Andean Geology 45 (2): 111-129. May, 2018
doi: 10.5027/andgeoV45n2-3059

Andean Geology
www.andeangeology.cl

First record of the Valanginian positive carbon isotope anomaly in the Mendoza shelf, Neuquén Basin, Argentina: palaeoclimatic implications

***Alejandro R. Gómez Dacal[1], Lucía E. Gómez Peral[1], Luis A. Spalletti[1], Alcides N. Sial[2], Aron Siccardi[1], Daniel G. Poiré[1]**

[1] *Centro de Investigaciones Geológicas (CONICET-UNLP), Diagonal 113 N° 275, 1900 La Plata, Argentina. agomezdacal@cig.museo.unlp.edu.ar; lperal@cig.museo.unlp.edu.ar; spalle@cig.museo.unlp.edu.ar; aron@fcnym.unlp.edu.ar; dgpoire@gmail.com*

[2] *Brasil NEG-LABISE, Department of Geology, Federal University of Pernambuco, Recife, PE, 50740-530, Brazil. sial@ufpe.br*

* *Corresponding autor: agomezdacal@cig.museo.unlp.edu.ar*

ABSTRACT. The Tithonian-Valanginian time interval in the Mendoza Shelf (Neuquén Basin, Argentina) is well exposed in the Río Salado, Puesto Loncoche and Cuesta del Chihuido sedimentary sections. From those localities, more than fifty preserved oyster shells of the genus *Aetostreon* sp. were selected and sampled in order to perform the first $\delta^{13}C$ curves for this particular time interval. Mineralogical and cathodoluminiscence properties, inner micromorphology of the valves, added to major and trace element geochemistry were analyzed in order to highlight the best C-O isotopic preservation. The $\delta^{13}C$ isotope curves show values varying between 0 and -3‰ VPDB for the Tithonian-Berriasian basal section, and a positive excursion of ~2.4-2.7‰ VPDB in the Valanginian upper section. This $\delta^{13}C$ up section trend is here considered in order to reveal eminent correlations with other sections from the Neuquén Basin, as well as the Weissert Event from the Tethys area, also on the basis of their ammonite faunal zones. The palaeotemperatures obtained from $\delta^{18}O$ preserved values, added to a detailed sedimentological study suggest that observed $\delta^{13}C$ anomaly may responds to a global climatic change from warm and dry to warm and humid conditions.

Keywords: Chachao Formation, Oyster shells, $\delta^{13}C$, Valanginian anomaly, Cretaceous climate.

RESUMEN. Primer registro de la anomalía isotópica positiva de carbono del Valanginano en la Plataforma Mendocina, Cuenca Neuquina. Argentina: implicaciones paleoclimáticas. El intervalo Titoniano-Valanginiano en la Plataforma Mendocina (Cuenca Neuquina, Argentina) se encuentra muy bien representado en las secciones sedimentarias estudiadas de Río Salado, Puesto Loncoche y Cuesta del Chihuido. En estas localidades más de cincuenta valvas de ostras del género *Aetostreon* sp. fueron seleccionadas y muestreadas con el objeto de obtener las primeras curvas de $\delta^{13}C$ de este particular intervalo temporal. Las propiedades mineralógicas, la respuesta a la catodoluminiscencia, así como la micromorfología interna de las valvas, sumado al análisis geoquímico de los elementos mayoritarios y trazas fueron utilizados para indicar las zonas con el más alto grado de preservación isotópica del C y O. La curva de $\delta^{13}C$ muestra valores que varían entre 0 y -3‰ VPDB para la sección basal de edad titoniana-berriasiana y una excursión positiva de ~2.4-2.7‰ VPDB para la sección cuspidal de edad valanginiana. Esta tendencia del $\delta^{13}C$ hacia el tope de la sección revela una eminente correlación con otras secciones de la Cuenca Neuquina como así también con el Evento Weissert para el área del Tetis, también respaldada por la fauna de amonites presente. Las paleotemperaturas obtenidas aquí a partir de los datos de $\delta^{18}O$, sumado al estudio sedimentológico de detalle sugieren que la anomalía de $\delta^{13}C$ podría ser la respuesta a un cambio climático desde condiciones cálidas y áridas a cálidas y húmedas registrado a nivel global.

Palabras clave: Formación Chachao, Ostras, $\delta^{13}C$, Anomalía valanginiana, Clima cretácico.

1. Introduction

The Valanginian positive $\delta^{13}C$ excursion was first recorded by Cotillon and Río (1984) in the Gulf of Mexico (DSDP Site 535). It was then described by many authors in different basins throughout the northern hemisphere (Lini *et al*., 1992; Weissert *et al*., 1998; Hennig *et al*., 1999; Melinte and Mutterlose, 2001; Bartolini, 2003; Erba *et al*., 2004; Duchamp-Alphonse *et al*., 2007; Price and Nunn, 2010; Charbonnier *et al*., 2013; Meissner *et al*., 2015; Silva-Tamayo *et al*., 2016), and subsequently in the Neuquén Basin (Aguirre-Urreta *et al*., 2008; Gómez Peral *et al*., 2012) (Fig. 1), in the southern hemisphere. This global Valanginian positive $\delta^{13}C$ anomaly was chronologically situated by Lini *et al*. (1992) on the basis of calcareous nannofossils. The excursion (~139 My) started in the late early Valanginian *Busnardoites campylotoxus* Zone and ended in the early late Valanginian *Saynoceras verrucosum* Zone (Weissert *et al*., 1998; Hennig *et al*., 1999; Van de Schootbrugge *et al*., 2000; Föllmi, 2012).

The origin and features of this anomaly has been the subject of controversy. Lini *et al*. (1992) and Erba *et al*. (2004) link it to an increase in atmospheric CO_2 as a result of volcanism (especially the basalts of the Paraná-Etendeka emissions), which would have led to global warming. This hypothesis is supported by the mineralogical studies of Duchamp-Alphonse *et al*. (2011), who analyzed an increased kaolinite content related to a warm, humid climate in sedimentary deposits. On the other hand, Van de Schootbrugge *et al*. (2000), Pucéat *et al*. (2003), and Price and Mutterlose (2004) propose a cold climate for the anomaly, based on palaeotemperatures derived from $\delta^{18}O$ data in belemnites and fish tooth enamels. Such hypothesis is supported by glendonites (Kemper, 1987; Tarduno *et al*., 2002), dropstones, as well as by the nature of calcareous nannofossils (Melinte and Mutterlose, 2001).

Erba *et al*. (2004) link the positive $\delta^{13}C$ excursion with the presence of black shales rich in organic carbon in the Southern Alps and in the Pacific Ocean, reinterpreting the Valanginan anomaly as an ocean anoxic event called the Weissert Event. Westermann *et al*. (2010) propose that the anoxic conditions would be circumscribed only to a few regions. Recently, Föllmi (2012) interprets the Valanginian anomaly as a short period (<1 My) of

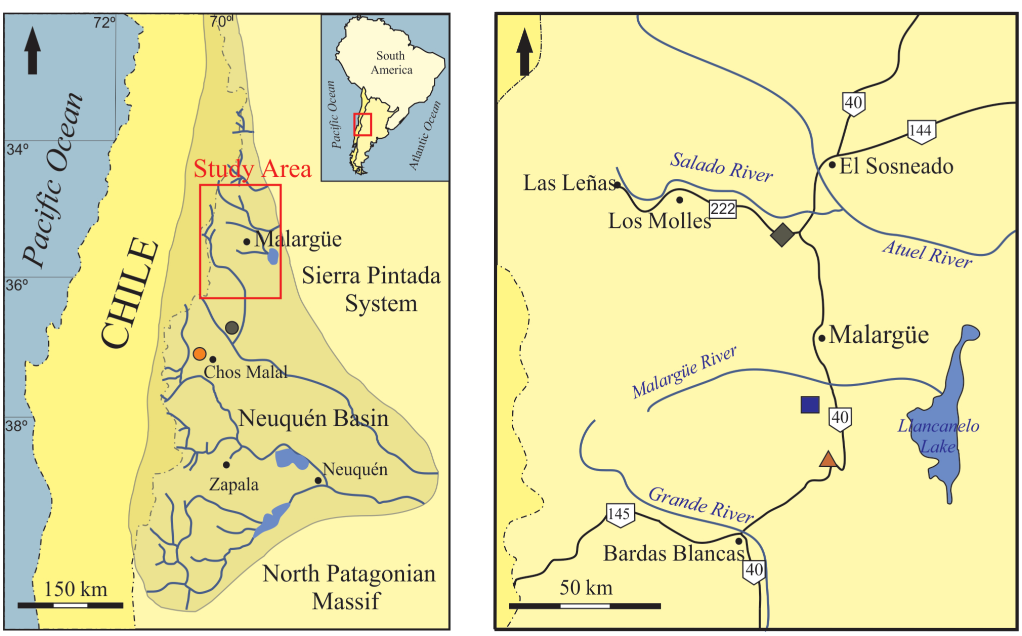

FIG. 1. To the left, the Neuquén Basin, located in west-central Argentina. Record of the Weissert Event in the Neuquen Basin: ● Cerro La Parva area (Aguirre Urreta *et al*., 2008), ● Buta Ranquil area (Gómez Peral *et al*., 2012). To the right, the study area, with the location of the studied sections: ◆ Río Salado, ■ Puesto Loncoche and ▲ Cuesta del Chihuido.

change in climate conditions from arid to humid in a warm context, classifying the Weissert Event as an episode of environmental change.

The combination of a decrease in shallow-marine carbonate production coupled with the enhanced burial of organic matter on the continent has been suggested to explain the global positive carbon excursion (Westermann *et al*., 2010). Enhanced detrital and dissolved continental fluxes to the ocean probably boosted marine primary productivity in marginal marine and epicontinental settings (Föllmi, 1995; Duchamp-Alphonse *et al*., 2007).

The main objective of this contribution is to provide the first record of $\delta^{13}C$ data from the Tithonian-Valanginian interval of the Mendoza Shelf (Neuquén Basin), with special emphasis on the positive excursion of the Valanginian. The palaeogeographic position of the section is of particular interest, since it was deposited in a near-shore setting. Palaeotemperature data obtained from $\delta^{18}O$ in calcareous fossils is also shown. Moreover, the integration of stable isotope data and the analyzed sedimentological aspects of the outcrops studied can contribute to the understanding of the climatic context of the Valanginian carbon excursion registered globally.

2. Geological setting

2.1. Neuquén Basin

The Neuquén Basin is located in west-central Argentina, and it constitutes the main oil basin in the country (Fig. 1). Two main depositional areas can be recognized in the Neuquén Basin: the Neuquén Embayment to the south, and the narrow Mendoza Shelf to the north (Doyle *et al*., 2005). The development of the Mendoza Shelf is favoured by the obliquity between the Andean arc and the axis of the basin, which is oriented NW-SE, and it is characterized by a significant reduction in the width of the basin (Spalletti *et al*., 2000; Doyle *et al*., 2005). In this area, an important sedimentary succession (4,000 m) was deposited during the Upper Jurassic-Lower Cretaceous interval, initially called "Mendociano" by Groeber (1947) and currently known as "Mendoza Group". It comprises the Vaca Muerta, Chachao and Agrio formations of the Mendoza Shelf (Mombrú *et al*., 1976) (Fig. 2).

The Vaca Muerta Formation was originally defined by Weaver (1931) to designate a set of Tithonian layers consisting of dark grey calcareous shales (Spalletti *et al*., 2015). This unit represents the stratigraphic succession of the Mendoza Group with the largest extension, the highest degree of lithological uniformity and continuity and of huge regional economic importance due to its potential oil and phosphate content (Leanza *et al*., 1977). The Vaca Muerta Formation is underlain by the continental deposits of the Tordillo Formation, and the contact between both formations is marked by the Tithonian transgression (Leanza, 1981). In the Mendoza Shelf, overlying the Vaca Muerta Formation, marine carbonates and shales of the Chachao Formation are recorded. The Vaca Muerta

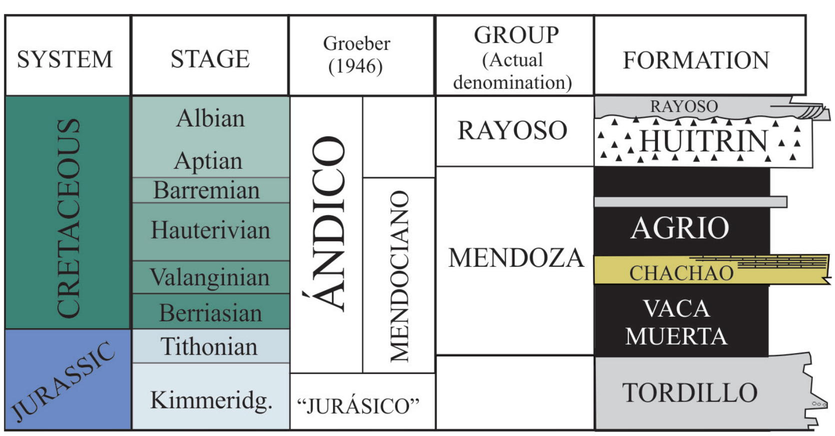

FIG. 2. Chronostratigraphic scheme of the Neuquén Basin (Upper Jurassic- Lower Crateceous). Based on Groeber (1946) and Gulisano and Gutiérrez Pleimling (1994).

Formation was deposited between the end of the early Tithonian (*Virgatosphinctes mendozanus* Ammonite Zone) (Riccardi, 2015) and the beginning of the early Valanginian (*Neocomites wichmanni* Ammonite Zone) (Kietzmann *et al*., 2015).

The Chachao Formation (Groeber, 1946) consists of bioclastic wackestones, packstones, grainstones, floatstones and rudstones. This unit overlies the Vaca Muerta Formation and is overlain by the Agrio Formation, both with concordant contacts (Mombrú *et al*., 1978; Carozzi *et al*., 1981). The Chachao Formation was deposited during the early Valanginian and part of the late Valanginian. It contains the *Lissonia riveroi* Ammonite Zone (beginning of the early Valanginian) (Aguirre-Urreta and Rawson, 1997; Palma and Lanés, 2001) and the *Olcostephanus atherstoni* Ammonite Zone (end of the early Valanginian and beginning of the late Valanginian) (Legarreta and Kozlowski, 1981; Aguirre-Urreta *et al*., 2011).

2.2. Geological setting of the studied dataset

Fieldwork was carried out in three localities of the Mendoza Shelf, near the city of Malargüe (Fig. 1): Río Salado, Puesto Loncoche and Cuesta del Chihuido. In these localities, the sedimentary succession studied is composed of mixed ramp deposits (Mitchum and Uliana, 1986; Legarreta and Uliana, 1991; Spalletti *et al*., 2000; Kietzmann *et al*., 2008; among others) of the Vaca Muerta and Chachao formations (Tithonian-Valanginian).

2.2.1. Río Salado area

In the Río Salado area (35°11' S and 69°46' W), a mixed succession of sedimentary rocks with a vertical coarsening-upward trend has been described (Doyle *et al*., 2005). This unit consists of a 176-m-thick succession composed of an alternation of black shales and carbonates. Carbonates are arranged in 10-70-cm-thick layers composed of bioclastic wackestones, packstones, floatstones and rudstones (Fig. 3). The formational boundaries and environmental characterization of these deposits were proposed by Doyle *et al*. (2005).

The Vaca Muerta section at Río Salado area is characterized by the presence of black shales interbedded with marls and scarce wackestones and packstones near of the base. Based on these lithological attributes and the recognized trace fossil associations, Doyle *et al*. (2005) interpreted this section as the result of sedimentation under an anoxic to suboxic seafloor in a basinal environment. This siliciclastic and carbonate particles may have been deposited from suspension under an anoxic to suboxic seafloor, with evidences of storm reworking at the top. The middle interval consists of black shales, marls, heterolithic beds and packstones, with primary sedimentary structures (such as lamination and hummocky cross-stratification), and deformational structures (water escape features, ball-and-pillow), all this features strongly suggest deposits of a distal outer ramp system. The upper part of Vaca Muerta Formation is characterized by black shales and marls, marking a restoration of the basinal conditions. Meanwhile, the Chachao Formation consists of floatstones, rudstones, shales and marls. The skeletal carbonates are interpreted as oysters shell beds that developed in a proximal outer ramp (Doyle *et al*., 2005).

2.2.2. Puesto Loncoche area

In the Puesto Loncoche area (35°36' S and 69°37' W), the studied deposits were previously described in detail by Kietzman *et al*. (2008). The same vertical coarsening-upward trend observed in the Río Salado section is recognized here, accompanied by a thickening-upward arrangement that culminates in a 25-m-thick oyster bank, corresponding to Chachao Formation (Fig. 3).

A detailed palaeoenvironmental analysis of the Vaca Muerta Formation in the Puesto Loncoche area proposed by Kietzmann *et al*. (2008) divides the unit, from base to top, into four sub-environments: basin, distal outer ramp, proximal outer ramp and distal middle ramp. The basin sub-environment is composed of black shales, massive marls and siltstones, together with laminated mudstones and wackestones deposited by decantation in anoxic-suboxic environments. The distal outer ramp consists of black shales, marls, nodular mudstones and bioclastic wackestones (massive and laminated). The fine-grained siliciclastic and mixed siliciclastic carbonate deposits were essentially accumulated from suspension fall out. The outer ramp bioclastic wackestones represent distal storm-induced layers. In the proximal outer ramp, in addition to the association described previously, the above mentioned authors identified floatstones and packstones interpreted as proximal tempestites. Finally, the distal middle ramp is composed by an association of suspension

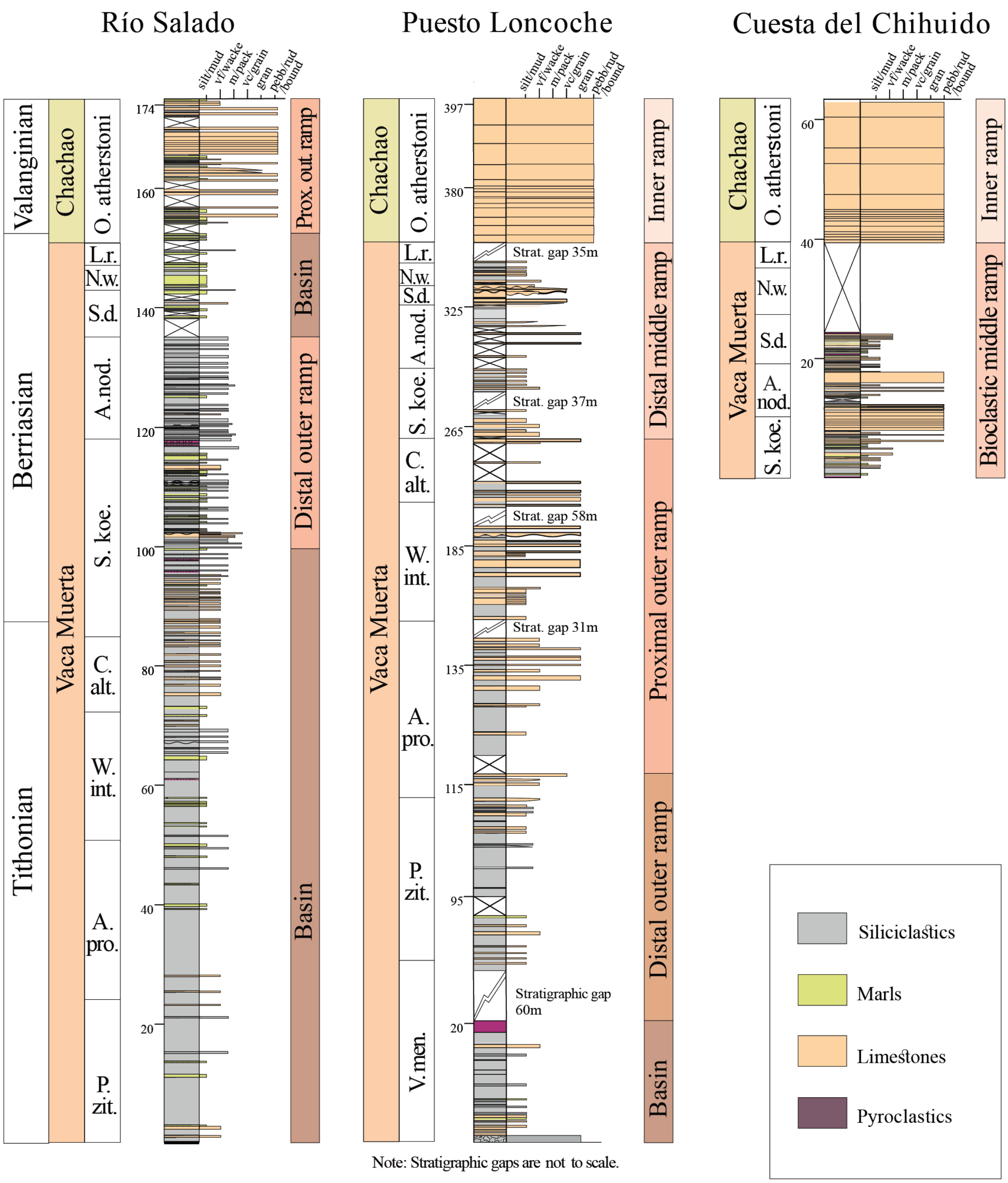

FIG. 3. Sedimentary sections of the studied localities; notice their formational boundaries and ammonites biozones. ***V. men:*** *Virgatosphinctes mendozanus;* ***P. zit:*** *Pseudolissoceras zitteli;* ***A. pro:*** *Aulacosphictes proximus;* ***W. int:*** *Windhauseniceras internispinosum;* ***C. alt:*** *Corongoceras alternans;* ***S. koe:*** *Substeuroceras koeneni;* ***A. nod:*** *Argentiniceras noduliferum;* ***S.d.:*** *Spiticeras damesi* ***N. w:*** *Neocomites wichmani;* ***L. r:*** *Lissonia riveroi;* ***O. atherstoni:*** *Olcostephanus atherstoni;* **Silt/mud:** silt/mudstone; **vf/wacke:** very fine sand/wackestone; **m/pack:** medium sand/packstone; **vc/grain:** very coarse sand/grainstone; **gran:** granule; **pebb/rud/bound:** pebble/rudstone/boundstone.

fall out deposits (shales, marls, nodular mudstones) and storm induced deposits (floatstones, massive bioclastic packstones and wackestones). Subsequently, the palaeoenvironmental interpretations were later reinforced with taphonomic, biofacies and sequence stratigraphic studies (Kietzmann and Palma, 2009; Kietzmann *et al*., 2014; Kietzmann *et al*., 2015).

The Chachao Formation is represented, in this area (Fig. 3), by an inner ramp environment, constituted by a coarse oyster bioclastic buildup of rudstones and floatstones, which shows vertical accumulation and a lateral stacking pattern after described by Palma and Lanés (2001). Within these bodies, slight signs of reworking were recognized from the original oyster banks, and can be characterized as an autoparabiostrome according to Kershaw (1994). Palma and Lanés (2001) performed a taphofacies analysis of carbonate bodies of the Chachao Formation, describing patterns of accumulation and dividing this unit into two sections: the lower section, with a low degree of reworking of the oyster beds, and the upper section, with a progressive increase in the intensity of disarticulation, bioerosion and fragmentation of the remains, accompanied by an increase in the matrix content.

2.2.3. Cuesta del Chihuido area

In the 63-m-thick Cuesta del Chihuido study section (35°44’ S and 69°34’ W), only the top of the Vaca Muerta Formation and the entire Chachao Formation crop out (Kietzmann *et al*., 2015). This section shows vertical arrangement, similar to the one described in Puesto Loncoche (Fig. 3). The Vaca Muerta Formation was studied in this region by Kietzmann *et al*. (2015), the cusp deposits were described as an oyster intercalation forming autoparabiostromes composed of bioclastic floatstones and rudstones, bioturbated wackestones, packstones, laminated wackestones and marls. This section is interpreted as a bioclastic middle ramp to proximal outer ramp, and an oyster biostrome dominated middle ramp.

The Chachao Formation in the Cuesta del Chihuido area has been extensively studied, from both the sedimentological and palaeontological points of view (Leanza *et al*., 1977; Mombrú *et al*., 1978; Legarreta and Koszlowsky, 1981; Uliana *et al*., 1979; Legarreta *et al*., 1981; Palma and Angeleri, 1992; Palma and Lanés, 2001), as well as by means of diagenetic analysis (Carozzi *et al*., 1981; Palma *et al*., 1999; Palma *et al*., 2008). It was described as an accumulation of floatstones and rudstones rich in benthic fauna (serpulids, oysters, brachiopods, and occasional ammonites) (Palma and Lanés, 2001), forming thick bioclastic accumulations associated with an inner carbonate ramp, with similar characteristics to those described for Puesto Loncoche.

3. Materials and methods

3.1. Sampling

Three sedimentary sections from three selected areas were studied in detail in order to recognize the sedimentary facies, fossil content and their palaeoenvironmental features. Fifty-seven (57) samples of fossil oysters (11 from Río Salado, 29 from Puesto Loncoche and 17 from Cuesta del Chihuido) were selected from sedimentary logs, taking as the main criteria the sampling equidistance (subject to fossil presence) and the degree of fossil preservation. Samples of *Aetostreon* sp. were selected to obtain accurate C and O isotope data and also to avoid the variations due to the “vital effect” (Fig. 4). Moreover in order to constrain these data with previous results obtained from samples of the same genus in other localities of the Neuquén Basin (Aguirre-Urreta *et al*., 2008).

Samples were carefully selected based on their mesoscopic features. The best criteria for choosing the fossil material were the taphonomic characteristics (avoiding material which shows a high degree of fragmentation and corrasion), and the size (microscopic observations showed that the larger individuals had better preservation of the internal layers); therefore, specimens larger than 5 cm were selected.

3.2. Petrography

Chips from the innermost oyster shell were covered with Au and analysed by SEM-EDS with a FEI Quanta 200 SEM (Laboratorio de Investigaciones de Metalurgia Física, Universidad Nacional de La Plata (UNLP), Argentina) with the objective of recognizing the original microtextures. In addition, sixteen thin sections in dorsoventral position were analysed under cathodoluminescence CITL Technosyn MKIII microscope of the Centro de Investigaciones Geológicas (CONICET-UNLP). Manganese emits a characteristic dull to bright luminescence during cathodic excitation of the calcitic shell layers and induces a typical orange colour, indicative of

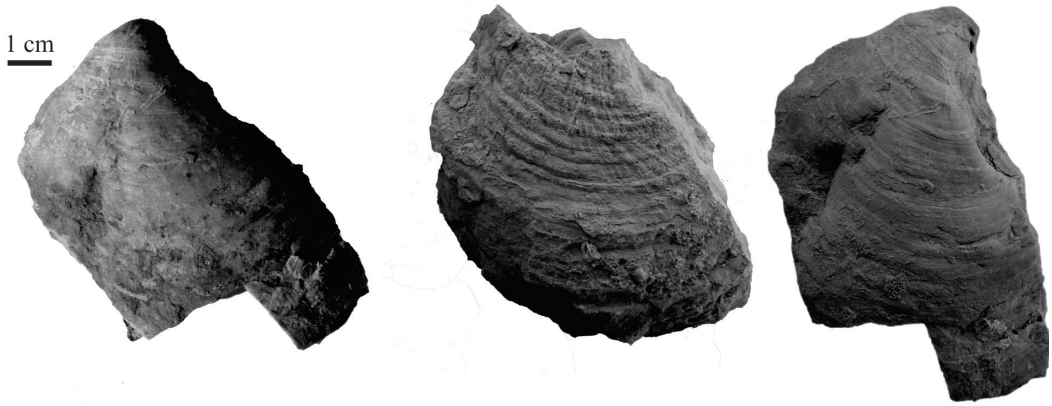

FIG. 4. Selected samples of *Aetostreon* sp. with a high degree of preservation. Notice the low grade of corrasion on external walls, this taphonomic feature suggest a better conservation of the inner layers.

diagenetic alteration, while primary calcite sectors appear neither luminescent nor blue (Ullmann and Korte, 2015; Marshall, 1992).

3.3. Geochemistry

Twenty-eight elemental analyses were performed in ~50 mg of powdered oyster samples (12 from Puesto Loncoche, 6 from Río Salado and 10 from Cuesta del Chihuido). The dissolution of the carbonate phase (5% HNO_3 solution for 2-3 h) was analyzed by ICP-MS, using a Perkin-Elmer ICP-MS fitted with a Meinhardt concentric nebulizer of the Centro de Investigaciones Geológicas geochemistry laboratories (CONICET- Universidad Nacional de La Plata) to determine Mn and Sr concentrations in ppm. Precision and reproducibility for all elements analyzed are better than 10%, based on replicate measurements of laboratory calcite and dolomite standards.

Fifty-seven microsamples of 0.1 gr of oysters (one sample per oyster) were taken with a microdrill. The microsamples were analyzed for C and O isotopes (29 from Puesto Loncoche, 11 from Río Salado and 17 from Cuesta del Chihuido). These analyses were performed at the Núcleo de Estudos Geoquímicos-Laboratório de Isótopos Estáveis (NEG-LABISE) of the Departamento de Geología, Universidade Federal de Pernambuco, Brazil. Extraction of CO_2 gas from selected unaltered samples was performed in a high-vacuum line after reaction with 100% orthophosphoric acid at 25 °C for one day. Released CO_2 was analyzed after cryogenic cleaning in double inlet, triple-collector SIRA II or Delta V Advantage mass spectrometers and results are reported in δ notation in per mil (‰) relative to the VPDB standard. The uncertainties of the isotope measurements were better than 0.1‰ for carbon and 0.2‰ for oxygen, based on multiple analyses of an internal laboratory standard (BSC). The $\delta^{13}C$ and $\delta^{18}O$ values obtained were calibrated against the internationally accepted International Atomic Energy Association carbonate standard NBS-19.

3.4. Palaeotemperatures

Palaeotemperature values obtained from the calcite samples were estimated using the modified version of the Epstein palaeotemperature equation (Epstein *et al*., 1953), given by Anderson and Arthur (1983), and then shown by Pirrie *et al*. (2004) as:

$$T(°C)=16.0-4.14(\delta c-\delta w)+0.13(\delta c-\delta w)^2$$

In this equation, $\delta c=\delta^{18}O$ (VPDB) of the analyzed carbonate at 25 °C, and $\delta w=\delta^{18}O$ (SMOW) of the water in which the carbonate precipitated, relative to the Standard Mean Ocean Water international standard. While δc is measured, δw has to be estimated as -1.2‰, the global average for periods of limited or no glaciation (Shackleton and Kennett, 1975). The $\delta^{18}O$ values higher than -5‰ VPDB were considered appropriate to estimate palaeotemperatures as seen in similar works (*e.g*., Zakharov *et al*., 2011). Those higher values indicate a low degree of diagenetic alteration (Brand and Veizer, 1981) and are therefore more accurate to show original features.

4. Results

From the photomicrographs obtained by SEM, oysters show foliated growth in layers with smooth-textured surfaces (Fig. 5). Cathodoluminescence photomicrographs make it possible to distinguished luminescent and non-luminescent zones (Fig. 6). Non-luminescent areas coincide with the growth of a foliated type of oysters, and were particularly selected for isotope microsampling.

Manganese, Sr, $\delta^{13}C$, and $\delta^{18}O$ values are shown in Table 1. The Mn/Sr ratio is below 1.5 (Table 1), except for three samples (PL88, CDC35 and CDC38, excluded from further interpretation), which are as high as Mn/Sr=6 and are considered as probably being diagenetically altered. Strontium concentrations vary between 300 and 700 ppm, very close to the data recorded by Korte *et al*. (2009) and Korte and Hesselbo (2011) for Jurassic oysters, with anomalously low values of up to 135 ppm.

Manganese concentrations reach 100 ppm on average, with some values of up to 282 ppm, which are also similar to those obtained by Korte *et al*. (2009) and Korte and Hesselbo (2011) for Jurassic oysters.

The $\delta^{13}C$ values vary between -4.93 and 2.66‰ VPDB, while $\delta^{18}O$ values are between -1.92 and -4.76‰ VPDB, with anomalous values of up to -11.56‰ VPDB (samples CDC 23 and 35-41, excluded from further interpretation (Table 1).

4.1. Isotopic preservation

The degree of isotopic preservation was evaluated considering the following parameters: (**i**) preservation of the original valve microtextures (Fig. 5); (**ii**) presence of non-luminescent areas (Fig. 6); (**iii**) $\delta^{18}O \geq -5$‰ VPDB; (iv) lack of correlation between $\delta^{13}C$ *versus* Mn/Sr (≤1.5), $\delta^{13}C$ *versus* Sr (ppm), $\delta^{18}O$ *versus* Mn (ppm) and $\delta^{13}C$ *versus* $\delta^{18}O$.

Selected layers with smooth-textured surfaces in oysters with foliated growth (observed by SEM) are considered as diagenetically unaltered (Korte and Hesselbo, 2011; Ullmann and Korte, 2015). Similarly, non-luminescent areas, which coincide

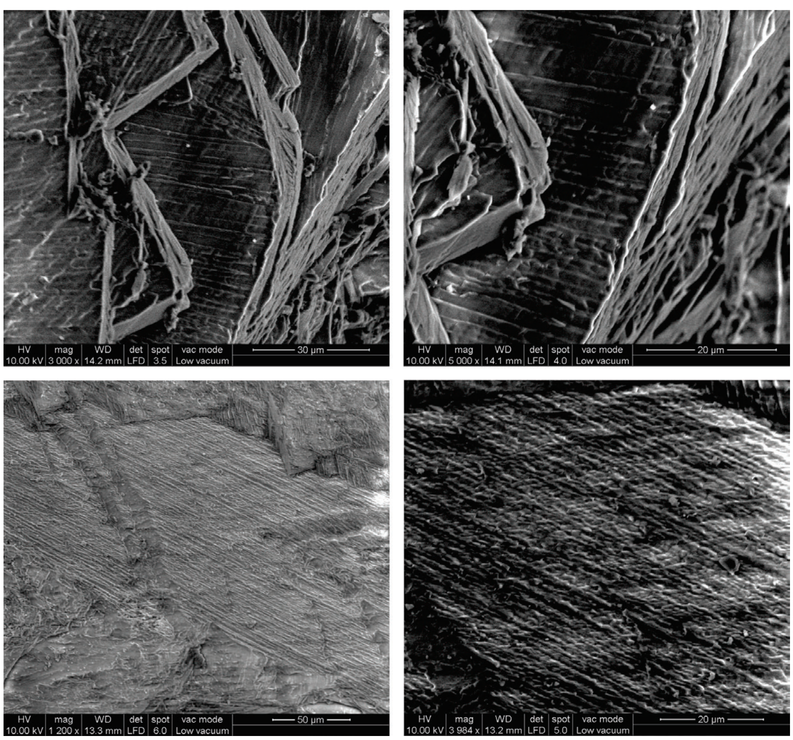

FIG. 5. Scanning electron microscopy images of oysters from the Puesto Loncoche sedimentary succession. It is possible to observe the “smooth textured” surfaces.

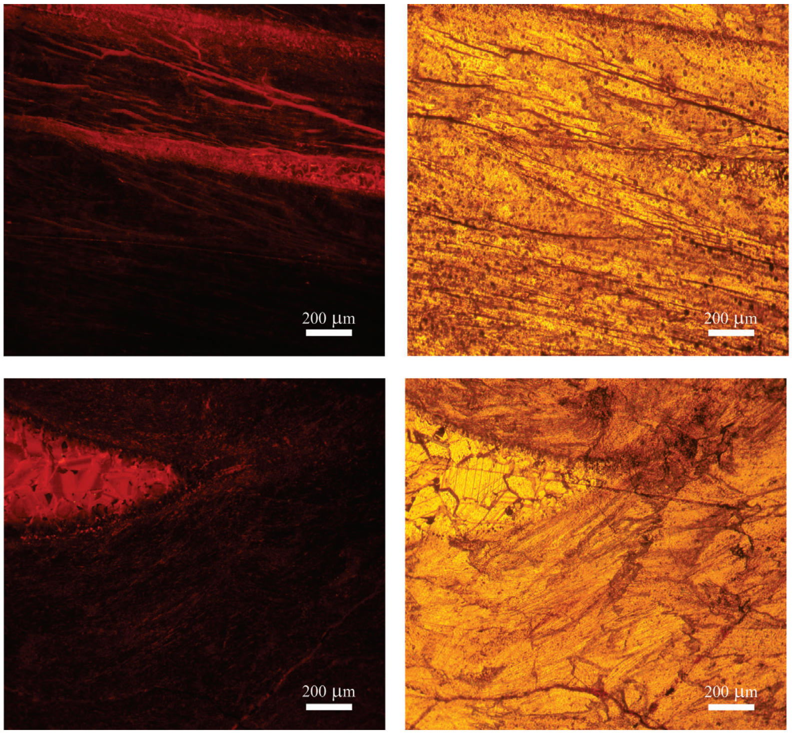

FIG. 6. Cathodoluminescence microscope images of oyster samples. Luminescent (right) and non-luminescent (left) areas are recognized; the non-luminescent areas match the foliated growth of oysters.

TABLE 1. GEOCHEMISTRY AND PALAEOTEMPERATURES VALUES.

Sample/weight	Mn (ppm)	Sr (ppm)	Mn/Sr	$\delta^{13}C‰_{VPDB}$	$\delta^{18}O‰_{VPDB}$	T(°C)
RS 248B	13	687	0.02	2.19	-2.40	21.77
RS 241B	-	-	-	2.53	-4.43	29.91
RS 237B	30	531	0.06	0.93	-3.15	24.78
RS 234A	-	-	-	0.86	-3.82	27.47
RS 232B	91	424	0.22	2.24	-3.97	28.07
RS 228B	27	516	0.05	1.31	-3.38	25.70
RS 227B	27	565	0.05	0.94	-2.86	23.62
RS 226C	-	-	-	0.94	-3.30	25.38
RS 223C	89	507	0.18	-0.39	-3.15	24.78
RS 221	-	-	-	0.43	-4.17	19.61
RS 220B	-	-	-	1.14	-4.08	28.51
PL 119	96	351	0.27	0.91	-2.69	22.94
PL 116	63	587	0.11	2.66	-2.92	23.86
PL 112	-	-	-	1.87	-4.37	29.67
PL 111	155	360	0.43	1.96	-3.55	26.38
PL 110B	99	430	0.23	1.66	-3.12	24.66
PL 108B	-	-	-	1.16	-5.80	-
PL 100	-	-	-	-0.75	-2.28	21.29

table 1 continued.

Sample/weight	Mn (ppm)	Sr (ppm)	Mn/Sr	$\delta^{13}C‰_{VPDB}$	$\delta^{18}O‰_{VPDB}$	T(°C)
PL 98B	-	-	-	-0.43	-1.92	19.85
PL 89B	99	394	0.25	-1.51	-2.05	20.37
PL 88C	-	-	-	-2.01	-2.62	22.65
PL 88	382	251	1.52	-4.51	-2.85	23.58
PL 83	-	-	-	-3.21	-4.76	31.24
PL 78	-	-	-	-2.11	-4.32	29.47
PL 76	-	-	-	-0.84	-3.46	26.02
PL 72B	-	-	-	-4.93	-1.97	20.05
PL 72	-	-	-	-2.14	-3.79	27.35
PL 68	72	476	0.15	-2.08	-4.32	29.47
PL 65	61	375	0.16	-4.54	-1.94	19.93
PL 61B	43	546	0.08	0.12	-2.10	20.57
PL 61	76	467	0.16	-0.12	-3.52	26.26
PL 60B	-	-	-	0.04	-2.35	21.57
PL 54	-	-	-	0.15	-2.41	21.81
PL 50	44	598	0.07	-1.18	-2.58	22.49
PL 44B	45	499	0.09	0.33	-2.10	20.57
PL 44	-	-	-	0.04	-2.79	23.34
PL 42B	-	-	-	-2.58	-2.70	22.98
PL 38	-	-	-	-0.46	-2.73	23.10
PL 33B	-	-	-	0.99	-4.06	28.43
PL 22C	-	-	-	-0.20	-3.70	26.99
CDC 41	-	-	-	0.89	-7.68	-
CDC 40	117	249	0.47	2.13	-7.17	-
CDC 39	56	487	0.12	0.91	-5.94	-
CDC 38	479	86	5.58	1.33	-7.34	-
CDC 37	-	-	-	1.67	-7.14	-
CDC 36	163	274	0.60	-0.33	-11.56	-
CDC 35	314	53	5.93	-0.18	-8.78	-
CDC 24	-	-	-	-0.41	-2.96	24.02
CDC 23	282	284	0.99	-2.08	-7.22	-
CDC 22	-	-	-	-1.51	-3.52	26.26
CDC 18	18	374	0.05	0.04	-2.63	22.69
CDC 17	-	-	-	-0.98	-3.05	24.38
CDC 16	163	135	1.21	-0.53	-2.85	23.58
CDC 15	-	-	-	-1.10	-3.54	26.34
CDC 12	66	443	0.15	-0.53	-2.79	23.34
CDC 11B	-	-	-	-0.78	-2.79	23.34
CDC 10	221	235	0.94	-2.84	-3.38	29.47

Concentrations of Mn (ppm) and Sr (ppm), obtained by ICP-MS analysis. Mn/Sr ratios estimated as diagenetic proxies. Results of $\delta^{13}C$ (‰VPDB) and $\delta^{18}O$ (‰VPDB), and estimated palaeotemperatures (T °C) of samples from the three sedimentary sections (**RS:** Río Salado; **PL:** Puesto Loncoche; **CDC:** Cuesta del Chihuido).

with those of foliated growth, indicate a better degree of preservation, as mentioned above.

The data obtained from Mn and Sr showed there was no relative Sr impoverishment or Mn enrichment produced by diagenetic alterations in most of the samples, with three exceptions (samples PL 88, CDC 35 and CDC 38, Table 1) which show higher values of Mn, and depleted Sr, which can be associated with probable diagenetic alteration. Furthermore, the degree of correlation between the different variables was calculated considering the values of stable isotopes and Mn and Sr concentrations (Fig. 7 and Table 2).

The lack of covariation between $\delta^{13}C$ and Mn/Sr (Fig. 7a and Table 2) and $\delta^{13}C$ *versus* Sr (Fig. 7b

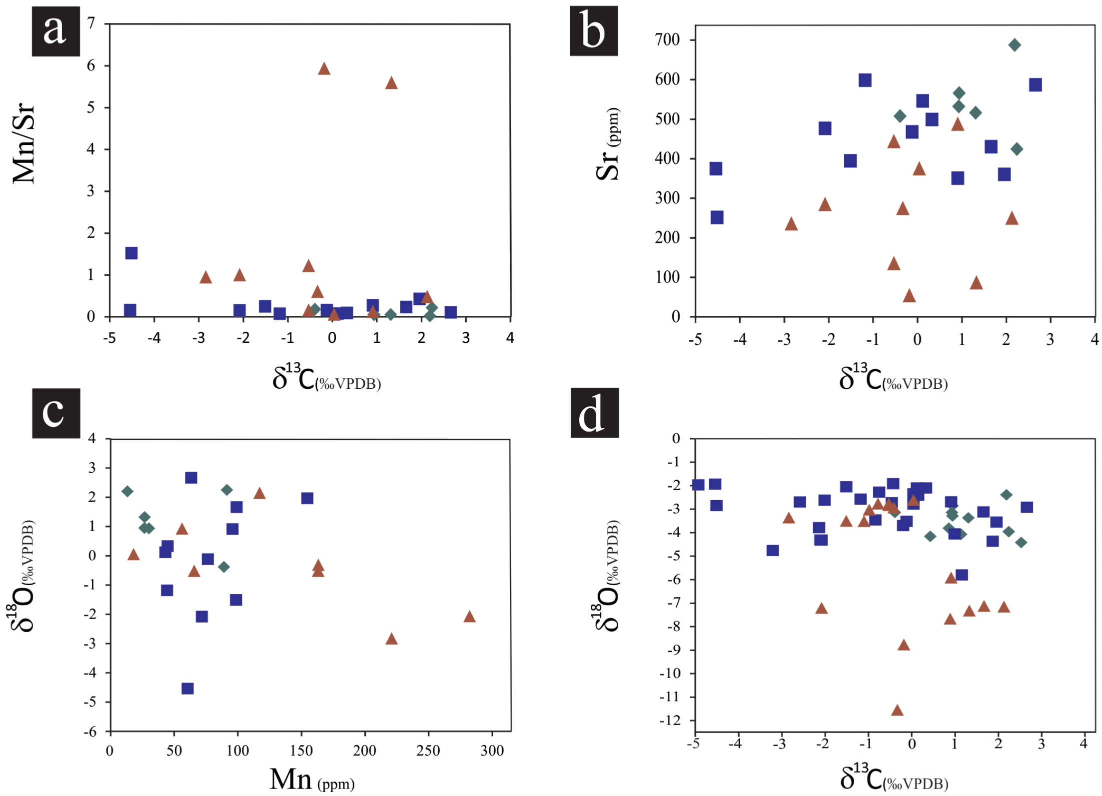

FIG. 7. Isotopic and element cross plots: **a.** Mn/Sr *versus* $\delta^{13}C$; **b.** Sr *versus* $\delta^{13}C$; **c.** $\delta^{18}O$ *versus* Mn; and **d.** $\delta^{13}C$ *versus* $\delta^{18}O$. ◆ Río Salado samples, ■ Puesto Loncoche samples and ▲ Cuesta del Chihuido samples.

TABLE 2. CORRELATION COEFFICIENT (R^2).

	$\delta^{13}C$ *versus* Mn/Sr	$\delta^{13}C$ *versus* Sr	$\delta^{18}O$ *versus* Mn	$\delta^{13}C$ *versus* $\delta^{18}O$
Río Salado	0.02	0.03	0.48	0.02
Puesto Loncoche	0.10	0.01	0.17	0.02
Cuesta del Chihuido	0.00	0.00	0.10	0.17

Estimated between the following variables: $\delta^{13}C$ *versus* Mn/Sr; $\delta^{13}C$ *versus* Sr; $\delta^{18}O$ *versus* Mn; and $\delta^{13}C$ *versus* $\delta^{18}O$, discriminated for the three sedimentary logs (Río Salado, Puesto Loncoche and Cuesta del Chihuido).

and Table 2) for the three localities studied suggest a high degree of isotopic preservation for the stable carbon isotopes (Marshall, 1992). Furthermore, the diagram of $\delta^{18}O$ *versus* Mn shows no correlation in the Puesto Loncoche and Cuesta del Chihuido localities, while in the Río Salado area it shows a slight positive correlation (Fig. 7c and Table 2).

4.2. Chemostratigraphy

The $\delta^{13}C$ values were represented in curves parallel to the sedimentary logs in order to compare the segments of the same age from the three localities under study (Fig. 8). The $\delta^{13}C$ curve for the Río Salado sector shows values obtained from the uppermost strata of the Chachao Formation, taking into consideration the presence and preservation of the fossil samples. In Puesto Loncoche, the $\delta^{13}C$ curve represents the complete section; however, data from the basal section of the Vaca Muerta Formation is not represented due to the absence of fossils of the genus *Aetostreon* sp. In Cuesta del Chihuido, the $\delta^{13}C$ curve represents the complete section of the Chachao Formation and the upper part of the Vaca Muerta Formation.

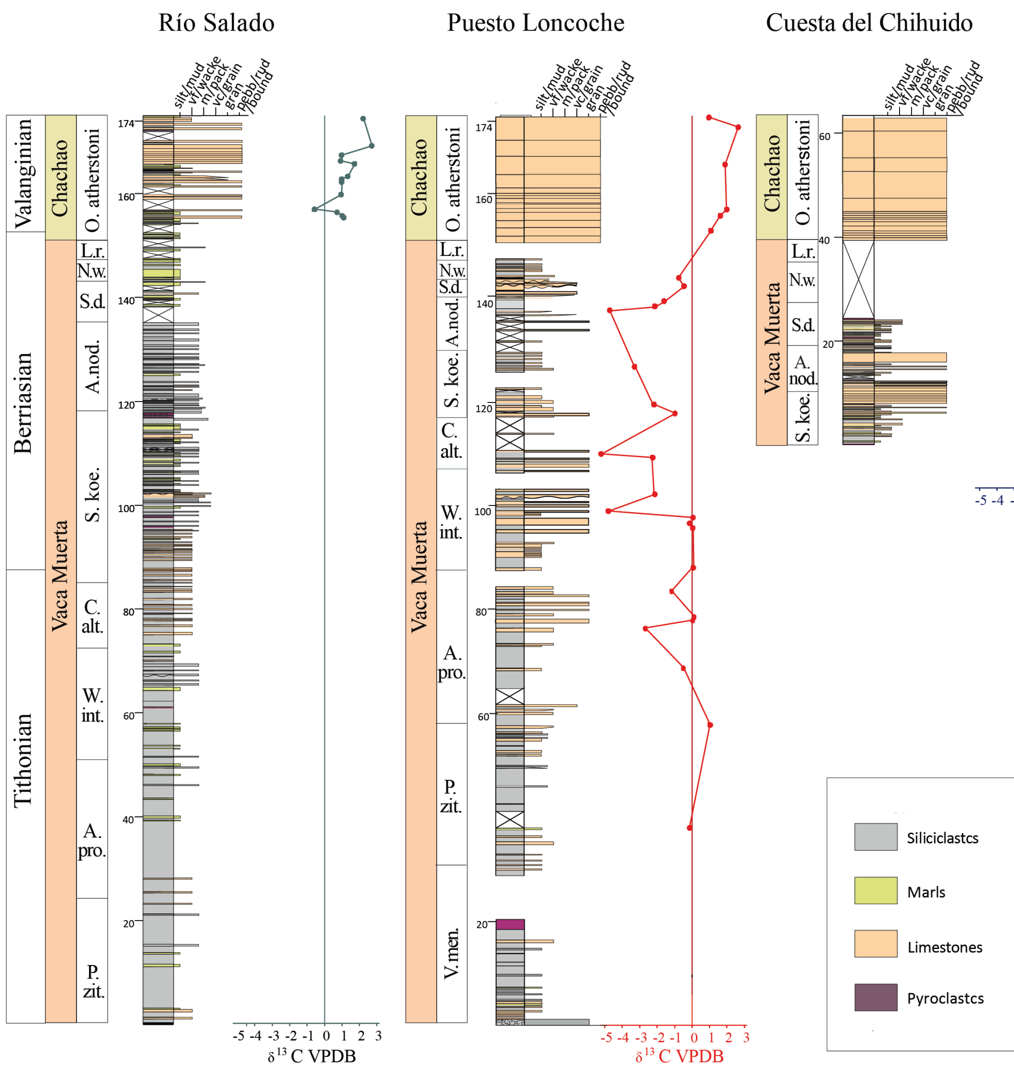

FIG. 8. Sedimentary sections with the $\delta^{13}C$ curves of the three areas under study (Río Salado in green, Puesto Loncoche in red and Cuesta del Chihuido in blue). Towards the top of the sequence, a carbon positive excursion can be recognized.

The $\delta^{13}C$ values from the early Tithonian (*V. mendozanus* Ammonite Zone) to the early Valanginian (*N. wichmanni* Ammonite Zone) range from slightly negative to ~0‰, with a single value that reaches 1‰. In the early Valanginian-early late Valanginian succession (*O. atherstoni* Ammonite Zone), a marked positive excursion in $\delta^{13}C$ values is recognized throughout the three studied sections, ranging between 0.94 and 2.53‰ (Río Salado), from 1.16 to 2.66‰ (Puesto Loncoche) and from 0.91 to 2.13‰ VPDB (Cuesta del Chihuido), with a decrease towards the upper sedimentary section (top of the Chachao Formation).

Estimated seawater palaeotemperatures, obtained from the $\delta^{18}O$ values (Table 1, Fig. 9), are on average 25 °C (26 °C in Río Salado, 25 °C in Puesto Loncoche and 25 °C in Cuesta del Chihuido); this value coincides with those specified for the Neuquén Basin by Lazo *et al*. (2008), based on isotopic studies in fossil oysters of the same genus, and Lazo *et al*. (2005), on the basis of fossiliferous associations of the Pilmatué Member of the Agrio Formation located to the south of the basin, in Province of Neuquén.

5. Discussion

The C and O-isotope chemostratigraphic curves compare variations from three different sections of the Chachao Formation (Fig. 7), Mendoza shelf area, which are well correlated with previous data presented by Aguirre-Urreta *et al*. (2008) and Gómez Peral *et al*., (2012) from other localities of the central area of the Neuquén Basin. Aguirre-Urreta *et al*. (2008) mentioned such a positive carbon anomaly (+2-3‰ VPDB) from the analysis of oysters from the Cerro La Parva locality (37º15’30’’- 70º26’30’’), characterized by the ammonite subzones of *O. (O.) atherstoni-Karakaschiceras attenuatum* (*O. atherstoni* Ammonite Zone). Subsequently, Gómez Peral *et al*. (2012) obtained a $\delta^{13}C$ curve with values that on average are of +1.6‰ with a positive excursion of +2.9‰. This analysis of oysters and micrite corresponds to deposits from Buta Ranquil (37º06’00’’- 69º49’00’’) characterized by the subzone of *K. attenuatum* (Schwarz *et al*., 2011). Therefore, the positive carbon anomaly recorded in *O. arthestoni* Zone deposits is clearly established in different areas of the Neuquén Basin, from the Mendoza Platform (this study) to the central area of the basin (Aguirre-Urreta *et al*., 2008; Gómez Peral *et al*., 2012).

According to Aguirre-Urreta and Rawson (1997) and Aguirre-Urreta *et al*. (2005), the ammonite faunas of *O. (O.) atherstoni-K. attenuatum* correlates with the *B. campylotoxus* to *S. verrucosum* Ammonite Zone described for the Mediterranean Province, where the positive carbon anomaly was defined by Weissert *et al*. (1998) and Hennig *et al*. (1999), among others (Fig. 10).

The origin of the carbon positive anomaly has been the cause of many controversies (Lini *et al*., 1992; Weissert *et al*., 1998; Hennig *et al*., 1999; Melinte and Mutterlose, 2001; Bartolini, 2003; Erba *et al*., 2004; Duchamp- Alphonse *et al*., 2007; Aguirre-Urreta *et al*., 2008; Price and Nunn, 2010; Gómez Peral *et al*., 2012; Charbonnier *et al*., 2013; Meissner *et al*., 2015; Silva-Tamayo *et al*., 2016). This contribution provides new C and O isotope data, as well as a record of the palaeotemperature data, which makes it possible to understand better the palaeoenvironmental context, considering the sedimentological and palaeontological features of the studied deposits.

The isotopic results indicate an average seawater palaeotemperature of 25º C, indicating a warm context for the Tithonian- Valanginian interval in the Neuquén Basin, which is consistent with data provided by Lazo *et al*. (2005, 2008) for other locality in the same basin. Duchamp-Alphonse *et al*. (2011) also proposed warm temperatures based in studies of kaolinite content of Valanginian sequences. Lini *et al*. (1992) and Erba *et al*. (2004) arrived at the same conclusion but linked to increase in pCO_2 from volcanism, especially the Paraná-Ethendeka continental flood-basalts. In the analyzed sections there is no evidence of vertical changes in temperature, so the enrichment in the $\delta^{13}C$ ratio to the top of the succession cannot be related to sudden changes in temperature.

Furthermore, black shales rich in organic matter or other evidence of anaerobic conditions are absent in the studied sections, which make to avoid a connection of the $\delta^{13}C$ anomaly with an ocean anoxic event (OAE).

Föllmi (2012) postulated that the $\delta^{13}C$ anomaly was in response to a change in the Cretaceous climate from warm and dry to warm and wet, which had occurred in the mid-Valanginian (*Busnardoites*

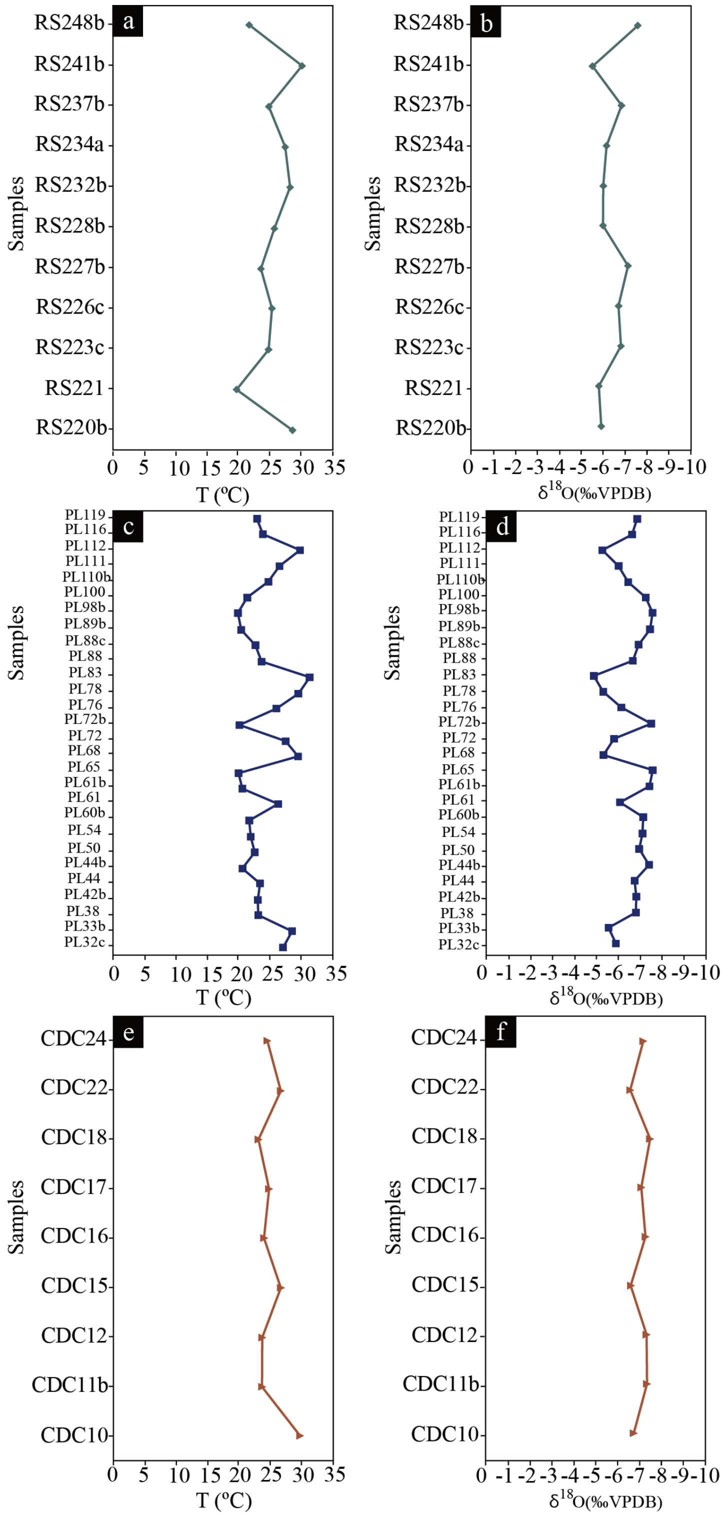

FIG. 9. Estimated palaeotemperatures (T °C) and results of $\delta^{18}O$ (‰VPDB) of samples from the three sedimentary sections. ◆ Río Salado samples, ■ Puesto Loncoche samples and ▲ Cuesta del Chihuido samples.

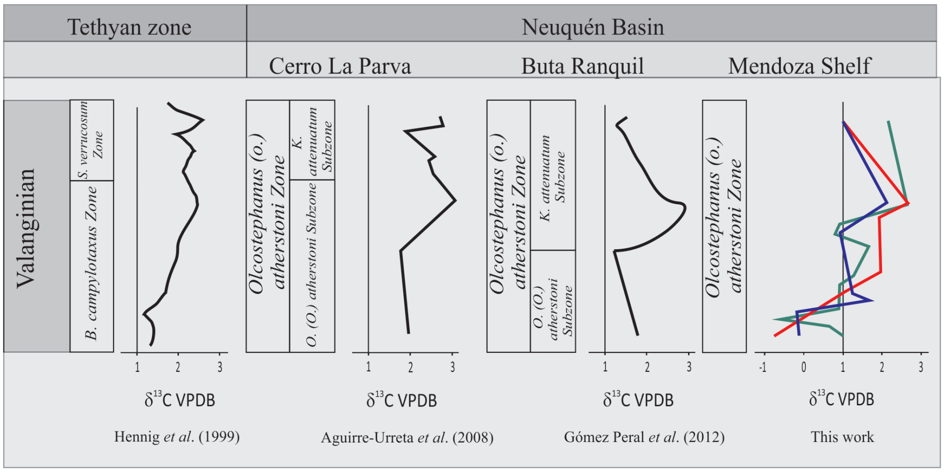

FIG. 10. Chemostratigraphic correlation between δ^{13}C curves and biozones of the Mendoza Shelf in Río Salado (green), Puesto Loncoche (red) and Cuesta del Chihuido (blue) here obtained, with curves reported for the Tethys (Hennig *et al*., 1999) and other localities of the Neuquén Basin in Cerro La Parva (Aguirre-Urreta *et al*., 2008) and Buta Ranquil (Gómez Peral *et al*., 2012).

campylotoxus Zone- *Saynoceras verrucosum* Zone, in the Tethys area). Among other factors, this variation in humidity regime would have produced a significant increase in the detrital input from the continent to the sea, with the consequent drowning of the carbonate platform (Westermann *et al*., 2010). The fact that the δ^{13}C anomaly is located just on the top of the buildup of Chachao Formation, reinforce the approach that this ultimate demise was in response to the climatic change suggested by Föllmi (2012). In this sense, Gómez Peral *et al*. (2012) showed a C isotope curve for Mulichinco Formation, located in a deeper portion of the basin (north of Neuquén). They place the Valanginian positive δ^{13}C anomaly in the top of the unit, which coincides with the basal siliciclastic parasequence immediately above the carbonate bodies that characterize the middle section of Mulichinco Formation. Furthermore, it is noticeable that the positive δ^{13}C excursion in the Neuquén Basin occurs as a regional event, which can be correlated with an increase in the detrital supply to the marine system, and as consequence this cause the cease in the development of the carbonate deposits. Therefore, it should not be ruled out, this event reflects a change towards higher humidity conditions as suggested by Föllmi (2012).

On the other hand, in the studied sections of the basin represented in the Mendoza Shelf area, the δ^{13}C anomaly shows no correlation with a facies change. In this case, the anomaly is recorded at the top of the biogenic carbonate bodies of the Chachao Formation and it is considered as signal of its imminent collapse.

6. Conclusions

Based on the foregoing, it can be concluded that:

The samples of *Aetostreon* sp. selected for C-O isotope analysis show a high degree of preservation validated by geochemical, cathodoluminescence and scanning electron microscopy studies.

The water palaeotemperature estimations for the Mendoza Shelf in the Neuquén Basin area during the Tithonian-Valanginian indicate a warm period, with seawater temperatures around ~25 °C on average, and sudden temperature changes are not recorded.

The occurrence of the well-established mid-Valanginian positive δ^{13}C excursion is documented, and it is recognized in the upper section of the Chachao Formation and characterized by the *O. atherstoni* Ammonite Zone in the Río Salado, Puesto Loncoche and Cuesta del Chihuido areas.

The positive δ^{13}C anomaly can be temporally correlated with the previously defined chemostratigraphic studies in other localities of the Neuquén Basin and can be also related to the event defined for the Tethys area.

The absence of black shale deposits or other indications of anaerobic conditions in Chachao Formation make it impossible to link the anomaly with an ocean anoxic event in the Mendoza Shelf.

The Chachao Formation, especially the upper section constituted by thick carbonates with a wide faunal diversity, can be correlated with the contemporary deposits of Buta Ranquil, where a marked decrease in carbonate content with the consequent drowning of the carbonate platform can be observed.

Finally, it can be concluded that the Upper Chachao Formation may constitute a scenario linked to an episode of environmental change, in which the positive $\delta^{13}C$ excursion must be related to a change in a warm context from arid to humid conditions.

Acknowledgments

The authors would like to thank Dr. E. Schwarz for his comments and suggestions, which improved the manuscript significantly. Special thanks to the NEG-LABISE, Departamento de Geología, Universidade Federal de Pernambuco, Recife, Brazil. We thank D. Mártire for the preparation of the thin sections, and Lic. C. Cavarozzi and Dr. M. Pedemonte for the ICP-MS analysis. We are also very grateful to Lic. M. Zalazar for assisting in the field and for their support in cathodoluminiscence. This research is part of the Ph.D. thesis of the first author. Fieldwork and laboratory analyses and materials were financially supported by LAS (PIP 112-201101-00322), DGP (PIP 112-201501-00866) and LEGP (PIP-0134 and PICT Pres. BID 2012) grants. Helpful reviews from Dr. G.D Price, and Editor Dr. W. Vivallo greatly benefited this manuscript.

References

Aguirre-Urreta, M.B.; Rawson, P.F. 1997. The ammonite sequence in the Agrio Formation (Lower Cretaceous), Neuquén basin, Argentina. Geological Magazine 134: 449-458.

Aguirre-Urreta, B.; Rawson, P.F.; Concheyro, G.A.; Bown, P.R.; Ottone, E.G. 2005. Lower Cretaceous (Berriasian-Aptian) biostratigraphy of the Neuquén Basin. *In* The Neuquén Basin Argentina: a Case Study in Sequence Stratigraphy and Basin Dynamics (Veiga, G.D.; Spalletti, L.A.; Howell, J.A.; Schwarz, E.; editors). Geological Society, Special Publication 252: 57-81. London.

Aguirre-Urreta, M.B.; Price, G.D.; Ruffell, A.H.; Lazo, D.G.; Kalin R.M.; Ogle, N.; Rawson, P.F. 2008. Southern Hemisphere Early Cretaceous (Valanginian-Early Barremian) carbon and oxygen isotope curves from the Neuquén Basin, Argentina. Cretaceous Research 29: 87-99.

Aguirre-Urreta, B.; Lazo, D.G.; Griffin, M.; Vennari, V.; Parras, A.M.; Cataldo, C.; Garberoglio, R.; Luci, L. 2011. Megainvertebrados del cretácico y su importancia bioestratigráfica. *In* Relatorio del Congreso Geológico Argentino, No. 18: 465-488. Neuquén.

Anderson, T.F.; Arthur, M.A. 1983. Stable isotopes of oxygen and carbon and their application to sedimentological and palaeoenvironmental problems. *In* Stable Isotopes in Sedimentary Geochemistry. (Arthur, M.A.; Anderson, T.F.; Kaplan, I.R.; Veizer, J.; Land, L.S.; editors). Society for Sedimentary Geology, Short Course Notes 10: 1-151.

Bartolini, A. 2003. Cretaceous radiolarian biochronology and carbon isotope stratigraphy of ODP Site 1149 (northwestern Pacific, Nadezhda Basin). *In* Proceedings of the Ocean Drilling Program Scientific Results (Ludden, J.N.; Plank, T.; Escutia, C.; editors) 185: 1-17.

Brand, U.; Veizer, J. 1981. Chemical diagenesis of a multicomponent carbonate sistem: stable isotopes. Journal of Sedimentary Petrology 51 (3): 0987-0997.

Carozzi, A.V.; Berkowski, F.; Rodríguez, M.; Sanckes, M.; Vonesht, T. 1981. Estudio de microfacies de la Formación Chachao (Valanginiano), Provincia de Mendoza. *In* Congreso Geológico Argentino, No. 8, Actas 2: 545-565. San Luis.

Charbonnier, G.; Boulila, S.; Gardin, S.; Duchamp-Alphonse, S.; Adatte, T.; Spangenberg, J.E.; Föllmi, K.B.; Colin, C.; Galbrun, B. 2013. Astronomical calibration of the Valanginian "Weissert" episode: The Orpierre marlelimestone succession (Vocontian Basin, southeastern France). Cretaceous Research 45: 25-42.

Cotillon, P.; Rio, M. 1984. Cyclic sedimentation in the Cretaceous of DSDP site 535 and 540 (Gulf of Mexico), 534 (central Atlantic) and the Vocontian Basin (France). *In* Initial Reports of the Deep Sea Drilling Project (Buffler, R.T.; Schlager, W.; Pisiotto, K.A.; editors). US Government Printing Office 77: 339-376. Washington DC.

Doyle, P.; Poiré, D.G.; Spalletti, L.A.; Pirrie, D.; Brenchley, P.; Matheos, S.D. 2005. Relative oxygenation of the Tithonian-Valanginian Vaca Muerta-Chachao formations of the Mendoza Shelf, Neuquén Basin, Argentina. *In* The Neuquén Basin, Argentina: a Case Study in Sequence Stratigraphy and Basin Dynamics (Veiga, G.D.; Spalletti, L.A.; Howell, J.A.; Schwarz, E.; editors). Geological Society, Special Publication 252: 185-206. London.

Duchamp-Alphonse, S.; Gardin, S.; Fiet, N.; Bartolini, A.C.; Blamart, D.; Pagel, M. 2007. Fertilization of the northwestern Tethys (Vocontian basin, SE France) during the Valanginian carbon isotope perturbation: evidence from calcareous nannofossils and trace element data. Palaeogeography, Palaeoclimatology, Palaeoecology 243: 132-151.

Duchamp-Alphonse, S.; Fiet, N.; Adatte, T.; Maurice, P. 2011. Climate and sea-level variations along the northwestern Tethyan margin during the Valanginian C-isotope excursion: mineralogical evidence from the Vocontian Basin (SE France). Palaeogeography, Palaeoclimatology, Palaeoecology 302: 243-254.

Epstein, S.; Buchsbaum, R.; Lowenstam, H.A.; Urey, H.C. 1953. Revised Carbonate-Water Isotopic Temeprature Scale. Geological Society of America Bulletin 64: 1315-1325.

Erba, E.; Bartolini, A.; Larson, R.L. 2004. Valanginian Weissert oceanic anoxic event. Geology 32: 149-152.

Föllmi, K.B. 2012. Early Cretaceous life, climate and anoxia. Cretaceous Research 35: 230-257.

Föllmi, K.B. 1995. 160 m.y. record of marine sedimentary phosphorus burial: coupling of climate and continental weathering under greenhouse and icehouse conditions. Geology 23: 859-862.

Gómez Peral, L.E.; Shwarz, E.; Sial, A.N.; Spalletti, L.A. 2012. Palaeo-proxies recording primary signature of C-O isotope data from the Valanginian Mulichinco Formation, Neuquen Basin, Argentina: First results. *In* Simposio Sudamericano de Geología Isotópica, No. 8: CD Actas. Medellín.

Groeber, P. 1946.Observaciones geologicas a lo largo del Meridiano 70. Hoja Chos Malal. Asociacion Geologica Argentina Revista 1: 177-208.

Groeber, P. 1947. Observaciones geologicas a lo largo del meridiano 70. III Hojas Domuyo, Mari Mahuida, Huarhuarco y parte de Epu-Lauken. Revista Asociación Geológica Argentina 2: 347-443.

Gulisano, C.A.; Gutiérrez Pleimling, A. 1994. Field Guide to the Jurassic of the Neuquén Basin, province of Neuquén. Secretaría de Minería de la Nación, Dirección Nacional del Servicio Geológico, Publicación 158: 1-111.

Hennig, S.; Weissert, H.; Bulot, L. 1999. C-isotope stratigraphy, a calibration tool between ammonite- and magnetostratigraphy: the Valanginian-Hauterivian transition. Geologica Carpathica 50: 91-96.

Kemper, E. 1987. Das Klima der Kreide-Zeit. Geologisches Jahrbuch 96: 5-185.

Kershaw, S. 1994. Classification and geological significance of biostromes. Facies 31: 81-91.

Kietzmann, D.A.; Palma, R.M. 2009. Tafofacies y biofacies de la Formación Vaca Muerta en el sector surmendocino de la Cuenca Neuquina: implicancias paleoecológicas, sedimentológicas y estratigráficas. Ameghiniana 46: 321-343.

Kietzmann, D.A.; Palma, R.M.; Bressan, G.S. 2008. Facies y microfacies de la rampa Tithoniana- Berriasiana de la Cuenca Neuquina (Formación Vaca Muerta) en la sección del Arroyo Loncoche-Malargüe, Provincia de Mendoza. Revista de la Asociación Geológica Argentina 63: 696-713.

Kietzmann, D.A.; Palma, R.M.; Riccardi, A.C.; Martín-Chivelet, J.; López-Gómez, J. 2014. Sedimentology and sequence stratigraphy of a Tithonian-Valanginian carbonate ramp (Vaca Muerta Formation): A misunderstood exceptional source rock in the Southern Mendoza area of the Neuquén. Sedimentary Geology 302: 64-86.

Kietzmann, D.A.; Palma, R.M.; Paula, M.; Llanos, I. 2015. Cyclostratigraphy of an orbitally-driven Tithonian-Valanginian carbonate ramp succession , Southern Mendoza , Argentina: Implications for the Jurassic-Cretaceous boundary in the Neuquén Basin. Sedimentary Geology 315: 29-46.

Korte, C.; Hesselbo, S.P. 2011. Shallow marine carbon and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic. Paleoceanography 26: 1-18.

Korte, C.; Hesselbo, S.P.; Jenkyns, H.C.; Rosalind, E.M.R.; Christoph, S. 2009. Palaeoenvironmental significance of carbon- and oxygen-isotope stratigraphy of marine Triassic-Jurassic boundary sections in SW Britain. Journal of the Geological Society 166: 431-445.

Lazo, O.G.; Cichowolski, M.; Rodríguez, D.L.; Aguirre-Urreta, M.B. 2005. Lithofacies, palaeoecology and palaeoenvironments of the Agrio Formation, Lower Cretaceous of the Neuquén Basin, Argentina. *In* The Neuquén Basin, Argentina: a Case Study in Sequence Stratigraphy and Basin Dynamics. (Veiga, G.D.; Spalletti, L.A.; Howell, J.A.; Schwarz, E.; editors). Geological Society, Special Publication 252: 295-315. London.

Lazo, D.G.; Aguirre-Urreta, M.B.; Price, G.D.; Rawson, P.F.; Ruffell, A.H.; Ogle, N. 2008. Palaeosalinity variations in the Early Cretaceous of the Neuquén Basin, Argentina: Evidence from oxygen isotopes and palaeoecological analysis. Palaeogeography, Palaeoclimatology, Palaeoecology 260: 477-493.

Leanza, H.A. 1981. Faunas de ammonites del Jurásico superior y del Cretácico inferior de América del Sur, con especial consideración de la Argentina. *In* Cuencas Sedimentarias del Jurásico y Cretácico de América del Sur (Volkheimer, W.; Mussachio, E.; editors). Museo Argentino de Ciencias Naturales 2: 559-597. Buenos Aires.

Leanza, H.A.; Marchese, H.; Riggi, J. 1977. Estratigrafía del Grupo Mendoza con especial referencia a la Formación Vaca Muerta entre los paralelos 35º y 40º L.S., Cuenca Neuquina-Mendocina. Revista de la Asociación Geológica Argentina 32: 190-208.

Legarreta, L.; Uliana, M.A. 1991. Jurassic- Cretaceous marine oscillations and geometry of back-arc basin fill, central Argentine Andes. Internacional Association of Sedimentology, Special Publication 12: 429-450.

Legarreta, L.; Kozlowski, E. 1981. Estratigrafía y sedimentología de la Formación Chachao, Provincia de Mendoza. *In* Congreso Geológico Argentino, No. 8, Actas 2: 521-543. San Luis.

Legarreta, L.; Kozlowski, E.; Boll, A. 1981. Esquema estratigráfico y distribución de facies del Grupo Mendoza en el ámbito surmendocino de la Cuenca Neuquina. *In* Congreso Geologico Argentino, No. 8, Actas 3: 389-409. San Luis.

Lini, A.; Weissert, H.L.; Erba, E. 1992. The Valanginian carbon isotope event: a first episode of greenhouse climate conditions during the Cretaceous. Terra Nova 4: 374-384.

Marshall, J.D. 1992. Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. Geological Magazine 129 (2): 143-160.

Meissner, P.; Mutterlose, J.; Bodin S. 2015. Latitudinal temperatura trends in the northern hemisphere during the Early Cretaceous (Valanginian-Hauterivian). Palaeogeography, Palaeoclimatology, Palaeoecology 424: 17-39.

Melinte, M.; Mutterlose, J. 2001. A Valanginian (Early Cretaceous) Boreal nannoplankton excursion in sections from Romania. Marine Micropaleontology 43: 1-25.

Mitchum, R.M.; Uliana, M. 1986. Seismic stratigraphy of carbonate depositional sequences, Upper Jurassic-Lower Createaceous, Neuquén Basin, Argentina. *In* Seismic Stratigraphy II. An integrated aproach to hidrocarbon analysis (Berg, B.R.; Woolverton, D.G.; editors). American Association of Petroleum Geologists, Memoir 39: 255-283.

Mombrú, C.; Bettini, F.; Vázquez, J. 1976. Significado estratigráfico y sedimentología de las acumulaciones biocarbonáticas del Cretácico inferior surmendocino. *In* Actas del Congreso Geológico Argentino, No. 6, 1: 685-700. Buenos Aires.

Mombrú, C.; Uliana, M.A.; Bercowski, F. 1978. Estratigrafía y sedimentología de las acumulaciones biocarbonáticas del Cretácico inferior surmendocino. *In* Congreso Geológico Argentino, No. 7, Actas 2: 695-709. Neuquén.

Palma, R.M.; Angeleri, M.A. 1992. Early Cretaceous serpulid limestones: Chachao Formation, Neuquén Basin, Argentina. Facies 27: 175-178.

Palma, R.M.; Lanés, S. 2001. Shell bed stacking patterns in the Chachao Formation (Early Valanginian) in Malargüe area, Mendoza province, Neuquén Basin-Argentina. Carbonates and Evaporites 16: 168-180.

Palma, R.M.; Lanés, S.; Miretzky, P.; Fazio, A.M. 1999. Evidencias geoquímicas y neomorfismo en rocas de la Formación Chachao (Valanginiano)-anticlinal Malargüe, Mendoza. Revista de la Asociación Geológica Argentina 54: 248-256.

Palma, R.M.; Bressan, G.S.; Kietzmann, D.A. 2008. Diagenesis of a bioclastic oyster deposit from the Lower Cretaceous (Chachao Formation), Neuquén Basin, Mendoza Province, Argentina. Carbonates and Evaporites 23: 39-49.

Pirrie, D.; Marshall, J.D.; Doyle, P.; Riccardi, A.C. 2004. Cool early Albian climates; new data from Argentina. Cretaceous Research 25: 27-33.

Price, G.D.; Mutterlose, J. 2004. Isotopic signals from late Jurassic -early Cretaceous (Volgian-Valanginian) sub-arctic belemnites, Yatria River, western Siberia. Journal of the Geological Society 161: 959-968.

Price, G.D.; Nunn, E.V. 2010. Valanginian isotope variation in glendonites and belemnites from Arctic Svalbard: transient glacial temperatures during the Cretaceous greenhouse. Geology 38: 251-254.

Pucéat, E.; Lécuyer, C.; Sheppard, S.M.; Dromart, G.; Reboulet, S.; Grandjean, P. 2003. Thermal evolution of Cretaceous Tethyan marine waters inferred from oxygen isotope composition of fish tooth enamels. Paleoceanography 18 (2): 1-12.

Riccardi, A. C. 2015. Remarks on the Tithonian-Berriasian ammonite biostratigraphy of west central Argentina. Volumina Jurassica 13: 23-52.

Schwarz, E.; Spalletti, L.A.; Veiga, G.D. 2011. La Formación Mulichinco (Cretácico Temprano) en la Cuenca Neuquina. *In* Relatorio del Congreso Geológico Argentino, No. 18: 131-144. Neuquén.

Shackleton, N.J.; Kennett, J.P. 1975. Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: oxygen and carbon isotope analyses in DSDP sites 277, 279 and 281. *In* Initial Reports of the Deep Sea Drilling Project (Kennett, J.P.; Houtz,

R.E.; editors). US Government Printing Office 29: 743-755. Washington DC.
Silva-Tamayo, J.C.; Ramírez, C.; Lara, M.; Sial A.N.; Trujillo, D.; Salazar, E. 2016. Sedimentology and chemostratigraphy of a Valanginian carbonate succession from the Baja Guajira Basin, northern Colombia. Brazilian Journal of Geology 20 (10): 1-18.
Spalletti, L.A.; Franzese, J.R.; Matheos, S.D.; Schwarz, E. 2000. Sequence stratigraphy of a tidally-dominated carbonate-siliciclastic ramp; the Tithonian of the southern Neuquén Basin, Argentina. Journal of the Geological Society 157: 433-446.
Spalletti, L.A.; Pirrie, D.; Veiga, G.D.; Schwarz, E.; Rollinson, G.; Shail, R.; Haberlah, D.; Butcher, A. 2015. Análisis mineralógico integrado (QEMSCAN y DRX) de lutitas negras: los depósitos Tithonianos basales de la Formación Vaca Muerta (Cuenca Neuquina, Argentina). Latin American Journal of Sedimentology and Basin Analysis 22 (1): 13-28.
Tarduno, J.A.; Cottrell, R.D.; Lippert, P.; Friedman, M. 2002. Extreme climates recorded in the Cretaceous High Arctic: JOI/USSAC. *In* Workshop on Cretaceous Climate and Ocean Dynamics: 76. Florissant, Colorado.
Uliana, M.A.; Mombrú, C.; Bercowski, F. 1979. Los abultamientos calcáreos del Cretácico inferior en el sur mendocino. *In* Congreso Geológico Argentino, No. 7, Actas 2: 895-709. Neuquén.
Ullmann, C.V.; Korte, C. 2015. Diagenetic alteration in low-Mg calcite from macrofossils: a review. Geological Quarterly 59: 3-20.
Van de Schootbrugge, B.; Föllmi, K.B.; Bulot, L.G.; Burns, S.J. 2000. Paleoceanographic changes during the Early Cretaceous (Valanginian-Hauterivian): evidence from oxygen and carbon stable isotopes. Earth and Planetary Science Letters 181: 15-31.
Weaver, C. 1931. Paleontology of the Jurassic and Cretaceous of West Central Argentine. University of Washington. Memoir 1: 1-496. Seattle.
Weissert, H.; Lini, A.; Föllmi, K.B.; Kuhn, O. 1998. Correlation of Early Cretaceous carbon isotope stratigraphy and platform drowning events: a possible link? Palaeogeography, Palaeoclimatology, Palaeoecology 137: 189-203.
Westermann, S.; Föllmi, K.B.; Adatte, T.; Matera, V.; Schnyder, J.; Fleitmann, D.; Fiet, N.; Ploch, I.; Duchamp-Alphonse, S. 2010. The Valanginian $\delta^{13}C$ excursion may not be an expression of a global oceanic anoxic event. Earth and Planetary Science Letters 290: 118-131.
Zakharov, Y.D.; Shigeta, Y.; Nagendra, R.; Safronov, P.P.; Smyshlyaeva, O.P.; Popov, A.M.; Velivetskaya, T.A.; Afanasyeva, T.B. 2011. Cretaceous climate oscillations in the southern palaeolatitudes : New stable isotope evidence from India and Madagascar. Cretaceous Research 32: 623-645.

Manuscript received: April 7, 2017; revised/accepted: October 18, 2017; available online: January 31, 2018.