Orbital Controls and High-Resolution Cyclostratigraphy of Late Jurassic–Early Cretaceous in the Neuquén Basin

Diego A. Kietzmann, María Paula Iglesia Llanos
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Abstract Detailed cyclostratigraphic analyses have been made from seven Tithonian–Hauterivian sections of the Vaca Muerta and Agrio Formations, exposed in southern Mendoza area of the Neuquén Basin. Both lithostratigraphic units are characterized by decimeter-scale rhythmic alternations of marlstones and limestones, showing a well-ordered hierarchy of cycles, including elementary cycles, bundles, and superbundles. According to biostratigraphic data, elementary cycles have a periodicity of ~18–21 ky, which correlates with the precessional cycle of the Earth's axis. Spectral analysis based on time series of elementary cycle thicknesses allowed us to identify frequencies of ~400 ky, and ~90–120 ky, which we interpret as the modulation of the precessional cycle by the Earth's orbital eccentricity. A third band frequency of ~40 ky was also identified that can be assigned to the obliquity cycle. Cyclostratigraphy enabled the construction of almost continuous floating astronomical time scale for the Tithonian–Hauterivian, for which a minimum duration of 5.67 myr for the Tithonian, 5.27 myr for the Berriasian, >3.45 myr for the Valanginian, and 5.96 myr for the Hauterivian have been assessed. Additionally, the likely transference mechanisms of the orbital signal to the sedimentary record are analyzed, proposing the coexistence of carbonate exportation and dilution as the dominant mechanisms.

Keywords Cyclostratigraphy · Astronomical time scale · Jurassic–Cretaceous · Neuquén basin

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1 Introduction

Cyclostratigraphy has become an important tool for determining Jurassic–Cretaceous geologic time and establishing floating astronomical time scales (ATS). Almost the entire Jurassic and Cretaceous have been calibrated using the long-term eccentricity cycle, which is the most stable cycle during the Phanerozoic. Many important works involving the Upper Jurassic–Lower Cretaceous were dedicated to demonstrating the presence of Milankovitch cycles in the sedimentary record. Nevertheless, only a few works have carried out detailed cyclostratigraphic studies for stratigraphic time calibration (Hinnov and Hilgen 2012; Ogg and Hinnov 2012a, b). Particularly, marlstone–limestone rhythmic successions have been cited as key examples of climate-forced sedimentation resulting from different palaeoenvironmental factors, including fluctuations in the supply of calcareous biogenic sediments produced by plankton (productivity cycles: Einsele and Ricken 1991), and fluctuations in the input of fine terrigenous sediments (dilution cycles: Arthur et al. 1984; Einsele and Ricken 1991). Additional potential mechanisms include diagenetic redistribution of calcium carbonate (dissolution cycles, Einsele and Ricken 1991; Westphal et al. 2010), fluctuations in carbonate-mud exportation from shallow areas (carbonate dilution cycles, Pittet and Strasser 1998), and fluctuations in superficial fertility (fertility cycles, Premoli Silva et al. 1989).

The Late Jurassic–Early Cretaceous in the Neuquén Basin represented a time of tectonic quietude that prompted the development of thick carbonate and mixed successions (Legarreta and Uliana 1991, 1996), included in the Mendoza Group (Figs. 1

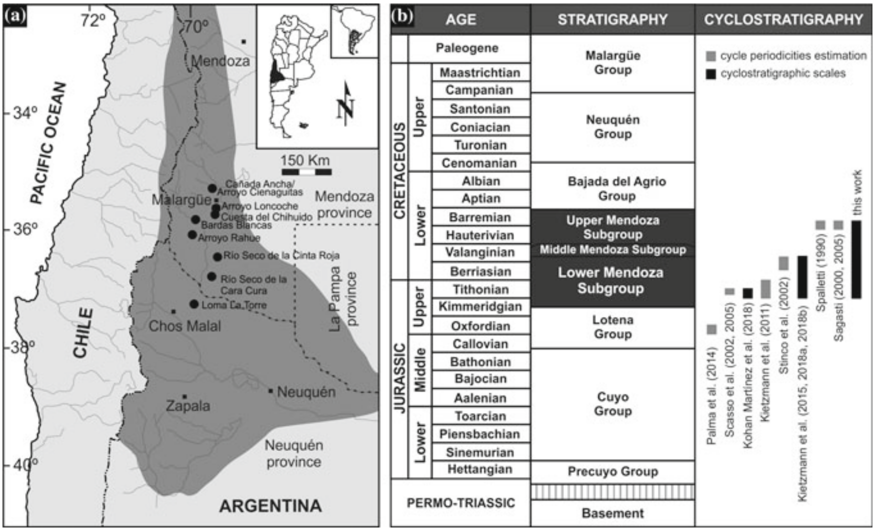


Fig. 1 **a** Location map of the Neuquén Basin showing studied localities. **b** Stratigraphic chart for the Neuquén Basin, showing stratigraphic coverage of cyclostratigraphic studies for the Upper Jurassic and Lower Cretaceous

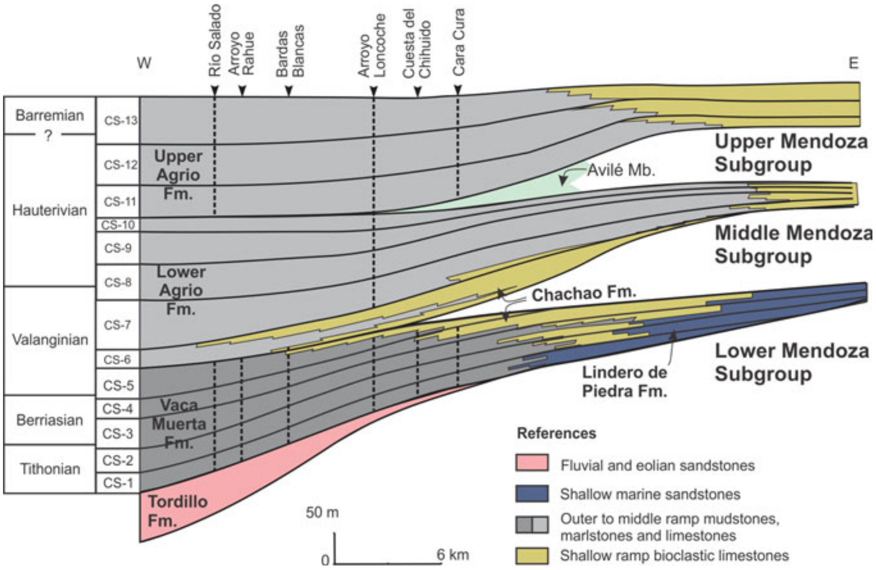


Fig. 2 Litostratigraphic subdivision of the Mendoza Group in the Southern Mendoza area, showing the location of the studied sections

and 2). Despite the notable limestone–marlstone rhythmicity of these successions, only a few works have dealt with this subject. The first study of cyclicity in Argentina was carried out by Spalletti et al. (1990) for the Upper Hauterivian–Lower Barremian interval using well logs data from the Upper Agrio Formation in the Filo Morado block. These authors recognized periodicities of 17–23, 114, 422, and 1143 ky, consistent with the Milankovitch frequency band. Later, Sagasti (2000, 2005) replicated these types of studies in outcrops of the same age, using lithological limestone–marlstone couples, and found similar periodicities of 10–30, 45–47, 103–127, and ~400 ky. At the same time, Scasso et al. (2002, 2005) estimated the periodicity for the rhythmicity of late Early–early Late Tithonian Los Catutos Member of the Vaca Muerta Formation, obtaining a periodicity of 18.2 ky for limestone–marlstone elementary cycles. Kietzmann et al. (2011) studied the Tithonian interval at the Arroyo Loncoche section, obtaining a periodicity of 21.1 ky for the elementary cycle, and 90–120 ky for bundles of elementary cycles, which is consistent with the modulation of the precessional cycle caused by the Earth's orbital eccentricity. A more detailed study was published later by Kietzmann et al. (2015), who analyzed four Tithonian–Early Valanginian sections of the Vaca Muerta Formation, and obtained an elementary cycle of ~20 ky, bundle periodicities of 90–120, and ~400 ky for superbundles. These authors proposed for the first time a floating orbital scale for the Tithonian–Lower Valanginian in the Neuquén Basin and established minimum durations of Andean ammonite zones. Under the light of new data provided by Kohan Martínez et al. (2018) from Los Catutos Member, Kietzmann et al. (2018a) revised this floating orbital scale introducing three new low-frequency eccentricity cycles and tied to the magnetostratigraphy obtained by Iglesia Llanos et al. (2017) (see Chap. "Magnetostratigraphy of the Jurassic Through Lower Cretaceous in the Neuquén Basin"). This enabled the calibration of the Tithonian–Berriasian in the Neuquén Basin, chronostratigraphically and temporally, with unprecedented precision. In fact, the combination of cyclostratigraphy with other stratigraphic disciplines, such as magnetostratigraphy, biostratigraphy, chemostratigraphy, and geochronology, is contributing to establishing an increasingly robust chronostratigraphic framework in the Andes (Iglesia Llanos et al. 2017; Kohan Martínez et al. 2018; and Kietzmann et al. 2018a, b).

The aim of this study is to provide an update on cyclostratigraphic studies performed in the Upper Jurassic–Lower Cretaceous of the Neuquén Basin, as well as discussing their applicability in the temporal calibration of the stratigraphic record. In this study, two new complete Early Tithonian–Early Valanginian stratigraphic sections are added to the high-precision correlation made by Kietzmann et al. (2018a). The same analysis is presented in the Late Valanginian–Early Barremian interval where two new sections are described in detail by the authors and compared with two sections published by Sagasti (2000). We also analyze the different proxies and mechanisms that allowed the accumulation and preservation of the orbital controls that acted in the Neuquén Basin during this time interval.

2 Upper Jurassic–Lower Cretaceous Stratigraphy

The Late Jurassic–Early Cretaceous in the Neuquén Basin is characterized by a generalized thermal subsidence regime interrupted by localized tectonic events (Legarreta and Uliana 1991; Vergani et al. 1995; Ramos and Folguera 2005; Ramos 2010). This tectonic regime allowed the depocenters to be filled by continental deposits during lowstands of sea-level, and marine mixed siliciclastic-carbonate, carbonate and evaporitic systems during transgressive and highstand sea-level stages (Legarreta and Gulisano 1989; Legarreta and Uliana 1991; Legarreta et al. 1993).

After a period of low sea-level stand, during the Late Oxfordian–Kimmeridgian, a rapid Early Tithonian transgression led to the development of two thick mixed-carbonate ramp systems. The first established during the Early Tithonian–Early Valanginian and is represented by the Lower Mendoza Subgroup, whose distal facies are included in the Vaca Muerta Formation (Legarreta and Uliana 1991; Kietzmann et al. 2008, 2014, 2016). The second system took place during the Early Valanginian–Early Barremian and is represented by the Middle and Upper Mendoza Subgroup that includes the other thick rhythmic alternation of the Agrio Formation (Legarreta and Uliana 1991; Spalletti et al. 2001; Sagasti 2000, 2005) (Fig. 2).

2.1 Tithonian–Early Valanginian

In the Mendoza area, the Lower Mendoza Subgroup starts with the continental deposits of the Tordillo Formation (Kimmeridgian–Lower Tithonian), on top of which the distal marine deposits of the Vaca Muerta Formation (Early Tithonian–Early Valanginian) were abruptly deposited. The latter includes basinal to middle carbonate ramp deposits, which laterally pass to shallow-water clastic marine facies of the Lindero de Piedra Formation (Tithonian) and the middle to inner ramp oyster-deposits of the Chachao Formation (Early Valanginian), making up an homoclinal carbonate ramp system (e.g., Carozzi et al. 1981; Mitchum and Uliana 1985). The top of the Lower Mendoza Subgroup is marked in the southernmost part of the basin by the so-called Intravalanginian unconformity, a tectonically diacronich unconformity, which is not recorded in the Mendoza sector, and the Vaca Muerta/Chachao system is followed by the Agrio Formation.

Biostratigraphy is well defined based on ammonites (Leanza and Hugo 1977; Riccardi 2008, 2015; Riccardi et al. 2011). Calcareous nannofossils, radiolarians, organic and calcareous dinoflagellates, and calpionellids (Quattrocchio et al. 2003; Bown and Concheyro 2004; Ballent et al. 2004, 2011; Kietzmann and Palma 2009; Ivanova and Kietzmann 2017; Kietzmann, 2017) are also important markers for the calibration of ammonite zones, but still need a thorough review to accurately establish the stratigraphic position of the most important bioevents.

In the Vaca Muerta Formation, a magnetostratigraphic study has been carried out by Iglesia Llanos et al. (2017). These authors recognized 11 reverse and 10 normal polarity zones, which were calibrated based on the correlation between Andean and Tethyan ammonite zones, and the Geomagnetic Polarity Time Scale compiled by Ogg and Hinnov (2012a, b). Accordingly, the authors conclude that the deposition of the Vaca Muerta Formation took place during the M22r.2r to M15r Subchrons (see Chap. "Magnetostratigraphy of the Jurassic Through Lower Cretaceous in the Neuquén Basin").

A sequence stratigraphic framework was established by Kietzmann et al. (2014, 2016) for the southern Mendoza and northern Neuquén sectors. These authors recognized two hierarchies of depositional sequences: (1) composite depositional sequences (CS) for large-scale sequences and (2) high-frequency depositional sequences (HFS) for those of small scale. Because of their average duration, composite sequences are considered equivalent to third-order sequences, whereas high-frequency sequences are interpreted as fourth-order sequences. In this chapter, we consider only composite sequences (Fig. 2), due to the importance of removing sea-level trends for spectral analysis. High-frequency sequences are too close to the superbundle hierarchy, and therefore, their removal could generate fictitious frequencies.

2.2 *Upper Valanginian–Lower Barremian*

In the Mendoza area, the Middle Mendoza Subgroup involves the upper part of the Chachao Formation and the Lower Agrio Formation (Pilmatué Member). The Upper Mendoza Subgroup includes the Avilé and Upper (Agua de la Mula) Members of the Agrio Formation, extending up to the top of the Chorreado Member. The Chorreado Member should be considered from a lithostratigraphic point of view, as part of the Agrio Formation, although it should be included within the Huitrín Meseosequence based on genetic relationships from sequence stratigraphy (Gutiérrez Pleimling et al. 2011).

Biostratigraphy of this interval is well defined based on ammonites (Leanza and Hugo 1977; Aguirre-Urreta et al. 1999, 2005, 2011). Microfossils, especially calcareous nannofossils, organic-walled dinoflagellates, and foraminifera are well tied to ammonite zones (Bown and Concheyro 2004; Aguirre-Urreta et al. 2005; Ballent et al. 2011; Lescano and Concheyro 2014).

The Middle Mendoza Subgroup was divided into five depositional sequences by Legarreta and Gulisano (1989), while the Upper Mendoza Subgroup was divided into other five sequences (Fig. 2). However, with the purpose of removing eustatic trends for spectral analysis, we only considered the tendencies generated by the two second-order sequences that define both subgroups.

3 Methodology

Detailed sedimentological sections from the Vaca Muerta and Agrio formations were described bed-by-bed and studied for cyclicity. Cyclostratigraphic analysis is based on the differentiation of decimetric-scale carbonate/siliciclastic lithofacies couplets or elementary cycles. Bundles and superbundles of cycles were also recognized in the field but searched applying time-series analysis with the software PAST3.21 (Hammer et al. 2001; Hammer and Harper 2006) using the REDFIT procedure of Schulz and Mudelsee (2002). The thickness of the elementary cycles was used as a proxy. Time was introduced as constant time intervals once the duration of the elementary cycles was estimated: The time represented in the stratigraphic section divided by the total number of elementary cycles. The time series is introduced in the software in the form of two columns with time and thickness values, so that the periodicity of the elementary cycle is used as scale in both procedures (thickness/time conversion).

The following primary premises are assumed for spectral analyses: (1) Sections consist of a succession of elementary cycles with similar thickness within the range of 20–40 cm, so they are considered of similar time duration, (2) obtained spectrograms are statistically reliable, since the number of cycles is large enough to obtain statistically significant results. According to Weedon (2003), the sampling density must be at least 12 times the lowest frequency. In our sections, the time series is at least 25 times longer than the low-frequency eccentricity cycle, (3) vertical changes in facies and bed thicknesses throughout the sections are related to periodic climate factors and/or to other non-periodic factors. Each data set was corrected prior to spectral analysis, subtracting the mean value and trends generated by changes in sea-level, allowing data centering and variance stabilization.

4 Cyclostratigraphic Analysis

4.1 New Stratigraphic Sections for the Construction of the Upper Jurassic–Lower Cretaceous ATS in the Neuquén Basin

In this work, we added two new complete Early Tithonian–Early Valanginian stratigraphic sections from the Vaca Muerta Formation. The first one is located at Cañada Ancha on the margin of the Salado River (Figs. 1 and 2). This section extends from the Early Tithonian *Virgatosphinctes andesensis* Zone to the Early Valanginian *Olcostephanus (O.) atherstoni* Zone and is represented mainly by outer ramp facies (Kietzmann et al. 2014). The second section locates at the southern part of the Cara Cura range, in the dry bed of stream known as Río Seco de la Cara Cura. This section extends from the Early Tithonian *Virgatosphinctes andesensis* Zone to the Early Valanginian *Lissonia riveroi* Zone and is represented mainly by outer and middle ramp facies (Kietzmann et al. 2014).

For the cyclostratigraphic calibration of the Late Valanginian–Hauterivian, we used two detailed sections published by Sagasti (2000) for the Upper Hauterivian–Lower Barremian at the Salado River (Arroyo Cienaguitas) and the northern Cara Cura range (Río Seco de la Cinta Roja). In addition, we included a complete Upper Valanginian–Lower Barremian section from the Loncoche creek, and the lower part of the Pilmatue Member at Loma La Torre of Late Valanginian–Early Hauterivian age. Successions are dominated by similar outer ramp facies to those of the Vaca Muerta Formation (Sagasti and Poire 1998; Sagasti 2000, 2005; Kietzmann and Paulin 2019; Palazzolo 2019).

4.2 Cycles Staking Pattern

Both in the Vaca Muerta Formation and in the Agrio Formation, we recognized a well-ordered hierarchy of cycles, including elementary cycles, bundles of four or five elementary cycles, and superbundles (four or five bundles). Elementary cycles have a regular thickness in the order of 20–40 cm, and therefore, they can be considered as units of similar temporal duration. Each elementary cycle consists of two hemicycles of similar thickness, which can be represented by limestone/marlstone,

marlstone/marlstone, or marlstone/mudstone combinations depending to the facies in which occurs.

Elementary cycles are grouped into sets of 4–5 elementary cycles (bundles), which are grouped into sets of 4–5 bundles (superbundles). The 5:1 ratio (5 elementary cycles per bundles) is commonly attributed to high-frequency eccentricity (95 and 125 ky), while the 4:1 ratio (4 bundles per superbundles) as low-frequency eccentricity (405 ky). Bundles and superbundles start with a thick elementary cycle and show a higher proportion of marlstones toward the top. This characteristic stacking pattern is well exhibited in stratigraphic sections with low sedimentation rates, such as in Cuesta del Chihuido and Arroyo Loncoche (Fig. 3). Bundles and superbundles can be dominated by marlstone/marlstone or limestone/marlstone elementary cycles. This descriptive division correlates with facies and system tracts, so that variations in the proportion of marlstones or limestones have no real genetic connotation respect to the transference mechanisms of the orbital signal to the sedimentary record. Yet, it relates with the proximal-distal trend within the carbonate ramp system: Basinal to outer

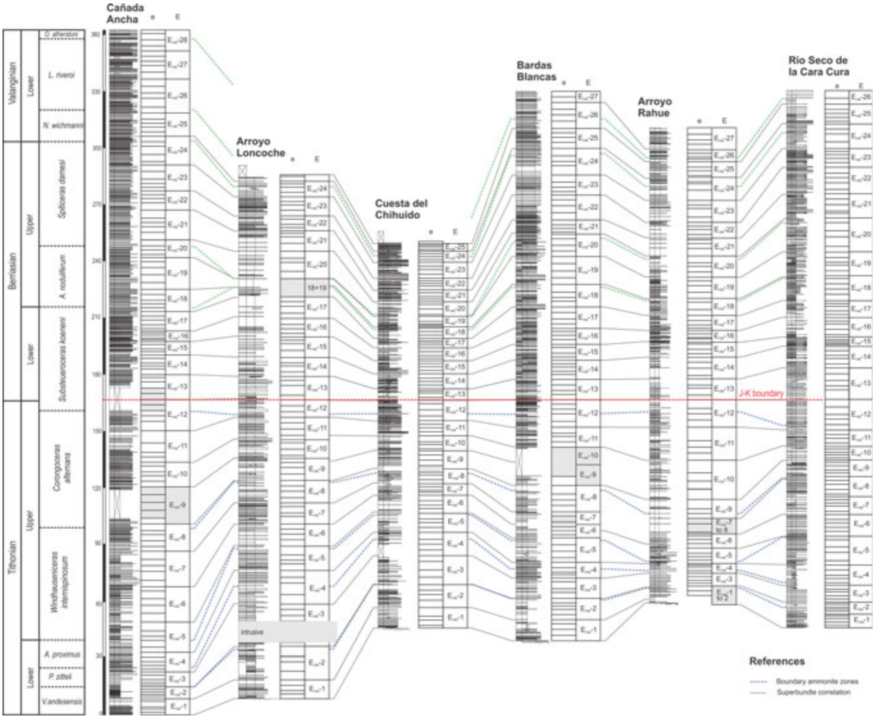


Fig. 3 High-resolution cyclostratigraphic correlation of studied stratigraphic sections of the Vaca Muerta Formation, using low-frequency eccentricity cycle (E) and high-frequency eccentricity cycle (e) (modified from Kietzmann et al. 2018a). Jurassic–Cretaceous boundary according to magnetostratigraphy (Iglesia Llanos et al. 2017; see Chap. "Magnetostratigraphy of the Jurassic Through Lower Cretaceous in the Neuquén Basin"), ammonite zones after Kietzmann et al. (2014, 2018a)

ramp deposits are dominated by marlstone/marlstone elementary cycles. Bundles or superbundles can occasionally start with a limestone/marlstone elementary cycle, and conversely, outer to middle ramp deposits are dominated by limestone/marlstone elementary cycles (Figs. 3, 4 and 5).

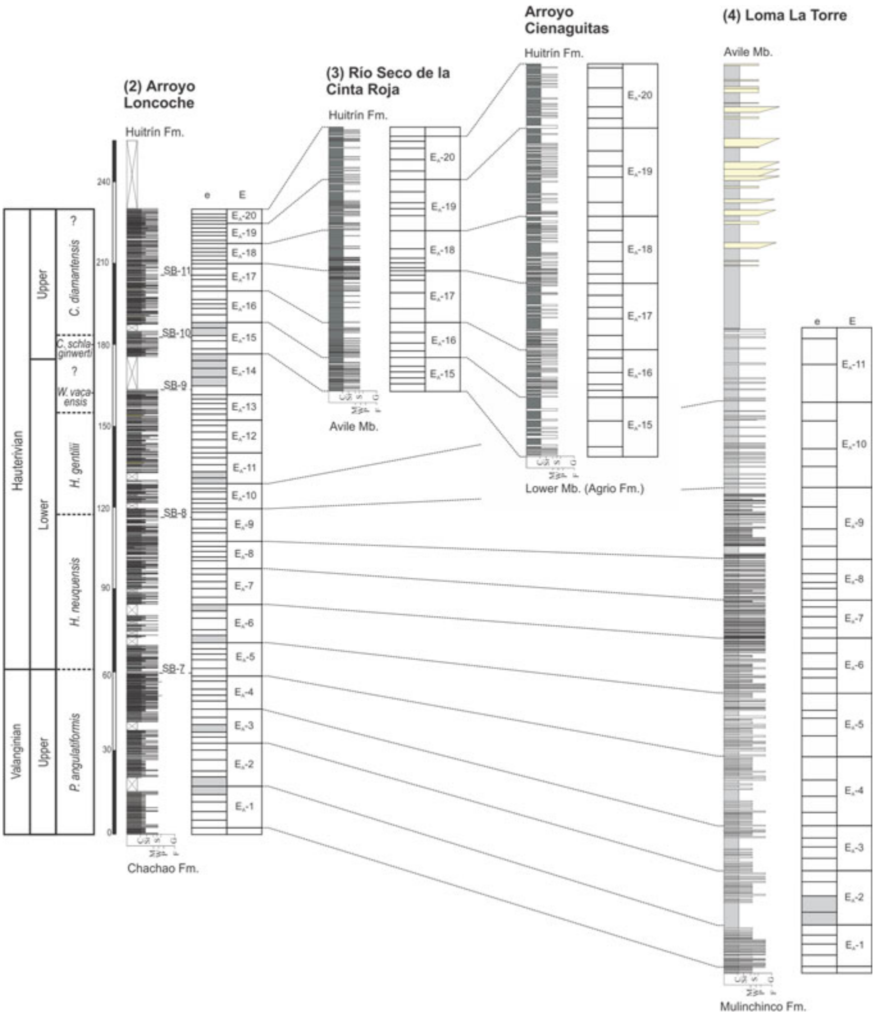


Fig. 4 High-resolution cyclostratigraphic correlation of studied stratigraphic sections of the Agrio Formation, using low-frequency eccentricity cycle (E) and high-frequency eccentricity cycle (e). Ammonite zones after Sagasti and Poire (1998), and Sagasti (2002, 2005)

4.3 *Elementary Cycle Periodicity and Spectral Analysis in the Vaca Muerta Formation*

According to ammonite biostratigraphic data from the studied sections, the Vaca Muerta Formation spans the Early Tithonian–Early Valanginian (Leanza and Hugo 1977). Detailed magnetostratigraphic correlations by Iglesia Llanos et al. (2017) in the Tithonian–Berriasian Arroyo Loncoche section indicate that the Vaca Muerta Formation spans the M22r.2r–M15r Subchrons (uppermost *Hybonoticeras hybonotum* to *Subthurmannia boissieri* Standard Zones). These data point to a time interval of *c.* 13 Ma (Ogg et al. 2016) for the Vaca Muerta Formation in Cañada Ancha and Río Seco de la Cara Cura sections. The Cañada Ancha section contains 654 elementary cycles, which are grouped in 130 bundles and 28 superbundles, whereas the Río Seco de la Cara Cura section includes 635 elementary cycles, 127 bundles, and 26 superbundles. Dividing the time-length of these sections by the number of elementary cycles, the periodicity of limestone/marlstone cycles has duration of ~21 ky, which can be attributed to the precessional cycle of the Earth. Data from the previous studied sections are consistent with this average value (Table 1).

Spectra obtained from time series of elementary cycle thickness are very consistent with each other (Fig. 4). At Cañada Ancha, REDFIT spectrum shows a peak above

Table 1 Cycle periodicities from the Vaca Muerta Formation (Lower Tithonian–Lower Valanginian)

Stratigraphic section	Estimated time (My)	Number of elementary cycles	Elementary cycle periodicity (ky)	Bundle periodicity (ky)	Superbundle periodicity (ky)
Previous studies					
Arroyo Loncoche	~10	487	20.53	118 91	410
Cuesta del Chihuido	~10	495	20.20	95	403
Bardas Blancas	~11	501	21.9	111	390
Arroyo Rahue	~11	510	21.56	89	395
El Ministerio	~3	168	18	120	400
This study					
Cañada Ancha	~13	654	19.9	102 84	480
Río Seco de la Cara Cura	~13	635	20.47	97	406

Data from previous studies include works of Kietzmann et al. (2011, 2015, 2018a) and Kohan Martínez et al. (2018)

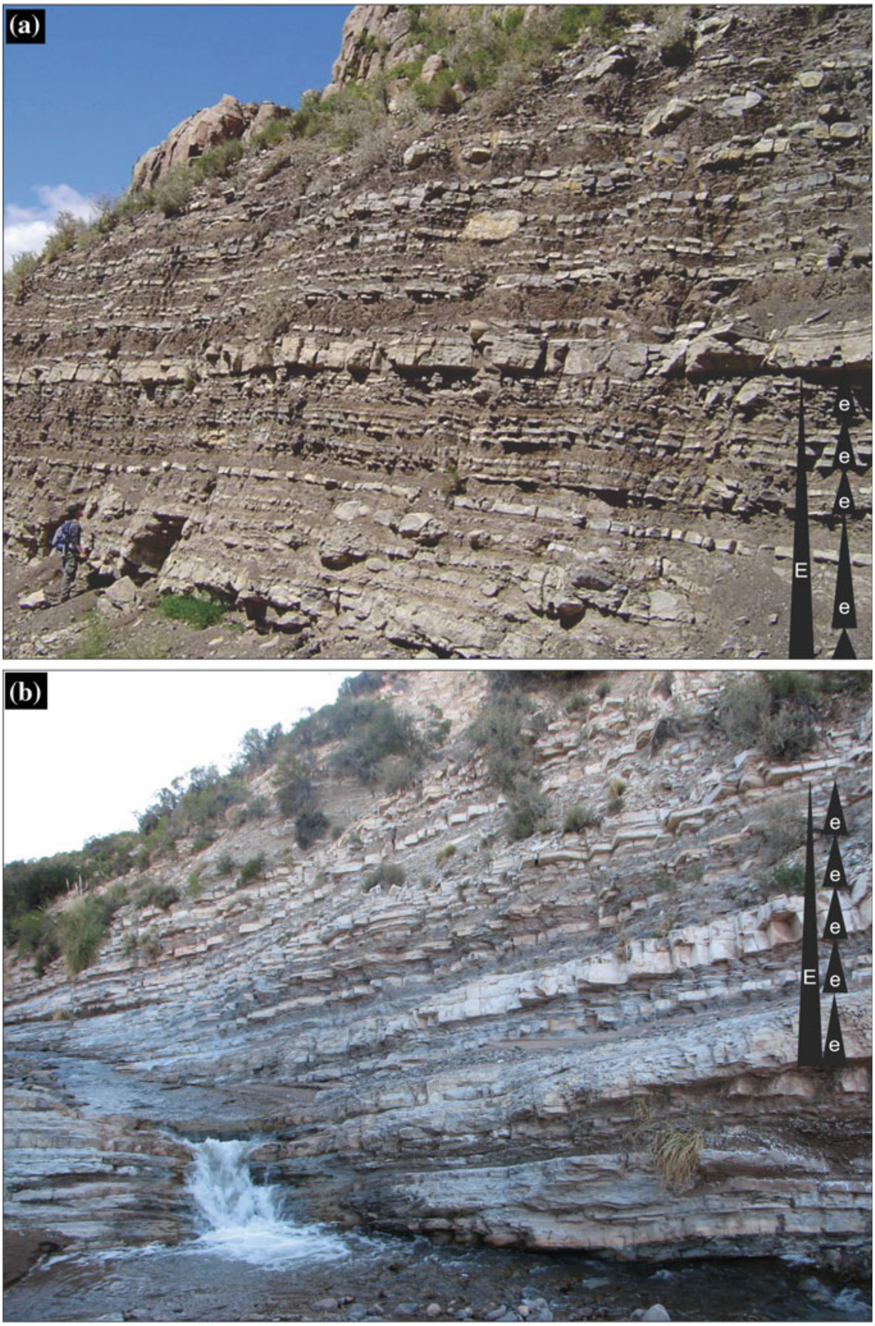


Fig. 5 Limestone–marlstone rhythmic successions in the Neuquén Basin: **a** Upper Tithonian at Cuesta del Chihuido section (Vaca Muerta Formation). **b** Lower Hauterivian at Arroyo Loncoche section (Agrio Formation). References: (E) superbundles or low-frequency eccentricity cycles (e) bundles or high-frequency eccentricity cycles

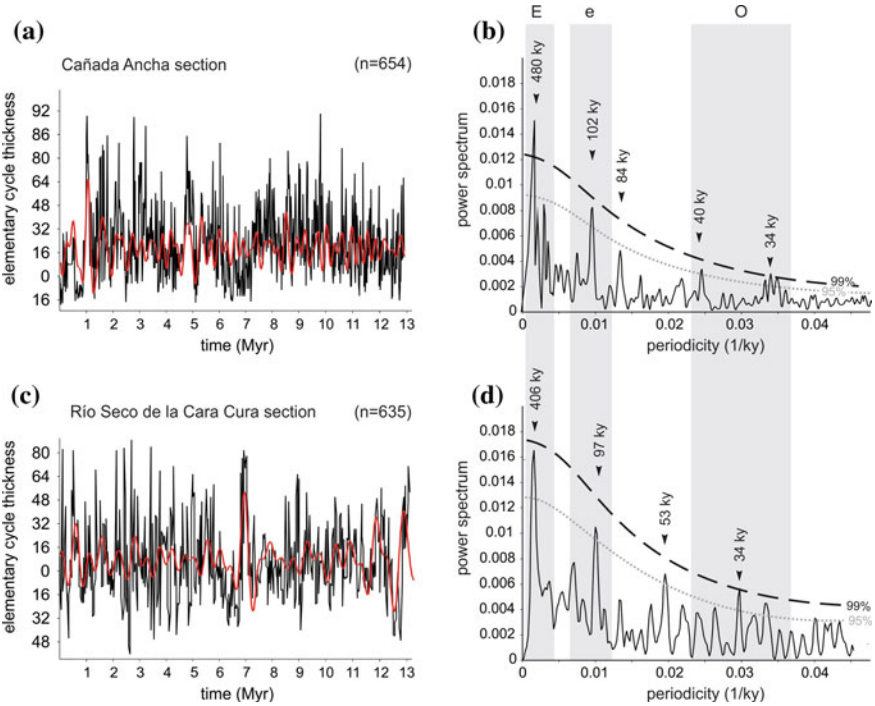


Fig. 6 Time series of elementary cycle thicknesses and REDFIT spectrum of new studied localities from the Vaca Muerta Formation, showing: low-frequency (E) and high-frequency (e) eccentricity cycle, obliquity (O) cycle and precession (P) cycle. **a**, **b** Cañada Ancha Section; **c**, **d** Río de la Cara Cura section. In **a** and **c,** red line indicates the modeled low-frequency eccentricity

the 95% confidence level and two peaks above the 99% confidence level (Fig. 6a, b). The first one has a periodicity of 403 ky which is consistent with the low-frequency eccentricity cycle. The other two peaks reveal periodicities of 103 cycles ky and 86 ky, respectively. These periodicities can also be attributed to the high-frequency eccentricity cycle. At Río Seco de la Cara Cura, a first peak of 410 ky and two peaks of 111 and 91 ky were observed, but an additional peak of 39 ky is observed above the 95% confidence level that can be assigned to the obliquity signal (Fig. 4). Similar results were observed in the other five sections of the Vaca Muerta Formation by Kietzmann et al. (2015, 2018a, b) for the Arroyo Loncoche, Cuesta del Chihuido, Bardas Blancas and Arroyo Rahue sections, as well as in El Ministerio section (Kohan Martínez et al. 2018) (Table 1). The calculated periodicities fit well with the so-called precession-eccentricity syndrome (PES) defined by Fischer et al. (2004), which is characteristic of mid- and low latitudes (Berger and Loutre 1994).

4.4 Elementary Cycle Periodicity and Spectral Analysis in the Agrio Formation

The Agrio Formation in the studied sections spans the Late Valanginian–Late Hauterivian (Leanza and Hugo 1977; Sagasti and Poire 1998; Sagasti 2000, 2005). Ammonite biostratigraphy suggests the correlation with the *Busnardoites campylotoxus* to the *Pseudothurmannia ohmi* Standard Zones (Aguirre-Urreta et al. 2005). However, magnetostratigraphic studies still need to be carried out in the Agrio Formation to tie the Andean ammonite zones in the international chronostratigraphic scale. These data point to a time interval of *c.* 8 Ma for the Agrio Formation at Arroyo Loncoche. The other partial sections from the Agrio Formation comprise approximately 3 Ma at Río Seco de la Cinta Roja, Arroyo Cianaguitas, and Loma La Torre.

The Arroyo Loncoche section, which spans the Late Valanginian–Late Hauterivian, contains 435 elementary cycles, which are grouped in 87 bundles and 20 superbundles. The Late Hauterivian–Early Barremian is represented also in the Arroyo Cienaguitas and Río Seco de la Cinta Roja sections. The Arroyo Cienaguitas contains 155 elementary cycles, 31 bundles, and 6 superbundles, Río Seco de la Cinta Roja section 135 elementary cycles, 27 bundles, and 6 superbundles, and Loma La Torre section (Upper Valanginian–Lower Hauterivian) 164 elementary cycles, 41 bundles, and 11 superbundles. After dividing the time-length of these sections for the number of elementary cycles, the periodicity of limestone/marlstone cycles has durations of ~18 to 19 ky that can be also attributed to the precessional cycle of the Earth (Table 2).

Table 2 Cycle periodicities from the Agrio Formation (Upper Valanginian–Lower Barremian)

Stratigraphic section	Estimated time (My)	Number of elementary cycles	Elementary cycle periodicity (ky)	Bundle periodicity (ky)	Superbundle periodicity (ky)
Previous studies					
Arroyo Cienaguitas	~3	103	~25	126 103 69	378
Río Seco de la Cinta Roja	~3	112	~18	125 117 77.5 65	875 319
This study					
Arroyo Loncoche	~8	435	18.4	97	390
Loma La Torre	~3	164	18.3	90	400

Previous studies include works of Sagasti (2000, 2005)

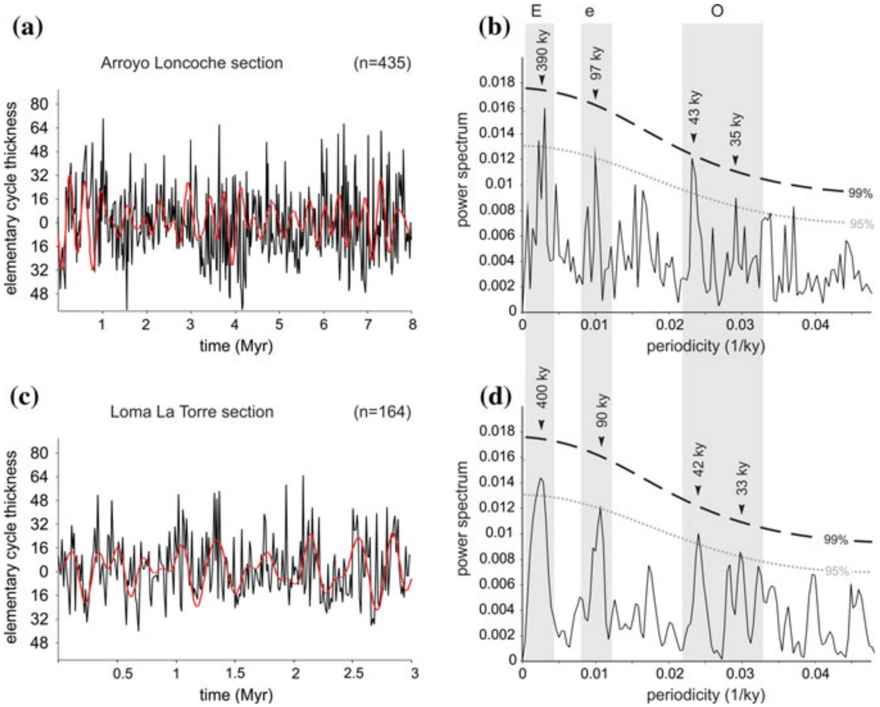


Fig. 7 Time series of elementary cycle thicknesses and REDFIT spectra of new studied localities from the Agrio Formation, showing low-frequency (E) and high-frequency (e) eccentricity cycles, obliquity (O) cycles and precession (P) cycles. **a**, **b** Arroyo Loncoche section; **c**, **d** Loma La Torre section. In **a** and **c,** red line indicates the modeled low-frequency eccentricity

Spectra obtained from time series of elementary cycle thicknesses are very consistent among each other (Fig. 7). At Arroyo Loncoche section, redfir spectrum shows four peaks above the 95% confidence level (Fig. 7a, b). The first one presents a periodicity of 390 ky which is consistent with the low-frequency eccentricity cycle. The other three peaks have periodicities of 97, 43 and 35 ky that can be attributed to the high-frequency eccentricity cycle and the obliquity cycle. At Loma La Torre section, a similar pattern is recognized (Fig. 7c, d), with a first peak of 400 ky and a second peak of 90 ky that are consistent with the low- and high-frequency eccentricity cycles, and two peaks of 42 and 33 ky that are assigned to the obliquity signal (Kietzmann and Paulin 2019).

4.5 High-Resolution Calibration of the Early Tithonian–Late Hauterivian in the Neuquén Basin

The cyclicity analysis of the ten studied stratigraphic sections enabled the construction of a floating astronomical scale for the Early Tithonian–Late Hauterivian in the Neuquén Basin (Fig. 8). Accordingly, minimum durations of ammonite zones within the Mendoza Group are the following:

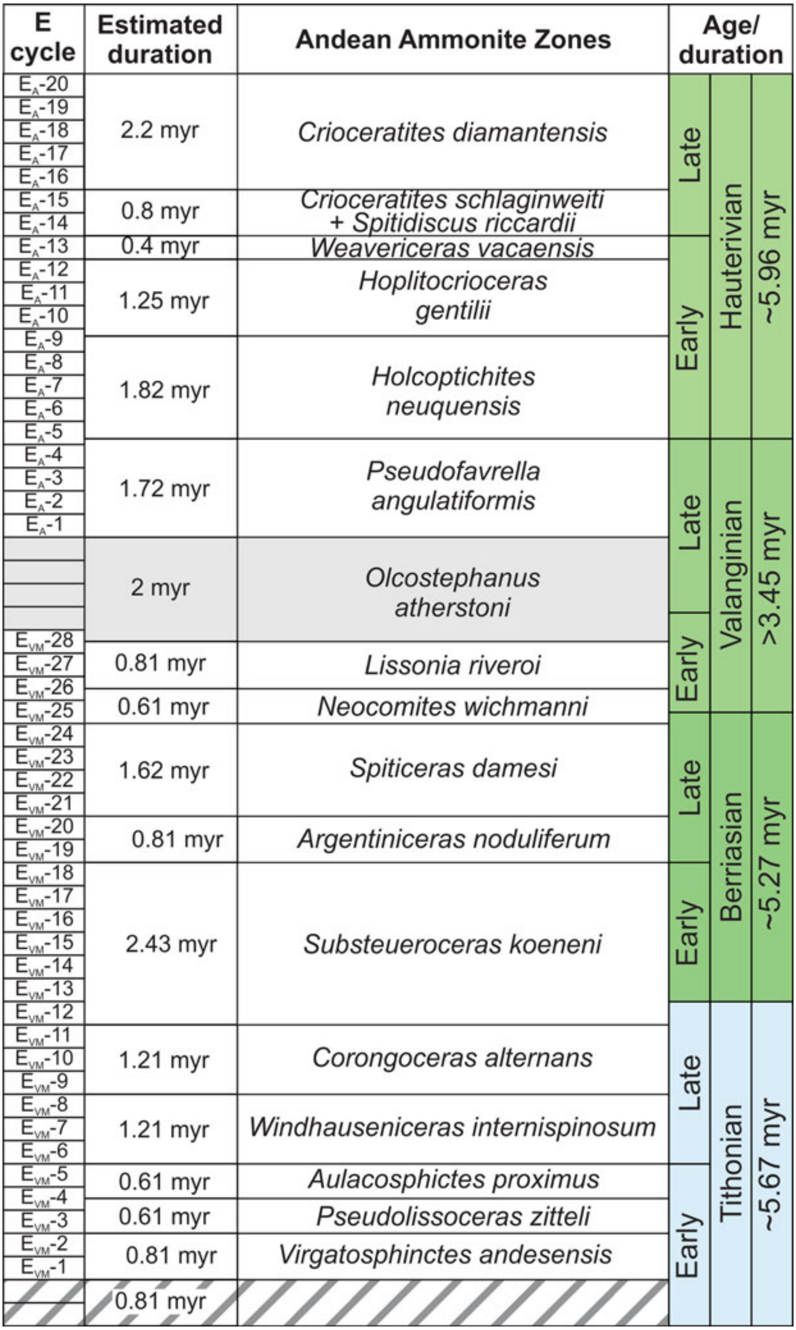
(1) The Lower Tithonian ammonite zones are distributed in 5 low-frequency eccentricity cycles (E-cycles) so that considering the 405 ky periodicity, this interval represents 2.025 myr. The lower part of the Lower Tithonian is not represented, and 2 E-cycles would thus be missing. The *Virgatosphinctes andesensis* Zone contains two E-cycles, with a minimum duration of 0.81 myr. The *Pseudolissoceras zitteli* Zone shows 1.5 E-cycles with a minimum duration of 0.61 myr, whereas the *Aulacosphinctes proximus* Zone shows 1.5 E-cycles with a minimum duration of 0.61 myr.

2) The Upper Tithonian comprises 7 E-cycles, representing 2.835 myr. The *Windhauseniceras internispinosum* Zone comprises 3 E-cycles with a minimum duration of 1.21 myr, whereas the *Corongoceras alternans* Zone contains also 3 E-cycles with a minimum duration of 1.21 myr. According to magnetostratigraphic data from the same section (Iglesia Llanos et al. 2017) the J-K boundary, in the middle part of Magnetosubzone M19n.2n, one E-cycle from the following *Substeueroceras koeneni* Zone is part of the Upper Tithonian.

(3) The Lower Berriasian comprises 6 E-cycles, representing 2.43 myr and corresponds to the *Substeueroceras koeneni* Zone. The Upper Berriasian includes 7 E-cycles, representing other 2.84 myr. The *Argentiniceras noduliferum* Zone shows 2 E-cycles with a minimum duration of ~0.81 myr, and the *Spiticeras damesi* Zone contains 4 E-cycles, with a minimum duration of ~1.62 myr. According to magnetostratigraphy (Iglesia Llanos et al. 2017), the lowermost part of the *Neocomites wichmanni* Zone should be included in the Upper Berriasian extending it in 1 E-cycle (0.405 myr).

(4) The Lower Valanginian represented in the Vaca Muerta Formation includes 3 E-cycles distributed in 3 ammonite zones. The upper part of the *Neocomites wichmanni* Zone contains 2 high-frequency eccentricity cycles (E-cycles) with a minimum duration of 0.203 myr. The *Lissonia riveroi* Zone contains 2 E-cycles with a minimum duration of 0.81 myr. The lowermost part of the *Olcostephanus (O.) atherstoni* Zone is also represented in the Vaca Muerta Formation with 2 E-cycles and a minimum duration of 0.203 myr. The rest of this zone is represented in the Chachao Formation and in the basal part of the Agrio Formation, but not in the studied sections of the latter formation, its minimum duration has not been assessed in this study. The Upper Valanginian is represented by the *Pseudofavrella angulatiformis* Zone that contains 4 E-cyles and at least 1 e-cycle, with a minimum duration of 1.72 myr.

(5) The Lower Hauterivian ammonite zones are distributed in 8 E-cycles and 4 E-cycles, so that this interval represents 3.6 myr. The *Holcoptichites neuquensis*



E cycle	Estimated duration	Andean Ammonite Zones	Age/ duration		
E_A-20 E_A-19 E_A-18 E_A-17 E_A-16	2.2 myr	*Crioceratites diamantensis*	Late	Hauterivian	~5.96 myr
E_A-15 E_A-14	0.8 myr	*Crioceratites schlaginweiti* + *Spitidiscus riccardii*			
E_A-13	0.4 myr	*Weavericeras vacaensis*	Early		
E_A-12 E_A-11 E_A-10	1.25 myr	*Hoplitocrioceras gentilii*			
E_A-9 E_A-8 E_A-7 E_A-6 E_A-5	1.82 myr	*Holcoptichites neuquensis*			
E_A-4 E_A-3 E_A-2 E_A-1	1.72 myr	*Pseudofavrella angulatiformis*	Late	Valanginian	>3.45 myr
	2 myr	*Olcostephanus atherstoni*			
E_{VM}-28 E_{VM}-27	0.81 myr	*Lissonia riveroi*	Early		
E_{VM}-26 E_{VM}-25	0.61 myr	*Neocomites wichmanni*			
E_{VM}-24 E_{VM}-23 E_{VM}-22 E_{VM}-21	1.62 myr	*Spiticeras damesi*	Late	Berriasian	~5.27 myr
E_{VM}-20 E_{VM}-19	0.81 myr	*Argentiniceras noduliferum*			
E_{VM}-18 E_{VM}-17 E_{VM}-16 E_{VM}-15 E_{VM}-14 E_{VM}-13 E_{VM}-12	2.43 myr	*Substeueroceras koeneni*	Early		
E_{VM}-11 E_{VM}-10 E_{VM}-9	1.21 myr	*Corongoceras alternans*	Late	Tithonian	~5.67 myr
E_{VM}-8 E_{VM}-7 E_{VM}-6	1.21 myr	*Windhauseniceras internispinosum*			
E_{VM}-5 E_{VM}-4	0.61 myr	*Aulacosphictes proximus*	Early		
E_{VM}-3	0.61 myr	*Pseudolissoceras zitteli*			
E_{VM}-2 E_{VM}-1	0.81 myr	*Virgatosphinctes andesensis*			
	0.81 myr				

Fig. 8 Astronomical calibration of the Tithonian–Hauterivian in the Neuquén Basin, using 405 ky low-frequency eccentricity cycles. The lowermost Tithonian interval (oblique stripes) is not represented in the Vaca Muerta Formation and the illustrated cycles are taken from Huang et al. (2010). Gray-shaded interval in the *Olcostephanus (O.) atherstoni* Zone does not present cyclostratigraphic data

Zone contains 4 E-cycles and 2 E-cycles with a minimum duration of 1.82 myr. The *Hoplitocrioceras gentilii* Zone includes 3 E-cycles and 1 e-cycle showing a minimum duration of 1.25 myr. The *Weavericeras vacaensis* Zone is poorly defined in the studied sections, but it contains at least one E-cycle, having therefore a minimum duration of 0.4 myr.

(6) The Upper Hauterivian ammonite zones ares distributed in 4.5 E-cycles with a minimum duration of 1.82 myr. The *Spitidiscus riccardi* and the *Crioceratites schlaginwerti* Zones are poorly defined in the studied sections, but they contain at least 2 E-cycle, having therefore a minimum duration of 0.8 myr, and the *Crioceratites diamantensis* Zone contains 5 E-cycles with a minimum duration of 2.2 myr. Nevertheless, more detailed studies are needed to determine whether the studied sections reach or not the Early Barremian.

Based on the number of low-frequency eccentricity cycles within the Vaca Muerta Formation, we estimated a minimum duration of each stage in the Neuquén Basin (Fig. 8):

1) The Tithonian would have a minimum duration of 4.86 myr; however, the basal part of the Tithonian is not represented in the Vaca Muerta Formation. Considering ammonite zones durations reported by Huang et al. (2010) for the Kimmeridge Clay Formation, Kietzmann et al. (2018a) interpreted that at least two low-frequency eccentricity cycles are missing, and therefore, the estimated minimum duration for the Tithonian is 5.67 myr.

(2) Considering the position of the Jurassic–Cretaceous boundary obtained by magnetostratigraphy (Iglesia Llanos et al. 2017; see Chap. "Magnetostratigraphy of the Jurassic Through Lower Cretaceous in the Neuquén Basin") the Berriasian presents a minimum duration of 5.27 myr (Kietzmann et al. 2018a).

3) The Valanginian should be studied in more detail, since the basal part (*Olcostepahus (O.) atherstoni* Zone) has not been analyzed yet. However, the results of this work indicate that it would have at least a minimum duration of 3.45 myr. Cyclostratigraphic studies in the Vocotian Basin (France) and the Subbetic Domain (Spain) indicate a minimum duration of 5.9 myr (Huang et al. 1993) and 5.08 myr (Martínez et al. 2013) so that this zone would comprise at least 4 E-cycles with a duration of c.a. 2 myr.

4) The minimum duration of the Hauterivian is estimated in 5.96 myr; however, it is necessary to carefully analyze the upper part of the studied sections to determine whether it can reach in fact the Early Barremian. Previous cyclostratigraphic studies in the Vocotian Basin (France) and the Subbetic Domain (Spain) indicate a minimum duration of 5.3 myr (Huang et al. 1993) and 5.9 myr (Martínez et al. 2015), very consistent with our results, but considerably longer than the durations proposed in the GTS2012 and 2016 (Ogg et al. 2016).

5 Orbital Controls on the Sedimentation in the Neuquén Basin

Marlstone–limestone rhythmic deposits are important examples of climate-forced sedimentation resulting from different palaeoenvironmental responses to orbital forcing (Arthur et al. 1984; Einsele and Ricken 1991; Berger and Loutre 1994). However, some authors have claimed a diagenetic origin for these cycles (Ricken 1986, 1987; Munnecke and Samtleben 1996; Westphal et al. 2000, 2004, 2010). Criteria for differentiating primary from diagenetic origin deposits were described by Einsele (1982) and Einsele and Ricken (1991), based on simple geological criteria. Recently, Westphal et al. (2010) stated that the occurrence of palynomorphs, calcite fossils in both calcareous and terrigenous hemicycles, sedimentary structures and textures, and variations in clay mineralogy constitute unequivocal criteria for interpreting a primary origin of the deposits. The Vaca Muerta Formation includes several groups of planktonic and benthic invertebrates of aragonitic, calcitic, and organic composition, which are present in both calcareous and clastic hemicycles. Additionally, although there is evidence of diagenetic overprint (Catalano et al. 2018), taphonomic, sedimentary structures, and petrographic evidences are irrefutable signals that support the primary origin of rhythmicity in the Vaca Muerta Formation (Kietzmann et al. 2015).

Four main transference mechanisms were proposed for primary rhythmic successions (Einsele and Ricken 1991), including fluctuations in the production of calcareous biogenic particles by plankton or “productivity cycles,” in the input of fine-grained terrigenous sediments or “dilution cycles,” of the lysocline or “dissolution cycles,” and in the minimum oxygen zone or “redox cycles.” The first two mechanisms were proposed in the Neuquén Basin: Productivity and dilution mechanisms were suggested in different intervals for the Vaca Muerta Formation by Concheyro et al. (2006) and Palma et al. (2008) based on the limestone/marlstone ratio, whereas the dilution mechanism was interpreted for the Agrio Formation by Sagasti (2000, 2005) based on sedimentological and geochemical data. However, Kietzmann et al. (2011, 2015) proposed that elementary cycles are driven by “carbonate exportation” (Pittet and Strasser 1998; Bádenas et al. 2003). These cycles are originated by fluctuation in shallow-water carbonate production, which in turn, involves changes in carbonate basinward exportation.

The estimated water depth for the Vaca Muerta and Agrio formations ranges between 50 and 200 m (Sagasti 2005; Kietzmann et al. 2008, 2014), so dissolution mechanism did not produce the rhythmicity, since the carbonate compensation depth (CCD) during the Upper Jurassic–Lower Cretaceous was at 2–3 km (Arthur et al. 1985). Similarly, redox cycles cannot be considered as a potential mechanism, since any changes in the icnological and faunal associations are observed at elementary cycles scale (Doyle et al. 2005; Kietzmann and Palma 2009; Kietzmann et al. 2014).

Productivity (sensu Einsele 1982) and fertility (sensu Premoli Silva et al. 1989) mechanisms would not explain the cyclicity in the Vaca Muerta Formation, since sedimentation was controlled by hydrodynamic factors instead of a strong pelagic input;

the abundance of transported skeletal particles and particles derived from shallow-water areas, such as dasycladacean algae, agglutinated foraminifera, and abundant crustacean microcoprolites in both carbonate and marly facies, are strong evidences of shallow-water input (Kietzmann et al. 2014, 2015). Similar observations were made by Sagasti (2005) for the Agrio Formation, where pelagic calcareous material is represented by a poorly diversified association of calcareous nannofossils that is considered by this author a subsidiary component. In fact, the most abundant components in mudstones and limestones are micritic pellet (Kietzmann and Palma 2011, 2014). Recent SEM studies show that these pellets are made up of coccoliths that can produce lamination and were produced by shrimps (callianassids) (Kietzmann et al. 2010; Kietzmann and Palma 2014). Callianassids dwell from shallow to deep marine areas and can be detritivorous or suspension feeders. In fact, the middle and outer ramp facies of the Vaca Muerta and Agrio formations are rich in pellets, but also show a high level of bioturbation produced by crustaceans, such as *Thalassinoides* or *Rhizocorallium* (Sagasti and Poire 1998; Doyle et al. 2005; Kietzmann and Palma 2009). As mentioned by Kietzmann and Palma (2011), pellets are mostly transported, appearing most frequently in medium-sand size, and hydrodynamically behaving as sand. Therefore, cyclicity can be interpreted in terms of "productivity" related to variations in carbonate exportation. The four productivity and dilution intervals identified in the Vaca Muerta Formation by Concheyro et al. (2006) and Palma et al. (2008) are related to changes in sea-level. The two marlstone-rich intervals attributed to dilution cycles coincide with transgressive system tracts, whereas carbonate-rich intervals attributed to productivity cycles coincide with regressive system tracts, where the increase in the proportion of carbonates results from a decrease in accommodation that induces an increase in carbonate basinward exportation from shallower areas (Kietzmann et al. 2015).

The dilution mechanism was proposed by Sagasti (2005) for the Agrio Formation, based on the idea of high-frequency paleoclimatic fluctuation in the North Patagonian Massif, which was the main active source area during the Agrio carbonate ramp deposition (Legarreta and Uliana 1991; Eppinger and Rosenfeld 1996; Sagasti 2005). In that model, fluctuations in clastic dilution occurred as from recurring latitudinal migration of climate zones forced by the precessional cycle. The alternation of humid and arid climatic conditions in the North Patagonian Massif caused changes in the amount of terrigenous sediment supply. During one phase of the precessional cycle, the humid conditions promoted an increase in rainfall, and consequently in runoff and sediment supply to the marine basin. During the arid phase, terrigenous input was inhibited, and carbonate material exported from shallow areas, and could be accumulated in the distal areas.

An important question for the Agrio dilution model is that even if orbital forcing would have provided the trigger, it is not clear if it was effective during the Late Jurassic–Early Cretaceous. Climate response during Neogene through Holocene was much more sensitive due to the presence of large polar ice masses and glaciers that increase sensitivity of the system to disturbance (Berger 2013). In contrast, carbonate systems were highly sensitive to orbitally induced temperature changes during greenhouse conditions (Fischer 1982; Goldhammer et al. 1990, Strasser et al.

1999), particularly in shallow water, where these fluctuations controlled the carbonate production rate and sea-level amplitude (Algeo and Wilkinson 1988; Drummond and Wilkinson 1993; Burgess et al. 2001; Kemp et al. 2016). In this scenario, the carbonate exportation mechanism would be more likely. However, since mudstone volume in units of the Mendoza Group is striking, it is difficult to asses which of the mechanisms remained constant and which one fluctuated, so that the sedimentary pattern observed in the Vaca Muerta and Agrio Formations would result from the coexistence of both mechanisms.

6 Conclusions

The Vaca Muerta and Agrio formations in southern Mendoza are characterized by decimeter-scale rhythmic alternations of marlstones and limestones, showing a well-ordered hierarchy of cycles, including elementary cycles, bundles, and superbundles. Based on spectral analysis, elementary cycles have a periodicity of ~21 ky, which correlates with the precessional cycle of Earth's axis; bundles and superbundles have periodicities of ~90 to 120 ky and ~400 ky, which we interpret as the modulation of the precessional cycle by the Earth's orbital eccentricity. Obliquity periodicities have also been recognized, but not in all the studied sections.

Cyclostratigraphic data allowed us to build a floating astronomical time scale for the Tithonian–Hauterivian in the Neuquén Basin: (1) The Tithonian would have a minimum duration of 5.67 myr. (2) Considering the position of the Jurassic–Cretaceous boundary obtained by magnetostratigraphy, the Berriasian presents a minimum duration of 5.27 myr. (3) The Valanginian should be studied in more detail, since the *Olcostepahus (O.) atherstoni* Zone has not been analyzed yet, however, it would have at least a minimum duration of 3.45 myr. (4) The minimum duration of the Hauterivian is estimated in 5.96 myr, which is very consistent with previous cyclostratigraphic studies in the Tethys but differs with the 3.1 myr in the GTS2012 and 3.9 y the GTS2016.

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