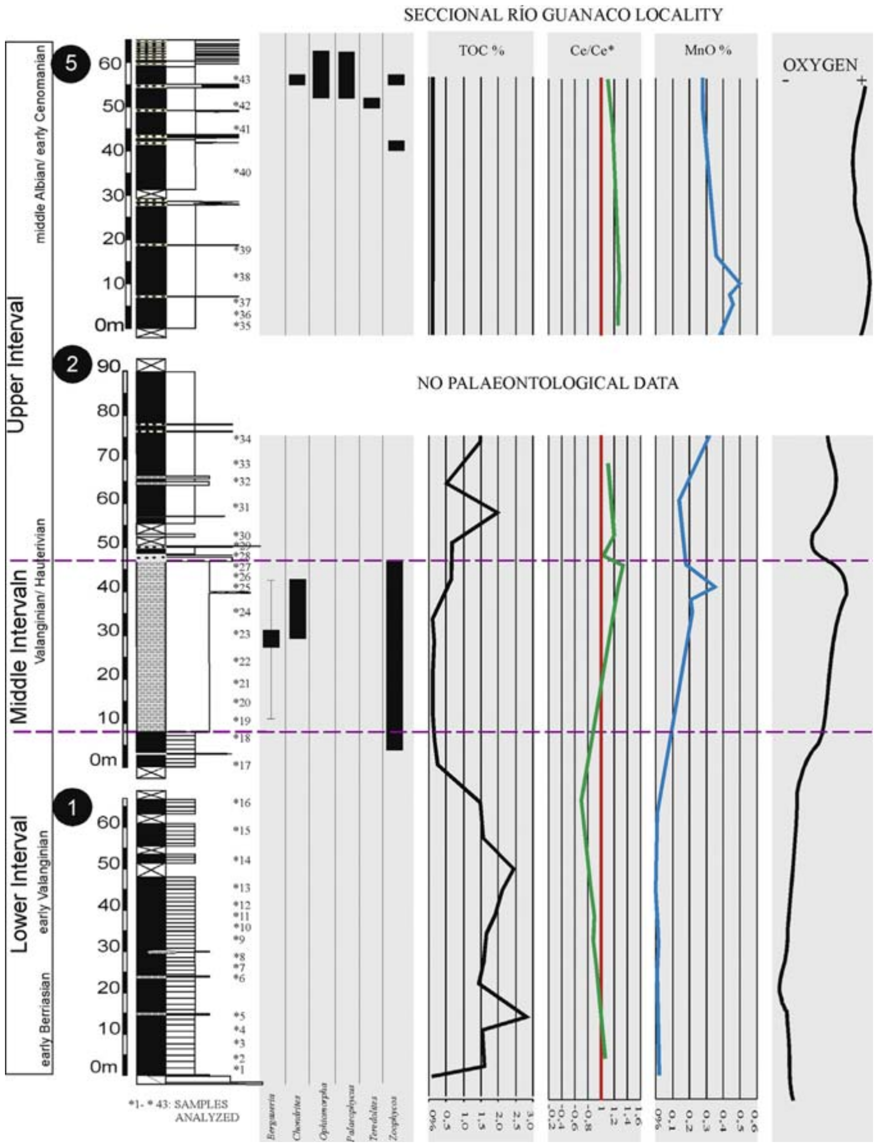

Fig. 7. Trace fossils distribution, the TOC (%), Ce anomaly (Ce/Ce*) and MnO (%) content in the Río Mayer Formation at Seccional Río Guanaco locality during the Lower Cretaceous. The reconstruction of the relative palaeo-oxygenation levels is in the right margin.

OAEs: the decrease in oxygen supply to the deepwater with increase in thermohaline stratification, and the increase in oxygen consumption in the deepwater with an increase in surface productivity (Misumi and Yamanaka, 2008). The most common assumptions suggested changes in the ocean circulation, ocean chemistry, bioproductivity, and climate (Misumi and Yamanaka, 2008). Probably many factors forced the worldwide change of the early Cretaceous anoxic conditions to the late Cretaceous oxic conditions (Jansa and Hu, 2009; Wagreich, 2009), but for the Austral Basin this change is strongly linked with two aspects: first, to the local restricted initial palaeogeography of the basin; and second, to the huge magnitude of the initial 2nd order transgression (Arbe, 2002), which promoted the restricted circulation at the deepest areas of the basin. In contrast, the less intense 2nd order transgression defined by Arbe (2002) during the Aptian-early Albian was in fact developed during the final stages of a 3rd order Highstand (Richiano, 2012), demonstrated by the progradation of the Piedra Clavada deltaic system. This sequence stratigraphic context is the responsible for the better oxygenation conditions after the Neocomian.

Similar oxygenation patterns to those obtained for the Río Mayer Formation have been recognized for the western Tethys deposits (Melinte-Dobrinescu and Roban, 2011). At the beginning of the early Cretaceous, anoxic-dysoxic conditions prevailed, while during the Aptian to the Cenomanian, more oxic palaeoenvironments were observed (Jansa and Hu, 2009; Wagreich, 2009; Melinte-Dobrinescu and Roban, 2011). Apart from some similarities in this topic with deposits from other places, many detailed studies are still to be carried out regarding the correlations with deposits of the northern hemisphere. In this sense, it is very necessary to have a better biostratigraphic framework (especially with microfossils) and/or radiometric ages that allow us to complete the current data available. On the other hand, as the main reasons for the anoxic palaeoenvironments here described are related to local conditions of the basin, the correlation of the curve proposed for the Lower Cretaceous of the Austral Basin with some of the global OAEs has several deficiencies solvable with more chronological and isotopic detail studies.

This study stands out as the first geochemical approach in the Austral Basin (south-western Gondwana) concerning palaeo-oxygenation conditions during the Early Cretaceous. In this respect, further studies and interpretations are needed for a better understanding of the matter here considered and for the identification of potential correlations of the anoxic conditions in the Austral Basin with the global OAEs.

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