10º Congreso de Exploración y Desarrollo de Hidrocarburos
Simposio de Recursos No Convencionales: Hacia una Nueva Convención

STABLE ISOTOPE SIGNATURE OF THE TITHONIAN-VALANGIAN STRATA OF THE VACA MUERTA-QUINTUCO SYSTEM IN THE NEUQUEN BASIN

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Keywords: **stable isotopes, outcrop, high-resolution curves, proximal-distal variation, paleoenvironment**

RESUMEN

Signatura de isótopos estables de los estratos Tithoniano-Valanginianos del Sistema Vaca Muerta-Quintuco en la Cuenca Neuquina.
Las composiciones de isótopos estables de C de los sedimentos carbonáticos han sido ampliamente utilizadas para la reconstrucción de las condiciones de CO_2 en los sistemas antiguos, y como método de correlación. Este trabajo presenta un registro $\delta^{13}C$ de alta resolución para el intervalo Tithoniano-Valanginiano en afloramientos de la Cuenca Neuquina, Argentina. Mediciones de roca total fueron tomadas a intervalos de 1m en una sucesión continua de ~650 m del intervalo Vaca Muerta-Quintuco en el área de Puerta Curaco. El marco crono-estratigráfico proviene de la bioestratigrafía de amonites de secciones cercanas publicadas. La curva de $\delta^{13}C$ en Puerta Curaco (PC) muestra una tendencia general creciente desde la zona de amonites V.mendozanus del Tithoniano Medio hasta la zona de L.riveroi en el Valanginiano temprano. Los primeros 420 m de la curva poseen valores muy negativos en 3 ciclos creciente-decrecientes de gran escala. Curvas de subsuelo de menor resolución muestran tendencias similares en el sistema Vaca Muerta-Quintuco. Existe una variación proximal-distal (entre los afloramientos de Picún Leufú, Sierra de la Vaca Muerta y Puerta Curaco) con los valores más negativos hacia la cuenca, lo que indica una mezcla entre material carbonatico de plataforma no afectado por diagénesis y carbonato precipitado o alterado en una cuenca disóxica/anóxica. A nivel de ciclos se observa que los hemiciclos transgresivos y con mayor contenido clástico muestran los mayores valores de TOC y mínimos de $\delta^{13}C$, mientras que lo opuesto ocurre en las porciones regresivas y más carbonáticas. Estos resultados sugieren una columna de agua estratificada, con los valores más negativos en aguas profundas, y una dilución de la materia orgánica producto del sedimento exportado de las plataformas carbonáticas que resulta en una mezcla composicional proximal-distal. Los valores de $\delta^{13}C$ han demostrado ser una herramienta de correlación muy útil dentro de la cuenca y un buen indicador de las condiciones paleoambientales de las aguas. Las curvas de $\delta^{13}C$ del Tethys muestran tendencias diferentes, ligeramente decrecientes y con valores entre +1 and +2‰. Una alteración diagenética causada por la adición de carbonato autigénico parecería sobreimponerse a la signatura original.

INTRODUCTION

The potential of marine carbonate isotope stratigraphy relies on the fact that 13C/12C ratios of marine carbonates vary over time, mainly as the result of partitioning of carbon between organic carbon and carbonate carbon reservoirs in the lithosphere (Kump and Arthur, 1999). While other factors such as diagenesis and sediment source are known to affect $\delta^{13}C$ values, their primary use in the carbonate record has been in the interpretation of the $\delta^{13}C$ values of the oceans and as stratigraphic tools (e.g. Saltzman and Thomas 2012).

The Tithonian-Early Valanginian strata of the Neuquén Basin consists of a mixture of siliciclastic and carbonate sediments deposited in a marine setting behind the proto-Andean arc. The succession is exposed along the current fold and thrust belt in excellent, highly continuous outcrops (Fig. 1A). An abundant fossil record constrains the age of the succession (Leanza 1973; Riccardi 2008; Aguirre Urreta *et al.* 2005, among others). The shelf deposits correspond to the Picún Leufú and Quintuco Formations while the slope and basinal deposits are the Vaca Muerta Formation (e.g. Gulisano *et al.* 1984; Leanza *et al.* 2011, Fig. 1B). The Picún Leufú and Quintuco

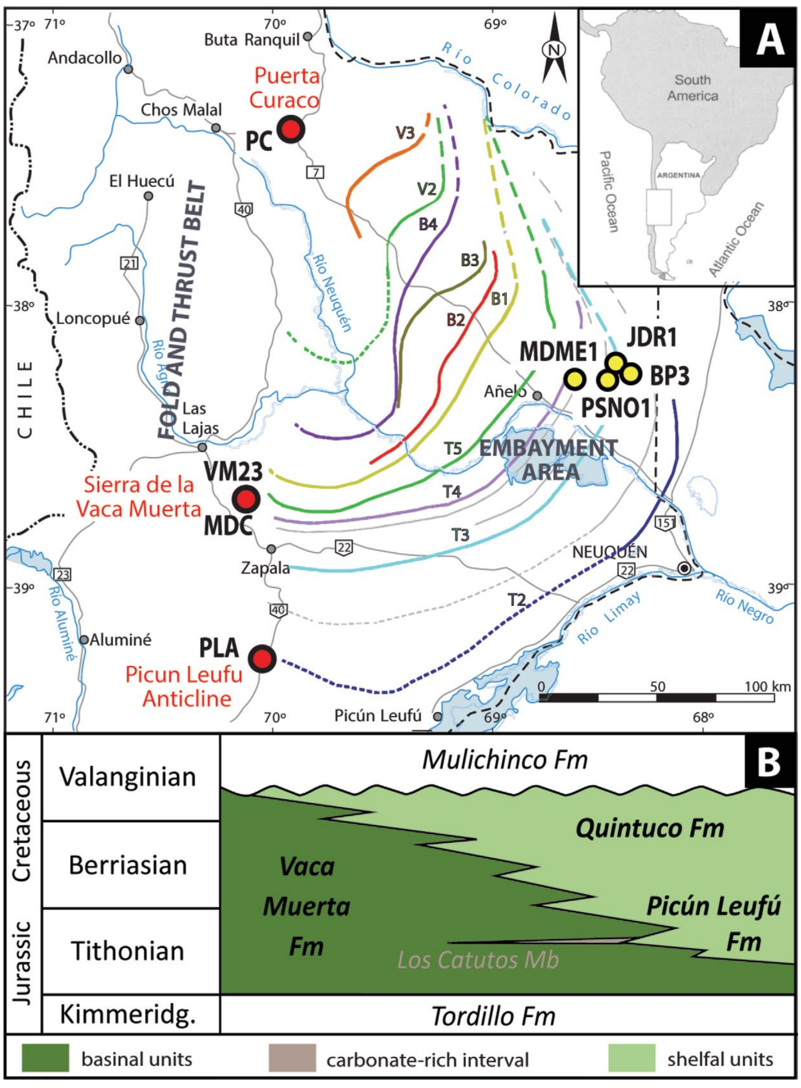

Figure 1. A) Location map of the Neuquén Basin with the studied outcrop (red dots) and well locations (yellow dots). Lines T2 to V3 are seismic clinoform breaks (modified from Dominguez *et al.* 2017) showing progradation of the Quintuco-Vaca Muerta system in the subsurface. B) Lithostratigraphic units. See text for citations.

Formations are the topsets of the prograding clinoforms that fill the basin, and the Vaca Muerta Formation corresponds to the foresets and bottomsets of the clinoforms (Mitchum and Uliana 1985; Zeller *et al.* 2015. Fig. 1B). The Los Catutos Member is a carbonate-rich interval within the Vaca Muerta Formation, which has been interpreted as deposited in an open shallow marine shelf environment below wave base (e.g. Leanza and Zeiss 1990) or a distal portion of a carbonate ramp (e.g. Spalletti *et al.* 2000). Recently, it has been interpreted as a periplatform deposit (Rodríguez Blanco 2016; Rodríguez Blanco *et al.* 2017).

The thick Tithonian-Early Valanginian succession with abundant ammonites makes the Neuquén basin an ideal location for detailed stratigraphic studies of the $\delta^{13}C$ record of the strata that straddles the Jurassic-Cretaceous boundary. This study provides the first high-resolution carbon isotope record of the Tithonian-Early Valanginian succession in outcrops of the Neuquén Basin. A 645m succession of Vaca Muerta and Quintuco Formations was sampled for isotopes at 1m intervals in the first 520m, and at 5m intervals in the subsequent 125 m in the Puerta Curaco area. Carbonate isotope ratios were measured via dissolution of whole-rock samples in phosphoric acid (Swart *et al.* 1991) and reported relative to the Vienna Pee Dee Belemnite (VPDB) scale. Samples were also analyzed for carbonate content and TOC, and spectral GR measurements were taken at 1m intervals in the outcrop. Shorter sections of the Picún Leufú and Vaca Muerta Formations in the Picún Leufú Anticline and the Sierra de la Vaca Muerta, respectively, were sampled in similar density to provide the record for the more proximal settings (Fig. 1A). All sections were analyzed for sedimentary facies and placed within a sequence-stratigraphic framework.

Cycles were determined in the field based on facies trends. Clastic (CO_3<15%) or calcareous (15-50% CO_3) mudstones dominate the transgressive portion of the cycles, while silty-mudstones or wackestone/packstone beds (sometimes stratigraphically-aligned concretions) commonly form their tops. The cyclic facies arrangement is noticeable in the weathering profile where the transgressive portion and turnaround are typically fissile and back-weathered, while the more cemented regressive tops tend to stick out. The cycles are arranged in coarsening upward cycle sets, with the top beds thickening upwards. Bioturbation and bivalve infauna are more abundant in the silty layers and carbonate beds, indicating more oxic conditions towards the top of the cycle sets. Increasing amounts of skeletal fragments raise the carbonate content towards the top of the cycle sets. Cycle sets group into sequences that show similar trends. Ages were constrained by nearby biostratigraphic sections from the literature (e.g. Aguirre Urreta and Vennari 2013; Aguirre Urreta *et al.* 2014).

The purpose of this study is to use 1) the $\delta^{13}C$ values for refinement of stratigraphic correlations within the basin and 2) to compare the record with published data of the same time period from other basins in the world. In the first case, the high-resolution isotope record was compared with shorter and/or lower-resolution curves measured in outcrops (Scasso *et al.* 2005; Rodríguez Blanco 2016) and subsurface wells (Morettini *et al.* 2015; Hernández Bilbao 2016). In the second case, the

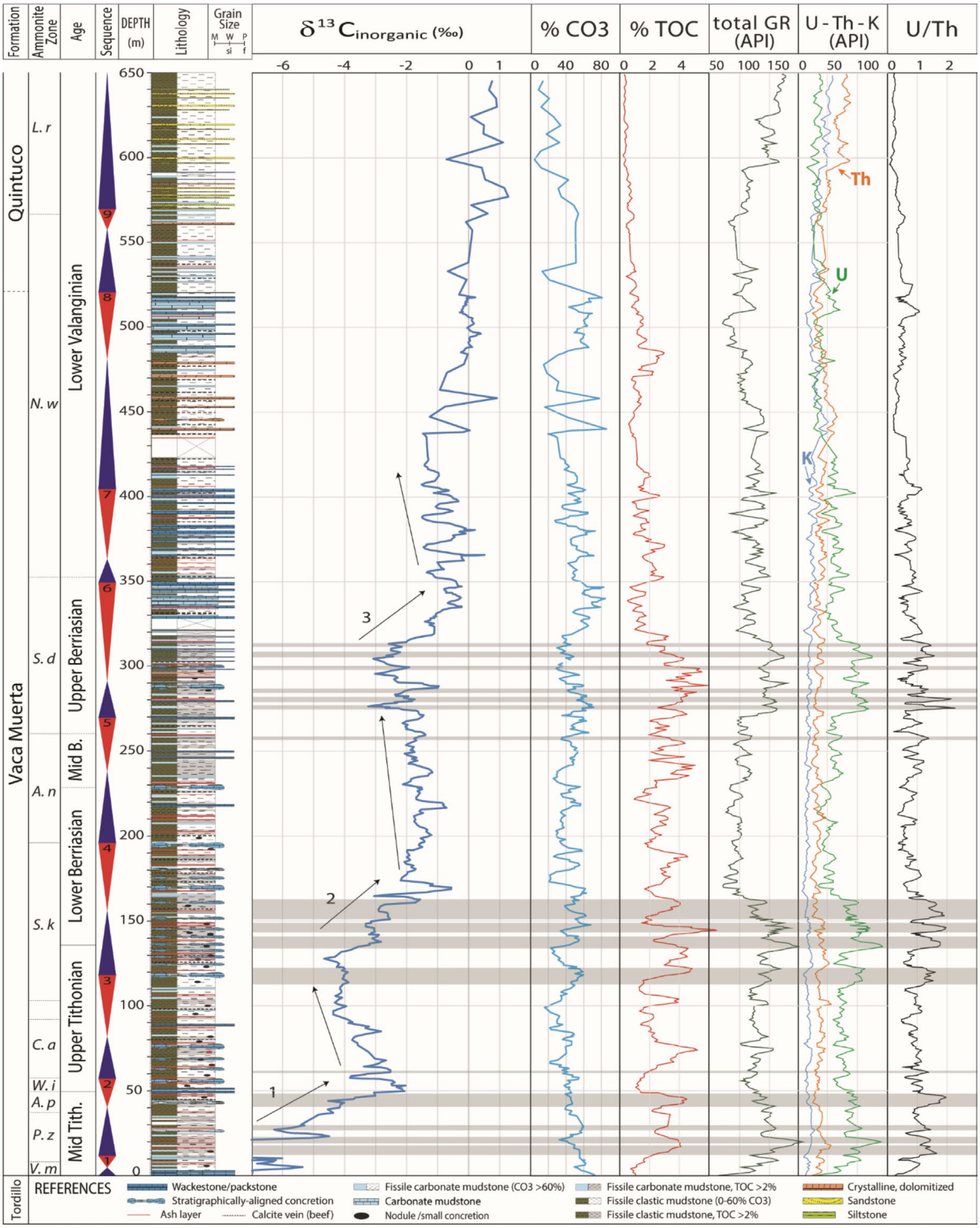

Figure 2. Stratigraphic section at Puerta Curaco (PC), modified from Rodríguez Blanco (2016) and Eberli *et al*. (2017). Large-scale $\delta^{13}C$ cycles are indicated with arrows and respective numbers. Highlighted intervals (grey) with U/Th > 1.2 coincide with turning points between those cycles, and transgressive portions of sequences 2, 4 and 6. Ammonite zones and ages were determined by correlation with sections from Aguirre Urreta and Vennari (2013) and Aguirre Urreta *et al*. (2014).

high-resolution curve was compared with Tethyan published data (Weissert and Erba 2004; Katz *et al*. 2005).

RESULTS

EARLY TITHONIAN TO EARLY VALAGINIAN CARBONATE ISOTOPE CURVE

The detailed curve of $\delta^{13}C$ values in Puerta Curaco (PC) (Fig. 2) shows an overall increasing trend from the Middle Tithonian V.mendozanus ammonite zone to the Early Valanginian L.riveroi. The first 420 m of the curve display highly negative values in 3 large-scale increasing-decreasing cycles. The initial minimum is very close to the base of the Vaca Muerta Formation, the second is near the Tithonian-Berriasian boundary, and the third falls within the Upper Berriasian. Minimum values tend to coincide with transgressive hemisequences while maximum values are frequently associated with sequence tops. The negative $\delta^{13}C$ values of the first 420 m of the section coincide with the most organic-rich part of the succession and with the highest amount of volcaniclastic intercalations. TOC in excess of 2% has been measured in the two lower cycles of $\delta^{13}C$ values and varies between 0.5 and 2% in the upper cycle. Though the organic-rich zone is quite continuous in the first 420 m of the PC section, the spectral gamma ray curve shows 3 distinct peaks that coincide with $\delta^{13}C$ minimums. These GR peaks are driven by the Uranium signal, and coincide with the highest U/Th ratios of the section. At the top of the 3rd large-scale cycle, between 420 and 460 m, another significant change occurs, which is masked by poor exposure and complete dolomitization of the carbonate beds. Above 460 m the $\delta^{13}C$ curve shows a slightly increasing trend with values between 0 and +2. Detailed sedimentological and sequence-stratigraphic analysis of this section can be found in Rodríguez Blanco (2016), Eberli *et al.* (2017) and Weger *et al.* (2017).

Comparison of the PC $\delta^{13}C$ values to Tethyan signatures is challenging both because of the much lower resolution of the available Tethyan data, and the high organic matter in the PC section. Figure 3 shows the integrated Tithonian-Valanginian curves of Weissert and Erba (2004), and Katz *et al.* (2005) from a review by Saltzman and Thomas (2012). Global isotope values vary between 0 and +3 similarly to other reports from Tethyan and Boreal realms with either bulk or belemnite measurements. In all the cases the Early Tithonian-Early Valaginian global range of $\delta^{13}C$ values is narrow with no significant variations but a strong negative spike in the middle Tithonian (Katz *et al.* 2005), and a more subtle one at the Tithonian-Berriasian boundary. Interestingly, both peaks seems to correlate with the highly negative signatures at the base of large-scale cycles 1 and 2 respectively. Except for those negative excursions, global curves are gently decreasing from near +3 to +1‰ during the Tithonian, and fairly stable between +2 and +1‰ during the Berriasian and lowest Valanginian. Instead, the first 420m of the PC curve display the previously mentioned 3 large-scale cycles within an overall increasing trend. A more detailed analysis shows that the most significant variations are produced in the increasing portion of the large-scale cycles near the turning points, where changes of 5, 4 and 3‰ are recorded in cycles 1 to 3 respectively. But the decreasing portions of the $\delta^{13}C$ cycles display more gentle trends with variations of 2.5‰ for

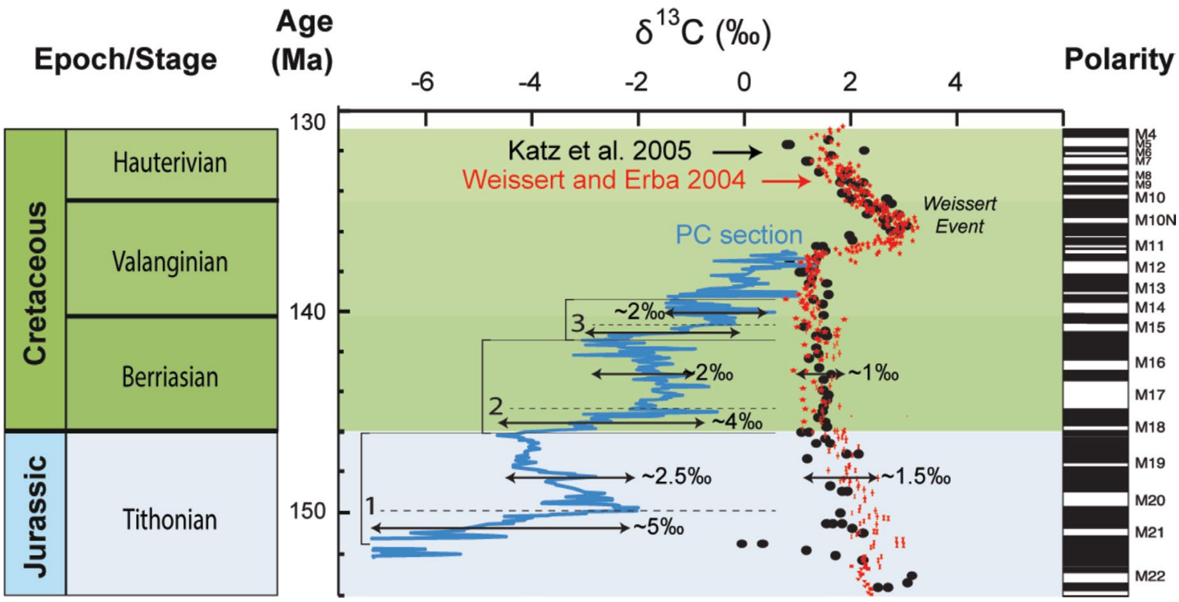

Figure 3. Comparison of Puerta Curaco (PC) isotope record to global curves from the Tethyan realm (Weissert and Erba 2004; Katz *et al.* 2005). Figure modified from Saltzman and Thomas (2012). Polarity data is from Weissert and Erba (2004). Positioning of PC is aproximate: base of the section was considered within the Darwini ammonite zone (Aguirre Urreta *et al.* 2014), in the middle portion of polarity chron M22 (e.g. Gradstein *et al.* 2012). Tithonian, Berriasian and Valanginian segments were stretched/shortened to match their respective boundaries (assumption of constant depositional rate). Top of the curve is placed earlier than the Weissert Event, which is younger than the analyzed PC succession (Aguirre Urreta *et al.* 2008). Large-scale cycles 1, 2 and 3 are indicated with brackets, while stippled lines limit increasing and decreasing portions. Ranges (‰) are displayed for each segment.

cycle 1, and 2‰ for cycles 2 and 3. These values are closer to the 1.5 to 1‰ ranges of the global isotope curve, though absolute values are more negative. In the uppermost PC section where organic content is lower (Fig. 2), both absolute values and ranges of variation are similar to the $\delta^{13}C$ compositions of the global curve (Fig. 3).

Correlation of the PC $\delta^{13}C$ values to other data sets in the basin is challenging because published data is scarce, with lower resolution and is derived mainly from relatively proximal areas either in the Sierra de la Vaca Muerta outcrops or in the subsurface Neuquén Embayment (Fig. 1A). The most significant constraint is that these proximal sections only represent the older part of the succession within the prograding system, showing relatively higher $\delta^{13}C$ values (Fig. 4). However, these curves from outcrop and subsurface display the same initial increase towards the W.internispinosum ammonite zone that can be observed in the coeval first $\delta^{13}C$ cycle in the PC section (Figs. 2 and 4). The highest $\delta^{13}C$ values in outcrop occur within the Los Catutos Member (MDC section, Sierra de la Vaca Muerta, Figs. 1A and 4). This carbonate-rich interval is characterized by a dominant south-north variation in carbonate content, bed thickness and $\delta^{13}C$ values that indicate a provenance from south (Rodriguez Blanco 2016 and Rodriguez Blanco *et al.* 2017). Hence, the periplatform ooze of the Los Catutos is not likely to reach the Embayment. However, the highest $\delta^{13}C$ values in subsurface are also associated with relatively higher carbonate contents (Hernández Bilbao 2016).

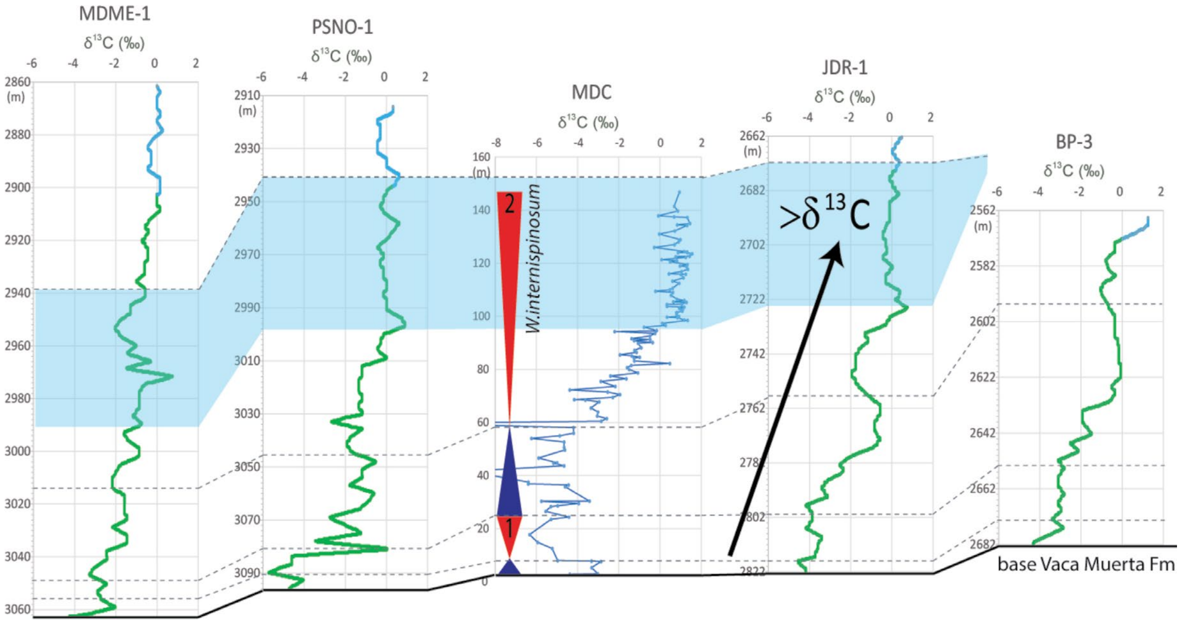

Figure 4. Isotope data from the Vaca Muerta Formation in Sierra de la Vaca Muerta (MDC section from Rodriguez Blanco 2016) and 4 wells from the Neuquén Embayment (from Hernandez Bilbao 2016). See Fig.1 for section and well locations. Sequence interpretation for the subsurface is modified from Hernandez Bilbao (2016). W.internispinosum zone (light blue) is placed for MDC section based on the literature (Los Catutos Member, Leanza and Zeiss 1990) and estimated for the wells relative to the interpreted sequences (stippled lines). The analyzed curves show similar increasing trends towards the W.i zone.

PROXIMAL-DISTAL VARIATIONS AND CYCLIC PARTITIONING

A north-south cross-section along the Puerta Curaco (PC), Sierra de la Vaca Muerta (MDC and VM23) and Picún Leufú Anticline (PLA) outcrops of the Neuquén Basin is displayed in Figure 5A. Here the interval of the W.internispinosum ammonite zone corresponds to the top of Sequence 2 and is a pure carbonate platform within the Picún Leufú Formation in the south (Leanza 1973; Spalletti *et al.* 2000; Zeller *et al.* 2015), a periplatform carbonate mud on the slope (Los Catutos Member) (Spalletti *et al.* 2000; Rodriguez Blanco 2016; Rodriguez Blanco *et al.* 2017), and a basinward decrease in skeletal and carbonate content to a siliciclastic-dominated interval in the Puerta Curaco area in the north (Vaca Muerta Formation) (Rodriguez Blanco *et al.* 2017). In all environments, individual cycles display more carbonates in the regressive than transgressive portions, indicating that the fine-grained carbonates are mostly shed during sea level highstands (here included in the regressive part of the cycle) when carbonate production was high in the shelf.

Carbonate $\delta^{13}C$ values display two trends. First they decrease basinward, and second they increase upward within each cycle and cycle set. Figure 5B displays the vertical variation of the $\delta^{13}C$ values in the studied sections. The PC, VM23 and MDC sections show overall gently increasing trends towards the top of the interval, which is the top of Sequence 2 (Figs. 2 and 4, respectively). The upward increase in $\delta^{13}C$ values is also observed in cycle sets (Fig. 5B). Detailed

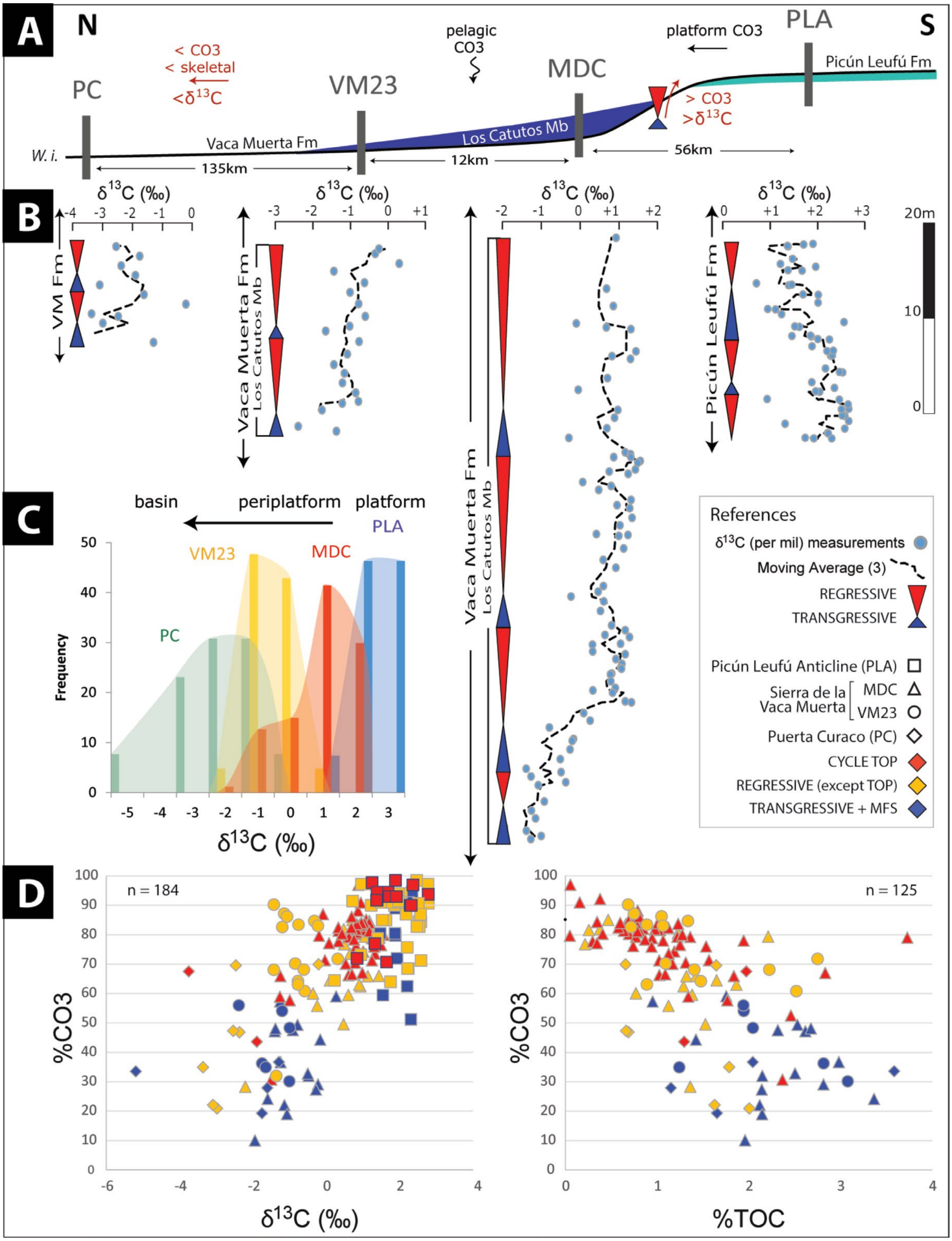

Figure 5. A) N-S outcrop cross-section (see Fig. 1 for location) for the W.internispinosum (W.i.) time-interval. Proximal-distal and cyclic behavior of carbonate (CO_3), skeletal content and isotopic signature are also schematized. B) Isotope curves and cycle sets of the studied sections. Notice that MDC and VM23 are sampled from base to top of the Los Catutos Mb, while PLA and PC curves only represent specific intervals (W.i zone) within the respective formations. C) Distribution of the isotopic values displayed in B). D) Cross-plots of TOC and $\delta^{13}C$ vs. CO_3 for the studied sections. See References for color-coding. CO_3 and part of the isotope data of PLA come from Afsar (2010). Notice that PLA lacks TOC measurements.

sedimentological and sequence-stratigraphic analysis of these sections can be found in Zeller (2013) for PLA, and in Rodriguez Blanco (2016), Eberli *et al.* (2017), and Weger *et al.* 2017 for MDC, VM23 and PC.

Isotope curve range is 2 to 3‰ in all the studied sections, with a noticeable decrease in absolute $\delta^{13}C$ values accompanying the basinward reduction in carbonate content. This proximal-distal trend is also observed in the $\delta^{13}C$ values of Figure 5C. The highest values correspond to the carbonate platform (PLA), which displays the same compositional range as the global Tithonian curve (Fig. 3). On the other end, the basinal PC section shows highly negative values probably affected by its relatively higher organic content. In between, slope (MDC) and distal periplatform deposits (VM23) are characterized by mixed compositions. In the case of MDC, the isotopic signature is very similar to that reported for other relatively proximal locations in the basin (Scasso *et al.* 2005; Morettini *et al.* 2015; Hernandez Bilbao 2016. Fig. 4). Cross-plots of $\delta^{13}C$ values vs. carbonate content (CO_3) and TOC vs. CO3 capture both the observed proximal-distal and the cyclic variations (Fig. 5D). Samples are identified by section, and color-coded by position within basic transgressive (blue)-regressive (red + yellow) cycles. The third color (yellow) was used to represent the transition that sometimes occurs along the regressive hemicycles. In other cases, the passage to the carbonate-rich top is abrupt. Increasing $\delta^{13}C$ values accompany the increase in carbonate content (CO_3) both towards proximal settings and cycle tops. The observed increase in carbonate content coincides with a decrease in TOC values towards more proximal settings and a relatively higher concentration of the organic matter in the more clastic-rich hemicycles (Fig. 5D). Similar cyclic partitioning of TOC has been described by many authors (e.g. Gonzalez *et al.* 2016; Tenaglia *et al.* 2017).

DISCUSSION

The most dramatic difference shown by the analyzed data are the large variations between the $\delta^{13}C$ values of the basinal section (PC) and the shelf carbonates. While the relatively positive values of the shelf carbonates, such as found at the PLA site, are consistent with the global $\delta^{13}C$ values published for the same time period (Weissert and Erba 2004; Katz *et al.* 2005), the values found in the basinal sites (PC and VM23) are more negative. Because the surface water of the Neuquén Basin is open marine (e.g Legarreta and Uliana 1996; Gasparini *et al.* 1997), the most plausible explanation for the negative values of the basinal sections is that the carbonate has been diagenetically altered or that authigenic carbonate with an isotopically negative value has been added to the sediments at the sea floor. This may be similar to the model envisaged by Schrag *et al.* (2013) in order to explain carbon isotopic anomalies during certain time periods, particularly the Neoproterozoic. While such processes are known to take place within the sediment pore space (Irwin *et al.* 1977), normally the amount of oxidants such as sulfate are limiting. Consequently, negative $\delta^{13}C$ values associated with authigenic carbonate precipitation are only present in sections with very low amounts of carbonate material or in sections with low rates of sediment deposition. Hence such an extensive low $\delta^{13}C$ values (~420 m-thick interval) together with a relatively high carbonate content (83% of measurements >30%CO_3) as present at the PC site can only be formed as a result of diagenesis within a region where the concentration of sulfate is not limited. This condition would be found in an anoxic basin. In modern oceans biogenic particles produced near the surface sink through the water column and are degraded by bacterial activity (Fig. 6). This process is enhanced by the stratification of the waters (Broecker and Peng 1982; Saltzman and Thomas 2012). If organic-carbon flux to the sea floor increases, bacterial processes will lead to progressive oxygen consumption and the eventual development of stratified waters with dysoxic or anoxic bottoms (e.g. Gruszczynski 1998; Jenkyns 2003).

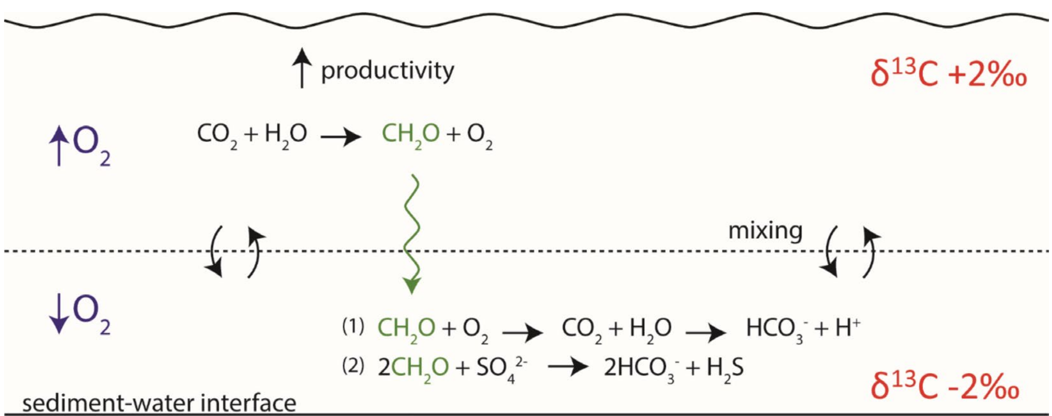

Figure 6. Proposed model to explain the basinal highly negative values measured. Organic matter (green) sink through the water column and undergo remineralization, either during sinking or when reaching the sea bottom. Whether the degradation of the organic matter takes place in the presence of oxygen (1) or sulfate (2), the result will be isotopically negative alkalinity. The HCO_3^- thus generated will combine with Ca_2^+ from the sea water to produce isotopically negative carbonates. Indicated $\delta^{13}C$ values are characteristic of normal sea water, but more negative values are expected if increasing deposition of organic matter occurs in stratified waters with anoxic/dysoxic bottoms.

The lateral change of the $\delta^{13}C$ values such as seen at location MDC can be best explained as a mixing signal between relative positive platform material reflecting carbonate precipitated in approximate isotopic equilibrium with oceanic dissolved inorganic carbon (DIC) and authigenic carbonates formed on the sea floor. As the platform gradually progrades into the basin or the precipitation of authigenic carbonate becomes reduced, the signal changes towards more positive values which are more reflective of the shallow water carbonate and perhaps reflective of the oceanic signal. This is similar to the mechanism proposed for the Bahamas (Swart and Eberli 2005; Swart 2008) with the exception that in the case of the Bahamas the distal end-member was proposed to be derived from pelagic carbonates. In the Neuquén Basin this pelagic end-member has been altered as it sinks into the anoxic bottom water and is recrystallized to authigenic carbonate producing isotopically negative carbonate material.

Interestingly, while the high deposition of organic matter may result in negative $\delta^{13}C$ values within anoxic basins, it can also be associated with time-synchronous carbonates with positive values as isotopically-negative carbon is removed and buried. Hence, the $\delta^{13}C$ values seen within the deeper portion of the Neuquén Basin are not global in nature as the rates of authigenic carbonate production are probably variable related to local conditions even if there were a large number of anoxic basins at this time. In contrast, the $\delta^{13}C$ values seen in the shallow water carbonates are probably more likely to be globally correlative as they are responding to a global change in the burial of organic carbon. As the position of relative sea level may be influential in the development of anoxia, this might have been a control of the extent of increase in the $\delta^{13}C$ values.

In the case of the Vaca Muerta Formation, the isotopically negative $\delta^{13}C$ values measured in the basin can be explained by an early diagenetic organic-matter driven alteration produced in a context of anoxic/dysoxic bottom waters and high productivity of surface waters. These depositional conditions are supported by multiple evidences from different authors: laminated mudstones with no bioturbation, very high organic matter content, presence of phosphate concentrations, dominance of planktonic/nektonic organisms and relative absence of benthic organisms, abundance of well-preserved marine reptile skeletons, etc. (Leanza 1973; Uliana and Legarreta 1993; Gasparini *et al* 1997, among others). However, there is abundant evidence that indicates bottom currents in the basin (e.g. Zeller 2013; Weger *et al.* 2017) suggesting that stagnant conditions would not have been prevalent. Also carbonate-rich intercalations within the shales are generally bioturbated reflecting system variations from anoxic to more oxygenated (suboxic) conditions (Doyle *et al.* 2005), that may reflect variations in productivity of surface waters, organic matter influx, climate-driven changes in water circulation, etc. Additionally, the maximum presence of ash intercalations in the higher TOC portion of the succession (Fig.2, 0 to 420m) seems to imply a relationship between volcanism and organic matter deposition. The incorporation of high fluxes of ^{12}C-enriched volcanogenic CO_2 into the atmosphere and waters might also contribute to the relative negative $\delta^{13}C$ values of the Vaca Muerta Formation.

Relationships between Uranium (U) and Thorium (Th) have been used extensively as anoxic indicators, based on the assumption that 1) under near-surface conditions Th is relatively immobile and found in the sediment associated with heavy minerals or clays, and 2) U in its 6+ valence is partly carried in solution but under anoxic conditions it may be precipitated to enrich the sediment in authigenic U provided a host mineral (e.g. carbonate and/or phosphate) or organic substrate is available (e.g. Adams and Weaver 1958; Jones and Manning 1994; Wignall and Myers 1988). Additionally, as Uranium accumulation occurs only within the sediment and not in the water column (e.g. Anderson *et al.*1989), slower sedimentation rates will allow more time for U to diffuse and precipitate into the sediment (Algeo and Maynard 2004). As a result, the enrichment in authigenic U under anoxic conditions will lead to higher U/Th ratios. In the case of the Vaca Muerta Formation, highest Th values coincide with ash layers present throughout the first 420 m of PC section, while highest U and U/Th values correspond to major GR peaks (Fig. 2). In light of the above discussion, highlighted intervals in Figure 2 might be interpreted as a reflection of the lowest oxygen levels and/or highest availability of deposited organic matter for uranium fixation and/or very low sedimentation rates. These high U/Th intervals (U/Th>1.2) also coincide with the turning points between large-scale $\delta^{13}C$ cycles and are immediately followed by significant positive excursions (Figs. 2 and 3). Hence, the large-scale $\delta^{13}C$ signal is probably driven by the highest accumulations of organic matter in very low oxygen conditions and low sedimentation rates. Positive excursions associated with organic matter sequestration are also mentioned for unpublished wells in the subsurface by Morettini *et al.* (2015).

A comparison between basinal (Fig. 2) and proximal (Fig. 4) $\delta^{13}C$ values, though limited by the short time-span represented in proximal areas, shows similar trends in the first large-scale cycle. Yet, absolute values increase towards proximal settings reflecting the decreasing influence of organic matter on the isotopic signal. The increase in carbonate content related to platform shedding, more significant near platforms and during highstands (Schlager *et al.* 1994), results on the one hand in dilution of organic matter and lower TOC values, and on the other hand heavier $\delta^{13}C$ signatures more influenced by surface waters (Fig. 5). The observed proximal-distal variations of $\delta^{13}C$ values are also displayed in the overall increasing trend of PC curve, which reflects the somerization of the system. This agrees with a depositional model of basin (0-320 m), periplatform (320 to 400 and 490 to 520m are carbonate-rich intervals similar to the periplatform Los Catutos Mb), and probable distal platform above 520m (Rodriguez Blanco 2016; Weger *et al.* 2017), similarly to what was interpreted by other authors both in outcrop and subsurface (Leanza and Hugo 1977; Gulisano *et al.* 1984; Mitchum and Uliana 1985; Kietzmann *et al.* 2014; Gonzalez *et al.* 2016, among others). Within the overall positive trend, minimum $\delta^{13}C$ values are associated with transgressive and maximum flooding intervals while sequence tops display heavier signatures (Figs. 2 and 4). The same behavior is observed at the scale of basic cycles and cycle sets (Fig. 5), where the organic-rich transgressive portions display lighter signatures than the carbonate-rich tops. Simplifying, the resulting isotopic compositions of Vaca Muerta samples may be explained by the interplay of 2 major processes: organic matter alteration and accumulation in oxygen-deficient bottoms, and organic matter dilution by platform-shedding of carbonate. Both processes act simultaneously but the former is enhanced during transgressions and the latter during regressions. Periodic mixing of waters must also play a role, as evidenced by variations in the inferred oxygen content and resulting degree of bioturbation.

CONCLUSIONS

The $\delta^{13}C$ values of the Vaca Muerta Formation show that two major processes that act in different parts of the system combine to control the measured $\delta^{13}C$ values: 1) organic-matter alteration in poorly-oxygenated basinal bottom waters (more negative values), and 2) platform-shedding of carbonate in a context of high productivity of surface waters (more positive values). The relative influence of these processes controls the resultant $\delta^{13}C$ values both in space and time. Positive shallow-water values on one end and negative organic-rich-influenced basinal values on the other result in mixed signatures along a proximal-distal trend. The carbonate-platform shedding process is recorded in two types of behavior that depend on the relative distance to the carbonate source: a basinward reduction in carbonate and skeletal contents, and a variable degree of organic-matter dilution. The higher productivity of platforms during highstands and the concomitant shedding increase are expressed in sequence-stratigraphic cycles as more carbonate-rich tops and more positive $\delta^{13}C$ values that are more influenced by surface water values than by alteration of the organic matter. Large-scale variations of $\delta^{13}C$ values reflect changes in the accumulation of organic matter and the resultant isotopic composition of the water from which carbonates precipitate. Negative spikes followed by positive excursions record moments of increased organic carbon sequestration. In combination with U/Th ratios, they provide insight into the environmental conditions of deposition such as water stratification, oxygen levels, and sediment rates. Isotopic variations are controlled by the sequence-stratigraphic framework, as minimum spikes immediately followed by positive excursions correspond to large-scale transgressive to maximum flooding periods. Major trends in $\delta^{13}C$ are similar in basinal and proximal positions. The large scale sequence-stratigraphic significance of $\delta^{13}C$ is replicated in the basic cycles, where a transgressive-regressive partitioning is observed. Hence carbonate isotope stratigraphy might be a powerful tool to refine correlations within the basin. Correlation with global signatures is challenging with only the complete record of the PC area and much lower resolution Tethyan curves to compare. In Puerta Curaco (PC) section, three major events were observed, which start with negative spikes and are followed by strong positive excursions: the one that represents the initial flooding of the basin and the one at the Tithonian-Berriasian boundary might be represented in Katz *et al.* (2005) records, though the latter with less significance. The third event, though, is not present in the curve of Weissert and Erba (2004) either. Further data would be necessary to assess how local the influence of the organic matter in the Neuquén Basin is, and if some of the observed events have a global significance.

ACKNOWLEDGEMENTS

The fieldwork and data analysis was a collaborative effort of a group from the CSL – Center for Carbonate Research with financial support from its industrial associates. L. Rodriguez Blanco acknowledges a Fulbright fellowship for partial support of this study.

CITED REFERENCES

Adams, J.A. and Weaver, C.E. (1958) Thorium-to-Uranium Ratios as Indicators of Sedimentary Processes: Example of Concept of Geochemical Facies. AAPG Bulletin 42 (2), 387-430.

Afsar, F. (2010) Einfluss petrographischer Merkmale auf akustische Geschwindigkeiten in gemischt siliziklastisch-karbonatischen Gesteinen (Picún Leufú-Formation, Neuquén Becken, Argentinien). Master-Thesis. Universität Bremen.

Aguirre Urreta, M.B. and Vennari, V.V. (2013) Amonites y bioestratigrafía de la Formación Vaca Muerta en tres pozos de El Trapial. Chevron internal report.

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

Aguirre Urreta, M.B., Price, G.D., Ruffell, A.H., Lazo, D.G, Kalin, R.M., Ogle, N. and 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, M.B., Vennari, V.V., Lescano, M., Naipauer, M., Concheyro, A. and Ramos, V.A. (2014) Bioestratigrafía y Geocronología de Alta Resolución de la Formación Vaca Muerta, Cuenca Neuquina. IX Congreso de Exploración y Desarrollo de Hidrocarburos. Mendoza. Trabajos Técnicos 2, 245-268.

Algeo, T.J. and Maynard, J.B. (2004) Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. Chemical Geology 206, 289– 318.

Anderson, R.F., Fleisher, M.Q. and LeHuray, A.P. (1989) Concentration, oxidation state, and particulate flux of uranium in the Black Sea. Geochimica et Cosmochimica Acta 53, 2215-2224.

Broecker, W.S. and Peng, T.H. (1982) Tracers in the sea. Eldigio Press, New York, p. 690.

Domínguez, R.F., Reijenstein, H., Kohler, G., Sattler, F., Moreno, M.J., Gómez Rivarola, L. and Borgnia, M. (2017) Distribución regional de quiebres de clinoformas del sistema Vaca Muerta-Quintuco. XX Congreso Geológico Argentino, Tucumán, Argentina. Actas Simposio Geología de la Formación Vaca Muerta, 38-45.

Doyle, P., Poire, D.G., Spalletti, L.A, Pirrie, D., Brenchley, P. and Matheos, S.D. (2005) Relative oxygenation of the Tithonian – Valanginian Vaca Muerta-Chachao formations of the Mendoza Shelf, Neuquén Basin, Argentina. In: Veiga, G.D., Spalletti, L.A., Howell, J.A. and Schwarz, E. (eds). The Neuquén Basin, Argentina: A Case Study in Sequence

Stratigraphy and Basin Dynamics. Geological Society, London, Special Publications 252, 185-206.

Eberli, G.P., Weger, R.J., Tenaglia, M., Rueda, L., Rodriguez Blanco, L., Zeller, M., McNeill, D.F., Murray, S. and Swart, P. (2017) The Unconventional Play in the Neuquén Basin, Argentina – Insights From the Outcrop for the Subsurface. URTEC Conference Paper: 2687581, Austin, TX.

Gasparini, Z., Spalletti, L. and De La Fuente, M. (1997) Tithonian Marine Reptiles of the Western Neuquén Basin, Argentina. Facies and Palaeoenvironments. Geobios, 30 (5), 701-712.

González G., Vallejo D., Kietzmann D., Marchal D., Desjardins P, González Tomassini F., Gómez Rivarola L., Domínguez R.F. (eds) (2016) Transecta Regional de la Formación Vaca Muerta. Integración de sísmica, registro de pozos, coronas y afloramientos, lAPG - AGA, p. 244, Buenos Aires.

Gradstein, F.M., Ogg, J.G., Schmitz, M.D., Ogg, G.M., 2012. The Geologic Time Scale. Elsevier, Oxford, p. 1144.

Gruszczynski, M. (1998) Chemistry of Jurassic seas and its bearing on the existing organic life. Acta Geologica Polonica, 48 (1), 1-29.

Gulisano, C.A., Gutiérrez Pleimling, A.R. and Digregorio, R.E. (1984) Análisis estratigráfico del intervalo Tithoniano-Valanginiano (Formaciones Vaca Muerta, Quintuco y Mulichinco) en el suroeste de la provincia del Neuquén. 9º Congreso Geológico Argentino, Actas 1: 221-235, San Carlos de Bariloche.

Hernandez Bilbao, E. (2016) High-resolution chemostratigraphy, sequence stratigraphic correlation, porosity and fracture characterization of the Vaca Muerta Formation, Neuquén Basin, Argentina. Colorado School of Mines. Dissertation 221, 10113602.

Irwin, H., Curtis, C. and Coleman, M. (1977) Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. Nature 269, 209-213.

Jenkyns, H.C. (2003) Evidence for rapid climate change in the Mesozoic-Palaeogene greenhouse world. Philosophical Transactions of the Royal Society A, 361, 1885-1916.

Jones, B. and Manning, D.A.C. (1994) Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chemical Geology, 111, 111-129.

Katz, M.E., Wright, T, J. D., Miller, K. G., Cramer, B. S., Fennel, K. and Falkowski, P.G. (2005) Biological overprint of the geological carbon cycle. Marine Geology 217, 323–338.

Kietzmann, D.A., Ambrosio, A.L., Suriano J., Alonso S., Vennari V.V., Aguirre-Urreta M.B., Depine G. and Repol D. (2014) Variaciones de facies de las secuencias basales de la Formación Vaca Muerta en su localidad tipo (Sierra de la Vaca Muerta), cuenca Neuquina. IX Congreso de Exploración y Desarrollo de Hidrocarburos, Mendoza. Trabajos Técnicos 2, 299-317.

Kump, L.R. and Arthur, M.A. (1999) Interpreting carbon-isotope excursions: carbonates and organic Matter. Chemical Geology 161, 181-198.

Leanza, H.A. (1973) Estudio sobre los cambios faciales de los estratos limítrofes Jurásico-Cretácicos entre Loncopué y Picún Leufú, provincia de Neuquén, República Argentina. Revista de la Asociación Geológica Argentina, XXVIII (2), 97–132.

Leanza, H.A. and Hugo C.A. (1977) Sucesión de amonites y edad de la formación Vaca Muerta y Sincrónicas entre los paralelos 35° y 40° L.S., cuenca Neuquina-Mendocina. Revista de la Asociación Geológica Argentina, XXXII (4), 248–264.

Leanza, H.A. and Zeiss, A. (1990) Upper Jurassic Lithographic Limestones from Argentina (Neuquén Basin): Stratigraphy and Fossils. Facies 22, 169–186.

Leanza, H.A., Sattler, F., Martínez, R.S. and Carbone, O. (2011) La Formación Vaca Muerta y equivalentes (Jurásico tardío-Cretácico temprano) en la Cuenca Neuquina. In: Congreso Geológico Argentino, No. 18 (Eds H. Leanza, J. Vallés, C. Arregui, J.C. Danieli). Geología y Recursos Naturales de la provincia del Neuquén, 12, 113-129. Neuquén.

Legarreta, L. and Uliana, M.A. (1996) The Jurassic succession in west-central Argentina: stratal patterns, sequences and paleogeographic evolution. Palaeogeography, Palaeoclimatology, Palaeoecology 120, 303-330.

Mitchum, R.M.Jr. and Uliana, M.A. (1985) Seismic Stratigraphy of Carbonate Depositional Sequences, Upper Jurassic-Lower Cretaceous, Neuquen Basin, Argentina. AAPG Memoir 39, 255-274.

Morettini, E., Godino, G., Smith, L.B. and Massaferro, J.L. (2015) The Vaca Muerta-Quintuco Mixed Depositional System: New Insights from Carbon Stable Isotopes (δ13Ccarb and δ13Corg) and Geochemical Data at the Jurassic-Cretaceous Boundary (Neuquén Basin, West Argentina). AAPG Search and Discovery Article 90216. AAPG Annual Convention and Exhibition, Denver, CO.

Riccardi, A.C. (2008) El Jurásico de la Argentina y sus amonites. Revista de la Asociación Geológica Argentina 63 (4), 625-643.

Rodriguez Blanco, L. (2016) Distribution and Source of Carbonate-Rich Intervals within the Vaca Muerta-Quintuco Mixed System, Neuquén Basin, Argentina. University of Miami. Open Access Theses, 622.

Rodriguez Blanco, L., Eberli, G.P. and Weger, R.J. (2017) Distribution and Source of Carbonate-Rich Intervals within the Vaca Muerta Formation. XX Congreso Geológico Argentino, Tucumán, Argentina. Actas Simposio Geología de la Formación Vaca Muerta, 135-138.

Saltzman, M.R. and Thomas, E. (2012) Carbon Isotope Stratigraphy. In: The Geologic Time Scale 2012 (Eds Gradstein, F.M., Ogg, J.G., Schmitz, M.D. and Ogg, G.M.), Elsevier, Oxford, 207–232.

Scasso, R.A., Alonso, M.S., Lanes, S., Villar, H.J. and Laffitte, G. (2005) Geochemistry and petrology of a Middle Tithonian limestone-marl rhythmite in the Neuquén Basin, Argentina: depositional and burial history. In: The Neuquén Basin, Argentina: A Case Study in Sequence Stratigraphy and Basin Dynamics (Eds Veiga, G.D., Spalletti, L.A., Howell, J.A. and Schwarz, E.). Geological Society, London, Special Publications 252, 207-229.

Schlager, W., Riejmer, J.J.G. and Droxler, A. (1994) Highstand shedding of carbonate platforms. Journal of Sedimentary Research 64 (3), 270-281.

Schrag, D. P., Higgins, J. A., Macdonald, F. A. and Johnston, D. T. (2013) Authigenic carbonate and the history of the global carbon cycle. Science 339, 6119, 540-543.

Spalletti, L.A., Franzese, J.R., Matheos, S.D. and Schwarz, E. (2000) Sequence stratigraphy of a tidally dominated carbonate-siliciclastic ramp; the Tithonian-Early Berriasian of the Southern Neuquén Basin, Argentina. Journal of the Geological Society, London, 157, 433-446.

Swart, P.K. (2008) Global synchronous changes in the carbon isotopic composition of carbonate sediments unrelated to changes in the global carbon cycle. Proceedings of the National Academy of Science 105, 13741-13745.

Swart, P. K. and Eberli, G. P. (2005) The nature of the d13C of periplatform sediments: Implications for stratigraphy and the global carbon cycle. Sedimentary Geology 175, 115-130.

Swart, P.K., Burns, S.J. and Leder, J.J. (1991) Fractionation of the stable isotopes of oxygen and carbon in carbon dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique. Chemical Geology 86, 89-96.

Tenaglia, M., Weger, R.J., Eberli, G.P., Rueda Sanchez, L.E., Rodriguez Blanco, L. and Swart, P. (2017) TOC Distribution and Prediction in the Vaca Muerta Formation, Neuquén Basin, Argentina. AAPG Search and Discovery Article 90291. AAPG Annual Convention and Exhibition, Houston, TX.

Uliana, M.A. and Legarreta, L. (1993) Hydrocarbons Habitat in a Triassic-to-Cretaceous Sub-Andean Setting: Neuquén Basin, Argentina. Journal of Petroleum Geology 16 (4), 397–420.

Weger, R.J., Rodriguez Blanco, L., and Eberli, G.P. (2017) A Basinal Reference Section and Lateral Variability of the Vaca Muerta Formation in the Neuquén Basin, Argentina. XX Congreso Geológico Argentino, Tucumán, Argentina. Actas Simposio Geología de la Formación Vaca Muerta, 179-184.

Weissert, H. and Erba, E. (2004) Volcanism, CO2 and palaeoclimate: a Late Jurassic–Early Cretaceous carbon and oxygen isotope record. Journal of the Geological Society, London, 161, 1-8.

Wignall, P.B. and Myers, K.J. (1988) Interpreting benthic oxygen levels in mudrocks: A new approach. Geology 16, 452-455.

Zeller, M. (2013) Facies, Geometries and Sequence Stratigraphy of the Mixed Carbonate-Siliciclastic Quintuco-Vaca Muerta System in the Neuquén Basin, Argentina: An Integrated Approach. University of Miami. Open Access Dissertations. Paper 1099.

Zeller, M., Verwer, K., Eberli, G.P., Massaferro, J.L., Schwarz, E. and Spalletti, L.A. (2015) Depositional controls on mixed carbonate-siliciclastic cycles and sequences on gently inclined shelf profiles. Sedimentology 62, 7, 2009-2037.

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