

PROVENANCE AND DEPOSITIONAL PROCESSES OF EXTRABASINAL (SILICICLASTIC) AND INTRABASINAL (CARBONATE) PARTICLES OF THE TITHONIAN–BERRIASIAN VACA MUERTA–QUINTUCO SYSTEM (NEUQUÉN BASIN, ARGENTINA)

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ABSTRACT

During the Early Jurassic–Early Cretaceous, between 32° and 40° S latitude, a steeply dipping active subduction zone along the western margin of Gondwana led to the development of a magmatic arc and a large back-arc depression known as the Neuquén Basin. A thick record of Tithonian–Berriasian organic rich sediments resulted from back-arc subsidence, expansion of the marine realm and flooding of the basin, which was presumably connected to the proto-Pacific Ocean through gaps in the magmatic arc. Widespread and persistent starved conditions in the basinal areas of the Neuquén Sea allowed the accumulation of a thick record of hybrid siliciclastic–carbonate sediments (“Vaca Muerta facies”), while along the eastern and southeastern cratonic basin margins, inner ramp deposits (“Quintuco facies”) were dominated by biogenic and clastic carbonates with subordinated muds, sands and salt deposits. The “Vaca Muerta Facies” is essentially composed of two (aggradational and progradational) accommodation sets. The aggradational set consists of hundred meters thick and widely distributed organic-rich silty and clayey mudstones with varying proportion of hemipelagic/pelagic siliceous and carbonate contribution, accumulated in the more distal sectors of the marine ramp under anoxic to suboxic conditions. The progradational sets, developed between the inner ramp and the deeper sectors of the basin, extend hundreds of kilometres both along and across the depositional dip, showing sigmoidal or clinoform geometries with well-defined topset, foreset, and bottomset configurations. In comparison with the aggradational sets, these intraplatform clinoforms are enriched in intrabasinal carbonate components and exhibit a reduction in organic matter content denoting a comparative increase in oxygenation of the marine bottom waters. If the productivity of pelagic biogenic carbonates was approximately constant at the basin level, the increase in the proportion of these components in the intraplatform clinoform deposits is attributed to the resuspension and dispersal of biogenic and clastic carbonate particles and grains from the internal ramp deposits (“Quintuco facies”) by cross-shelf oriented barotropic currents. These currents seem to be related either to storms and/or to deflection by the Coriolis Effect (Ekman component) of highly efficient geostrophic contour currents at depths above the pycnocline. In the

“Vaca Muerta facies” the supply of terrigenous siliciclastic particles has been voluminous and persistent, and the main source for these components was most probably the magmatic arc located to the western flank of the Neuquén Basin. Due to the marked stagnation and density stratification of the Neuquén Sea waters, much of the terrigenous fine-grained material was dispersed in the basinal and offshore settings of the basin by suspension plumes mobilised by baroclinic currents that travelled for long distances above the pycnocline.

INTRODUCTION

An epicontinental sea (epeiric sea) is a shallow-water inland sea or within a continental shelf almost surrounded by mainland, floored by continental crust, and usually connected to an ocean by rivers, straits or arms of sea. It is extensive (hundreds to thousands of kilometres), shallow, and with a very gentle slope (less than 1°) (Schieber, 2016). For the distal fine-grained deposits of epicontinental seas, two sedimentary models have been proposed: clear water and muddy water. The clear water model is dominated by (essentially biogenic) carbonate deposits, while the muddy water model is characterised by terrigenous clastic sediments (Feng, 1994, in Wang *et al.*, 2023). However, taken as a whole, the sedimentary record of the deeper settings (below wave-base) within epicontinental seas is far from being purely clear water or muddy water. The most common situation is the development of mixed or hybrid fine-grained sedimentary successions. These deposits can reach hundreds of meters thick and are composed of highly variable proportions of carbonate and siliciclastic components (Wei *et al.*, 2021; Schwarz *et al.*, 2022), depending on environmental factors such as the properties of marine waters, the sediment supply, and the climatic conditions (Tucker, 2003; Coffey and Fred, 2004; Seyedmehdi *et al.* 2016).

During the Tithonian–Berriasián, an epicontinental sea was laid down in the back-arc of the Neuquén Basin (central-western Argentina; Fig. 1A) in which marine ramp deposits accumulated. The more distal sectors of the ramp received the accumulation of pelagic and hemipelagic organic-rich sediments, essentially accumulated under anoxic conditions. The resulting black shale facies comprise the most important unconventional hydrocarbon reservoir in Argentina and the first

economical unconventional self-sourced play outside North America (Minisini *et al.*, 2020). In this paper, we analyse the characteristics and distribution of sediment types in the Tithonian–Berriasián marine ramp of the Neuquén Basin, the primary accumulation processes, the potential areas of terrigenous input, and the main drivers that could have produced the redistribution of fine-grained particles (=components of sedimentary rocks less than 62 µm; Teruggi, 1982) at a basin scale.

GEOLOGICAL SETTING

The Neuquén Basin is located in west central Argentina and eastern Chile between 36° and 40°S (Fig. 1A). The basin fill covers an area greater than 120,000 km² (Yrigoyen, 1991) and is composed of continental and marine siliciclastic deposits, carbonates and evaporites that range in age from Late Triassic to early Cenozoic (Gulisano and Gutiérrez Pleimling, 1995; Vergani *et al.*, 1995). During the Middle Jurassic and the Early Cretaceous, the basin behaved as a back-arc setting. It was limited to the east and south by the cratonic areas of the Sierra Pintada System and the North Patagonian Massif, while to the west it was linked to the magmatic arc generated by the subduction of the proto-Pacific oceanic plate along the active western margin of southern Gondwana (Digregorio *et al.*, 1984; Legarreta and Uliana, 1991) (Fig. 1A). Thermal subsidence and regional extension favoured the development of an epeiric sea connected with the proto-Pacific Ocean through gaps in the arc (Spallètti *et al.*, 2000; Macdonald *et al.*, 2003; Spallètti, 2013), and thick successions, characterised by transgressive-regressive cycles of different scales, were deposited as a result of changes in eustatic sea-level oscillations and subsidence rates (Vergani *et*

al., 1995; Howell *et al.*, 2005; Schwarz *et al.*, 2006, 2016).

The Neuquén Basin has a broadly triangular shape (Fig. 1A) and two main regions are commonly recognized: the Andean Region to the west, and the Neuquén Embayment to the east and southeast (Fig. 1A). In the Andean region a series of N-S-oriented

fold and thrust belts (Aconcagua, Marlargüe and Agrio fold and thrust belts) provide excellent outcrops of the Mesozoic successions (Howell *et al.*, 2005). In contrast, in the Neuquén Embayment most of the Mesozoic sedimentary record is in the subsurface and the beds are relatively undeformed (Howell *et al.*, 2005; Acevedo *et al.*, 2023).

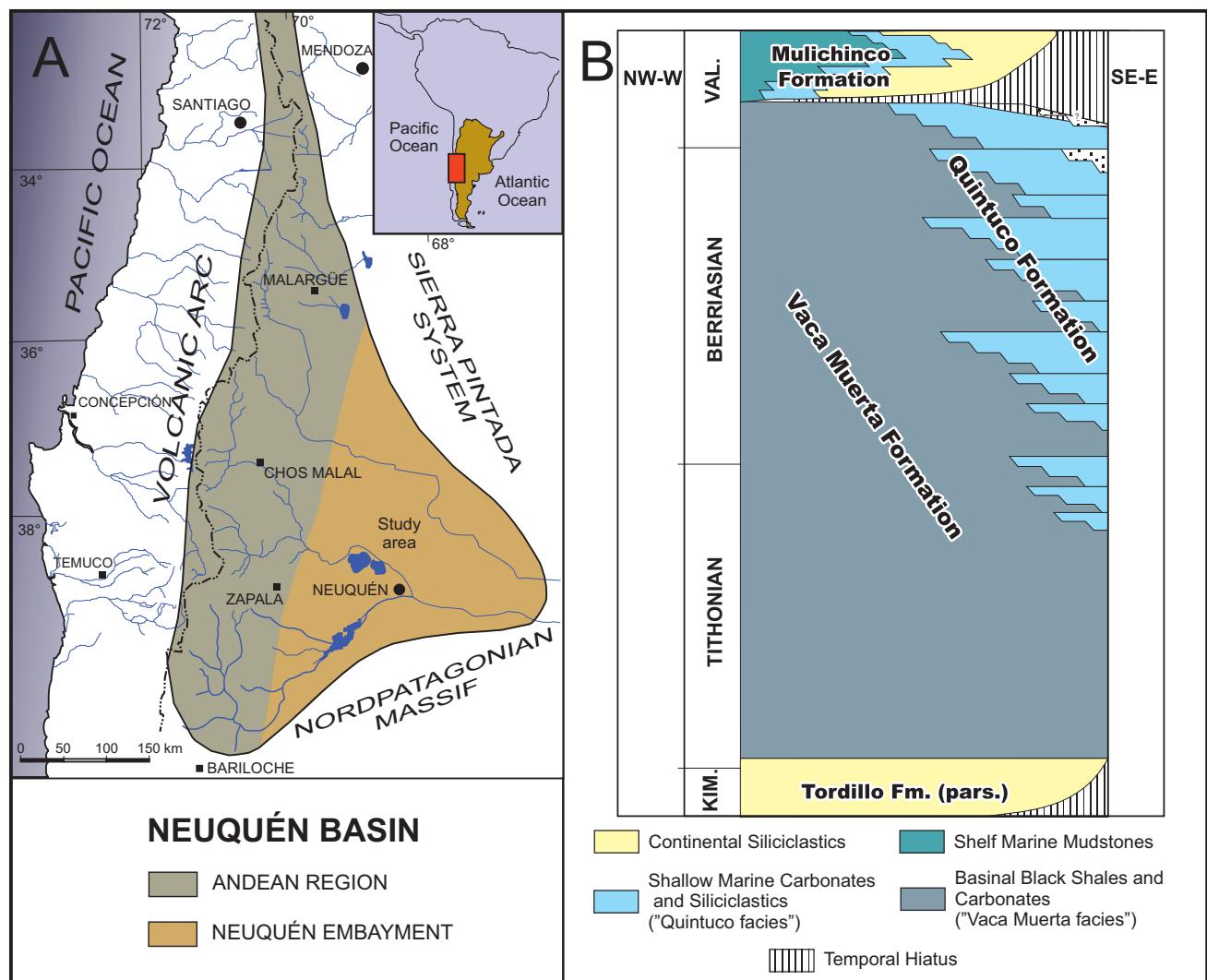


Figure 1. General context for the Neuquén Basin. **a)** Location map of the Neuquén Basin. **b)** Tithonian – Berriasian stratigraphy (Vaca Muerta – Quintuco System).

In the Neuquén Embayment the Upper Jurassic–Lower Cretaceous (Tithonian–Berriasian) sedimentary record is known as the Vaca Muerta–Quintuco mixed siliciclastic–carbonate system (Massaferro *et al.*, 2014). These deposits represent a shoreface to basin setting developed in a ramp-type interior sea. The Vaca Muerta Formation is an

alternating shale–marl succession rich in organic matter, accumulated in the mid-distal ramp and basinal sectors of the depositional system. The Quintuco Formation is essentially composed of shallow marine moderate to high-energy deposits, dominated by bioclastic carbonates (Fig. 1B).

DATASETS AND METHODOLOGY

This study is based on detailed bed-scale sedimentological logging of the Tithonian–Berriasián outcrops located in the central-western sector of the Neuquén Basin (Fig. 2). Detailed lithological descriptions of siliciclastic and carbonate deposits were made on a centimetre scale, and include texture, composition, sedimentary structures, degree of reactivity with acid, geometry of lithosomes, and vertical relationships between successive bedforms. The study was complemented by the results of earlier surveys on sedimentary facies and stratigraphic sequences (Gasparini *et al.*, 1997; Spalletti *et al.*, 1999, 2000, 2008, 2014, 2015, 2019; Zeller *et al.*, 2015b) and the reader is directed to those for additional details concerning methods and results. These data were compared to previous sedimentological surveys on the Upper Jurassic–Lower Cretaceous marine deposits of the Neuquén Basin (Leanza, 1973, 2003; Carozzi *et al.*, 1993; Scasso *et al.*, 2005; Armella *et al.*, 2007; Kietzmann *et al.*, 2008, 2014, 2015; Massaferro *et al.*, 2014; Zeller *et al.*, 2014, 2015a; Krim *et al.*, 2017, 2019; Iñigo *et al.*, 2018; Paz *et al.*, 2019, 2022a, 2022b, 2023; Otharán *et al.*, 2020; Rodríguez Blanco *et al.*, 2020; Capelli *et al.*, 2021).

ACCUMULATION SYSTEMS OF THE NEUQUÉN EPICONTINENTAL SEA DURING THE LATE JURASSIC - EARLY CRETACEOUS: STACKING PATTERNS AND CLINOFORM CONFIGURATION

During Tithonian–Berriasián times, the basinal areas of the epicontinental Neuquén Sea were dominated by widespread starved conditions, from anoxic to suboxic in the marine substrate, which favoured the sedimentation of mixed, siliciclastic–carbonate fine-grained pelagic and hemipelagic components (Spalletti *et al.*, 2019). These deposits are characterised as “Vaca Muerta facies” (Figs. 2 and 3). They have a wide regional distribution in the Neuquén Basin and are the product of restricted vertical circulation of the marine waters, generalized eustatic rise (Legarreta and Uliana, 1991, 1996), and warm water temperature resulting in a high nutrient productivity (Spalletti, 2013). The development of a marked pycnocline (controlled by both halocline and thermocline) and oxycline during the accumulation of the “Vaca Muerta facies” resulted

in stagnation of the deeper marine waters and hypoxia, with minimum levels of oxygenation on the substratum (Spalletti *et al.*, 1999), while surficial and shallow waters remained with a high degree of oxygenation that allowed the proliferation of abundant planktonic and nektonic biota (Gasparini *et al.*, 1997, 2002). These environmental conditions have been associated with global warming processes due to the increase in the level of atmospheric CO₂ and widespread transgressions on a planetary scale (Spalletti *et al.*, 2014).

It is worth noting that, while in the deeper areas of the basin anoxia-suboxia persisted during the entire studied interval with the accumulation of pelagic and hemipelagic fine-grained sediments, an extensive inner marine ramp environment occupied a continuous belt along the eastern and southeastern margins of the basin (Fig. 3). In contrast to the basinal areas, the substrate of the inner ramp was characterised by high levels of oxygenation. The resulting deposits were dominated by skeletal, ooidal, and peloidal carbonate sands together with tidal- and storm-related sands, algal carbonates, and gypsum/anhydrite deposits. These complex associations of shallow, marginal or nearshore marine settings together with sabkha, coastal plain and estuarine environments are known as the Quintuco, Loma Montosa and Picún Leufú formations (Leanza, 1973; Carozzi *et al.*, 1993; Massaferro *et al.*, 2014), and can be simplified as the “Quintuco facies” for the objective of this contribution (Figs. 2 and 3). Moreover, it is important to note that the studied stratigraphic interval does not include the late Berriasián–early Valanginian that clearly marks a change in depositional systems with the development of siliciclastic-dominated deltaic systems attributed to the Quintuco Formation (Olivo *et al.*, 2016). It is therefore possible to deduce that the pycnocline of the marine realm was placed around the depth limit between the nearshore and offshore areas of the basin.

Likewise, the overall stacking of the Tithonian–Berriasián sedimentary record shows a clear trend towards the dominance of the “Vaca Muerta facies” in the basal intervals of the succession (anoxic–suboxic starved basin state due to the Tithonian transgression), as well as a progressive increase in the participation of the “Quintuco facies” as a result of the gradual decrease in accommodation towards the younger sections of the sedimentary succession (Figs. 1 and 2).

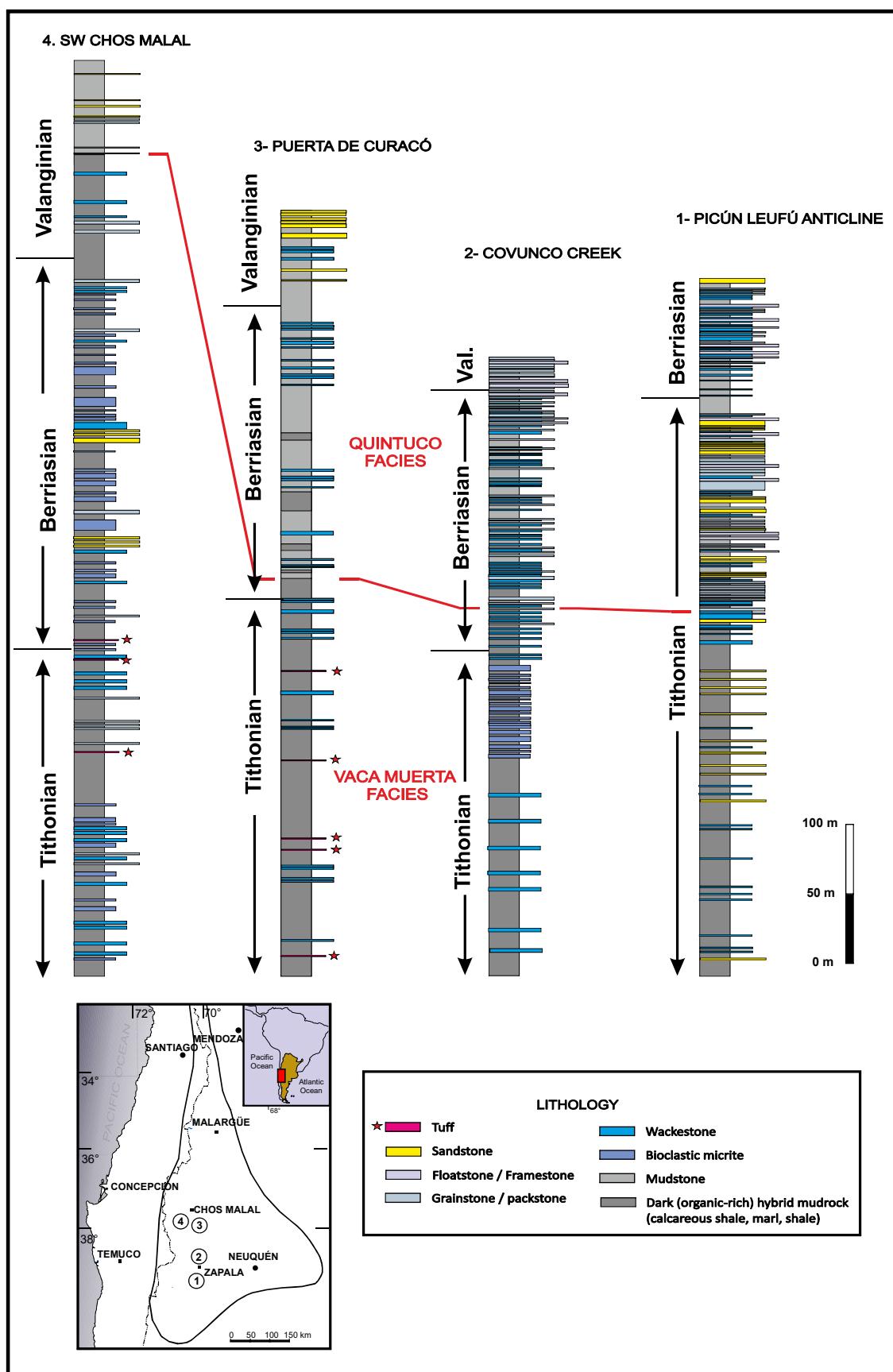


Figure 2. Graphic sedimentary logs of the “Vaca Muerta facies” and “Quintuco facies” exposed at four sections oriented N-S along the Andean Region of the Neuquén Basin.

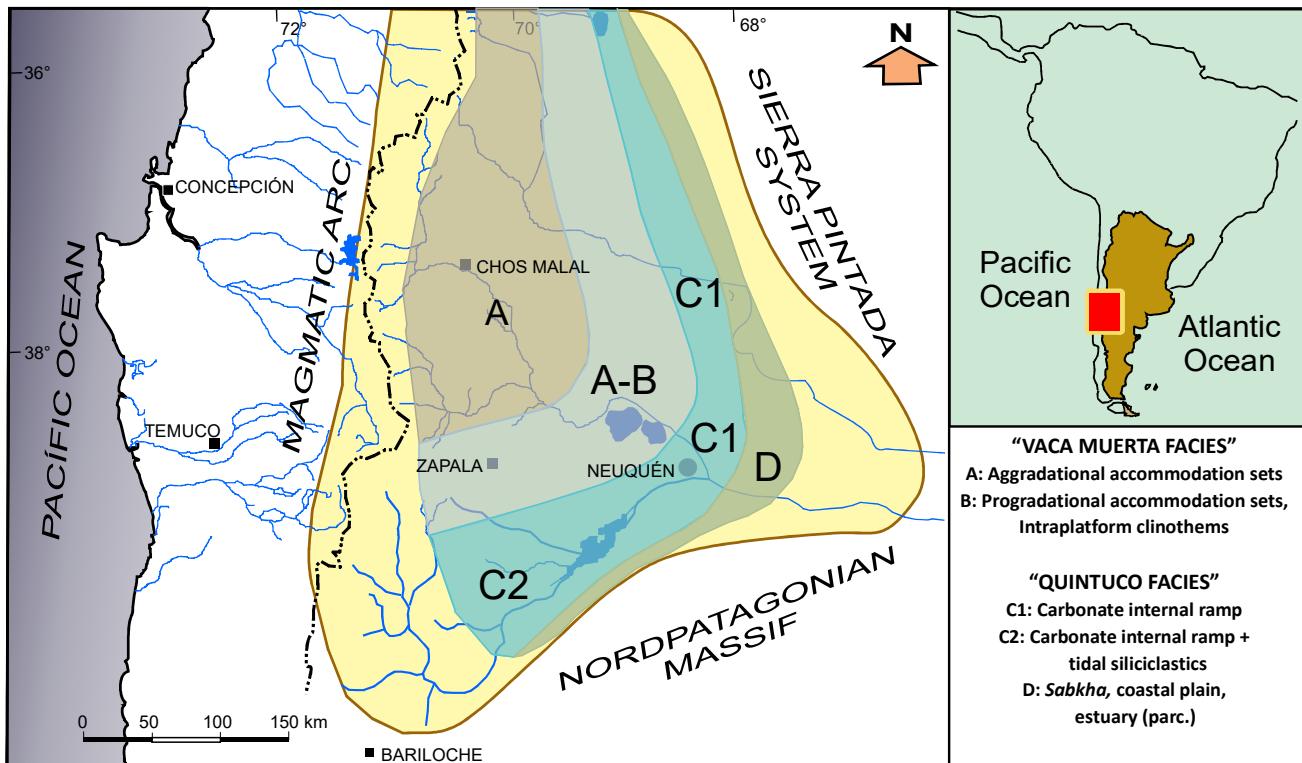


Figure 3. Regional distribution of the “Vaca Muerta facies” and “Quintuco facies”.

In the “Vaca Muerta facies”, Spalletti *et al.* (2019) have differentiated two accumulation models, which they called aggradational and progradational accommodation sets (Figs. 3 and 4). The aggradational accommodation set consists of clastic black shale successions composed of pelagic and hemipelagic deposits that reached a wide regional distribution occupying a large part of the marine basin during the Tithonian–Berriasián time. These aggradational sets are characterised by a typical tabular stacking, with thicknesses of hundreds of metres, and they represent accumulation processes occurring in the most distal sectors of the Neuquén Sea.

The progradational accommodation sets of the “Vaca Muerta facies” were accumulated in the middle sectors of the marine ramp (Spalletti *et al.*, 2019). Their sedimentary sequences show a typical sigmoidal or clinoform geometry (Mitchum and Uliana, 1985; Rodrigues *et al.*, 2009; Spalletti, 2013) with topset, foreset and bottomset configurations (Massaferro *et al.*, 2014; Reijenstein *et al.*, 2014; Zeller *et al.*, 2015a, b; Spalletti *et al.*, 2019) prograding towards the deeper sectors of the marine environment (Fig. 4). According to their location in the offshore settings of the basin, they are defined as intraplatform clinoforms (Hogdson *et al.*, 2017). Due

to their very low slope (0.5 to 1-1.3°; Zeller *et al.*, 2014; Reijenstein *et al.*, 2014), they can be appreciated only when the vertical scale of the stratigraphic and/or seismic sections is greatly exaggerated (Fig. 4).

These progradational accommodation sets are large-scale features, as they reach an extent of hundreds of kilometres and their deposits are on the order of hundreds of metres thick (Fig. 4). These wedges accumulated on top of transgressive deposits of the aggradational accommodation set; they correlate with inner ramp carbonate sediments towards the basin margin, and with aggradational accommodation set deposits accumulated under subpycnoclinal waters towards the deeper sectors of the epicontinental marine ramp (Spalletti *et al.*, 2006, 2019; Zeller *et al.*, 2015a, b; Krim *et al.*, 2017).

SEDIMENTARY DEPOSITS OF THE MIXED VACA MUERTA - QUINTUCO SYSTEM

The most characteristic sediments of the “Quintuco facies” occur along the marginal areas of the basin, particularly located towards the eastern and southern sectors of the Neuquén Embayment (Fig. 3), and from a stratigraphic point of view they are preferentially located above the “Vaca Muerta

A



B

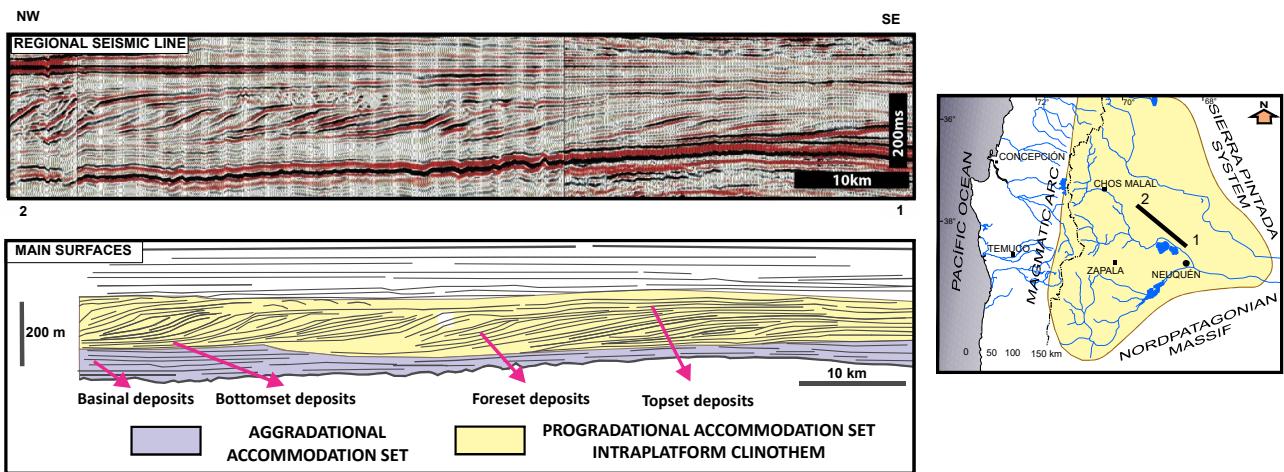


Figure 4. **a)** Regional geoseismic section of the Vaca Muerta–Quintuco System, after Rodrigues *et al.* (2009), modified from Mitchum and Uliana (1985). Check the large differences between vertical and horizontal scales. **b)** Regional seismic line and seismic interpretation from 1 to 2, based and modified from Massaferro *et al.* (2014) and Zeller *et al.* (2015b).

facies" (Figs. 1B and 4). The carbonates essentially consist of biogenic skeletal grains produced and accumulated in the shallow inner areas of the marine ramp. Volumetrically speaking, shell fragments are mainly derived from crinoids, echinoderms, shallow and deep infaunal bivalves, epifaunal bivalves (ostreids), and free-living bivalves (pectinids), gastropods, serpulids, and corals. They are associated with non-skeletal grains, such as peloids, ooids and carbonate mud. The most conspicuous varieties of resulting carbonate rocks are oolitic and bioclastic grainstones, packstones, mudstones, wackestones, paraautoctonous bioclastic rudstones, and float/framestones (Spalletti *et al.*, 2000; Armella *et al.*, 2007; Kietzmann *et al.*, 2008, 2014; Zeller *et al.*, 2015b; Paz *et al.*, 2019; Rodríguez Blanco *et al.*, 2020). Bodies of algal stromatolite bindstones, argillaceous dolostones, and massive and chickenwire anhydrite are also recorded in the region towards the eastern margin of the basin (Carozzi *et al.*, 1993; Iñigo *et al.*, 2018; Schwarz and Veiga, 2019). All these carbonate-dominated deposits are commonly associated with laterally continuous sigmoidal and mounded fine- to

coarse-grained sandstone bodies. Oolitic/bioclastic grainstones and packstones, as well as siliciclastic sandstones, show a great variety of sedimentary structures, particularly planar and trough cross-stratification, planar parallel lamination, hummocky cross-stratification, and herringbone cross-bedding (Spalletti *et al.*, 2000; Zeller *et al.*, 2015b, Schwarz and Veiga, 2019; Acuña Podestá, 2022; among others).

The Tithonian–Berriasian fine-grained sediments of the "Vaca Muerta facies" accumulated in a basinal marine environment are texturally homogeneous silty mudstones to clayey mudstones rich in organic matter and with minimal participation of sand grains, showing marked fissility, tabular geometry, and great areal continuity. Fine-grained ash layers occur interbedded within these deposits. The main accumulation process of the "Vaca Muerta facies" is settling from suspension, resulting in sediments of a mixed or hybrid nature, with varying proportions of siliceous and carbonate components, whereby carbonate-rich mudstones (> 66% carbonate), marls (33%–66%) and siliciclastic-rich mudstones (< 33% carbonate) are recognised (Fig. 5).

Siliceous components can be either hemipelagic, *i.e.* consisting of extrabasinal allotogenous particles (Spalletti *et al.*, 2014, 2015; Krim *et al.*, 2017), or pelagic, resulting from the accumulation of very fine biogenic debris (predominantly radiolarian skeletons). For the carbonates of the “Vaca Muerta facies”, it is essential to consider two main types of provenances, both typically intra-basinal. Pelagic components were supplied by planktonic microfossils, mostly derived from sponges (spicules), foraminifera, ostracods, and nannofossils (halophytic algae, calcispheres and juvenile foraminifera). These pelagic-derived carbonate debris prevailed in the deeper sectors of the Tithonian–Berriasiian ramp and were most likely

deposited by settling from suspension. The second provenance is represented by carbonate debris derived from biogenic nektonic fossils, such as ammonites, and skeletal remains of marine reptiles (ichthyosaurs, plesiosaurs, crocodiles, turtles) and fish. In contrast, the carbonate population of the topset, foreset and bottomset deposits of the progradational accommodation sets includes both the planktonic and nektonic components mentioned above and finely disaggregated grains of intra-basinal carbonates that are the product of erosion, remobilization and resedimentation of previously formed deposits in the shallow inner ramp regions (Krim *et al.*, 2017).

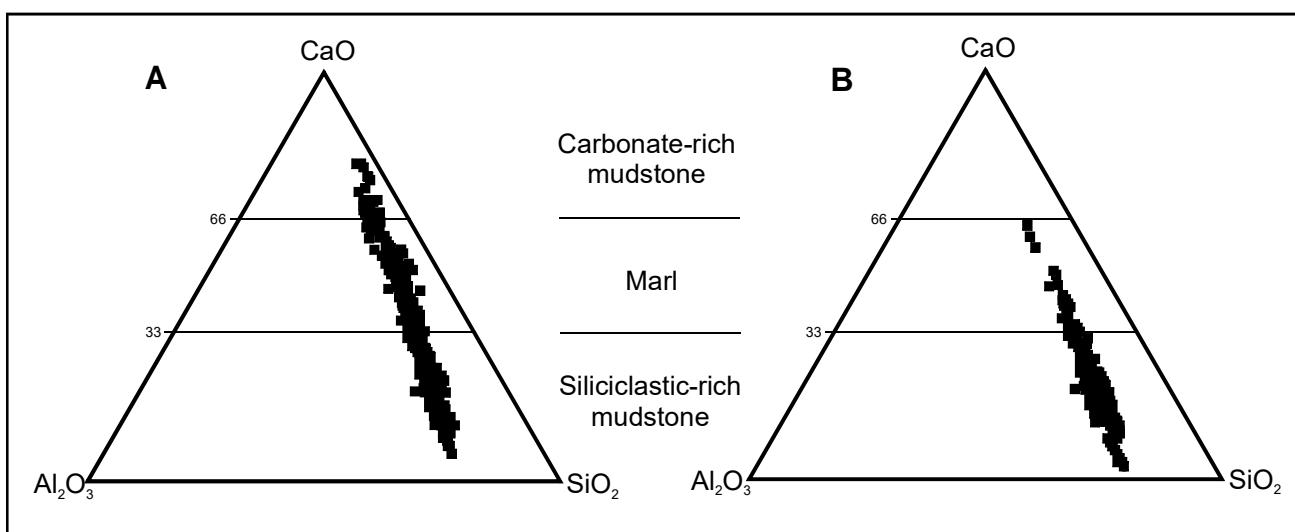


Figure 5. Ternary plots CaO–Al₂O₃–SiO₂ showing compositional differences between fine-grained samples of the “Vaca Muerta facies” (data from Spalletti *et al.*, 2019). **a)** Progradational and **b)** the aggradational accommodation set. Each point represents an individual sample.

The resulting sedimentary successions often have a rhythmic vertical stacking (Fig. 6). Elemental cycles, bundles and superbundles with frequencies in the Milankovitch band (Kietzmann *et al.*, 2015; Kohan Martínez *et al.*, 2018) were attributed to high and low frequency precession and eccentricity periodicities. In the fine-grained deposits of the aggradational accommodation sets, which represent the deepest sectors of the marine basin, the input of fine-grained terrigenous siliciclastic components was voluminous and may well have remained essentially constant. In contrast, the production of pelagic carbonate components showed significant variations related to global climatic changes, which

regulated nutrient supply from the ocean (Kietzmann *et al.*, 2015). In short, there was a clear trend towards differential accumulation in these fine-grained mixed successions, essentially driven by changes in biogenic productivity.

In addition to these deposits, sporadic fine-grained, non-bioturbated, massive strata with mud intraclasts are due to local remobilization and resedimentation of sediments by mudflows caused by underflows or hyperpycnal or frictional currents (cf. Paz *et al.*, 2019; Otharán *et al.*, 2020). These intercalations occur preferentially in progradational accommodation sets where mudflows are favoured by the gentle gradient of the intraplatform clinoforms (Fig. 7).

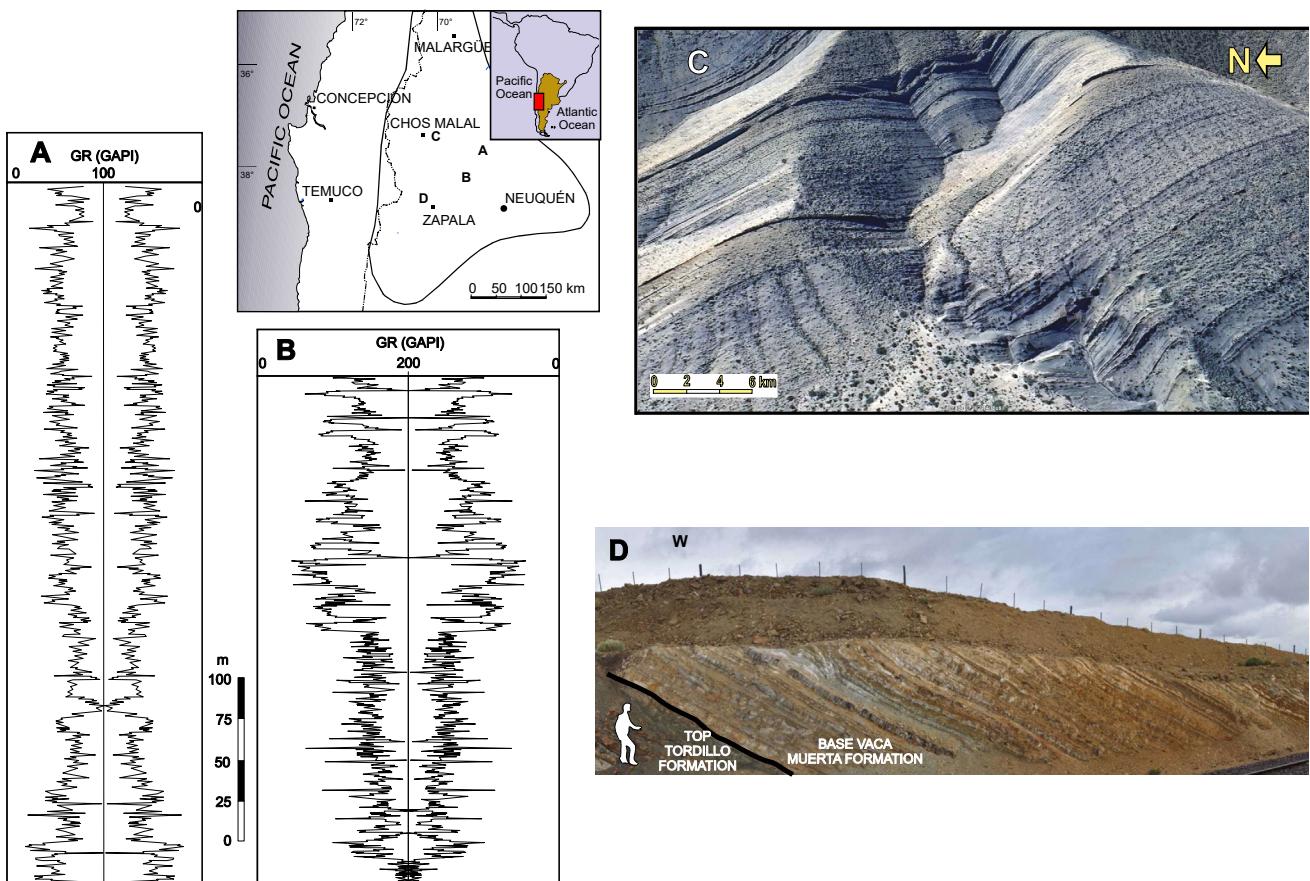


Figure 6. Rhythmic stacking of the Vaca Muerta fine-grained deposits. **a)** Gamma ray log at Aguada San Roque oil field. **b)** Gamma ray log at Aguada Pichana oil field. **c)** Satellite image of the Vaca Muerta outcrops at Puerta de Curacó locality. **d)** Cyclic stacking (bioclastic micrite/marl, marl/mudstone) within the Milankovitch spectrum band in the lowermost section of the Vaca Muerta Formation at Los Catutos (north of Zapala).

In the foresets and bottomsets of the progradational accommodation sets of the “Vaca Muerta facies”, isolated intercalations of thin-bedded sandstones, coarse mudstones and bioclastic mudstones with low-energy tractional structures (parallel, low angle cross-lamination, ripple cross-lamination) and bioturbation, as well as completed bioturbated mudstones, are also identified. Paz *et al.* (2022a, b) have interpreted these deposits as contourites. However, these sporadic deposits mentioned for the substratum of a basin essentially dominated by anoxic conditions and very poor water circulation have a very marked difference in comparison with the thick and very continuous contouritic successions developed on the slopes of continental margins (cf. Shanmugam, 2017, 2021; Stow and Smillie, 2020, and references therein). These latter deposits are formed by the quasi-continuous circulation of depth contour bottom currents driven by Coriolis

forces and temperature/salinity dependent density gradients. These processes are unlikely to occur persistently under restricted vertical circulation of the marine waters as occurred during the Tithonian–Berriasián in the Neuquén Basin (Fig. 7).

TRANSPORT-ACCUMULATION PROCESSES AND ORIGIN OF THE MAIN COMPONENTS OF THE “VACA MUERTA FACIES”

The fine-grained carbonate components

As the “Vaca Muerta facies” moves from the basinal deposits of the aggradational accommodation sets to the progradational accommodation sets of the intraplatform clinoforms (Fig. 4), progressive changes in the sedimentary deposits are recorded. The deeper, basinal and bottomset deposits of the clinoforms have comparatively higher organic-matter

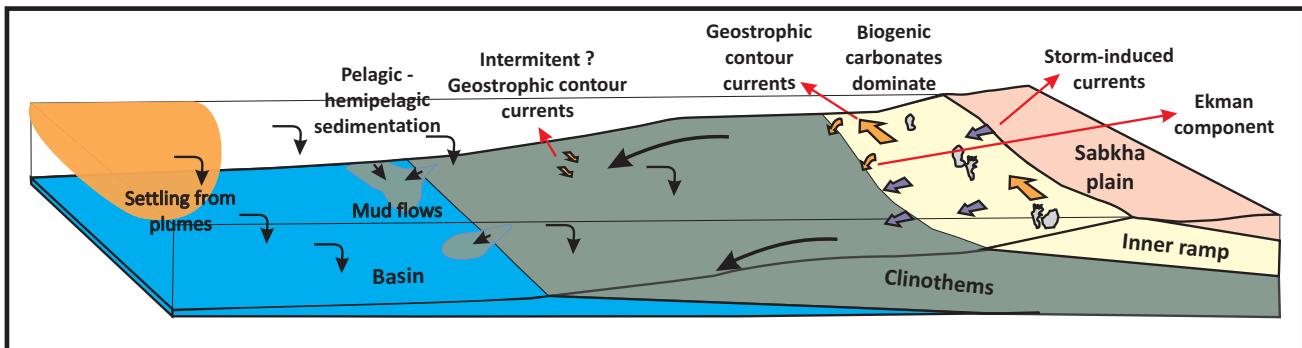


Figure 7. Schematic depositional model for the cratonic margin of the Neuquén Sea during the Tithonian–Berriasián interval.

content reflecting anoxic to suboxic conditions in the substratum. However, the bottomset deposits show a clear trend towards an increase in carbonate components when compared to the basinal deposits. On the other hand, the fine-grained sediments of the foresets and topsets exhibit a reduction in organic-matter content, which denotes a comparative increase in the oxygenation of the bottom waters (Spalletti *et al.*, 2019; Paz *et al.*, 2023), as well as a renewed increment in the proportion of carbonate components reflected by the greater participation of marl, micrite, carbonate mudstones, and bioclastic wackestones as dominant facies. These compositional changes in the sedimentary system are clearly reflected in the diagrams of Fig. 5.

Assuming that the productivity of pelagic biogenic carbonate components is approximately constant at the basin level, the increase in their proportion in the intraplatform clinoform deposits can be attributed to the supply of particles and grains from the shallower sectors of the marine environment, characterised by the high productivity of inner ramp carbonates, typical of the “Quintuco facies”. The remobilization of these components could be attributed to the action of cross-shelf oriented barotropic currents, this is towards the deeper zones of the clinoforms (Figs. 7 and 8). It is assumed that these currents mobilized the carbonate particles essentially by suspension and might have been induced either by geostrophic contour currents or by seaward-oriented, storm-driven relaxation flows (Figs. 7 and 8).

Thermohaline or wind-induced geostrophic currents are considered excellent redistributors of sedimentary load, as they move over distances of hundreds of kilometres essentially parallel to isobathymetric lines (Heezen, 1968; Shanmugam,

2017 and references therein). In the case of the Tithonian–Berriasián record of the Neuquén Basin, as it is currently the case in the Black Sea (Kershaw, 2015), due to the anoxic conditions in the deeper and stagnant marine waters of the basinal regions, these currents could have been highly efficient at depths above the pycnocline, *i.e.* only in the nearshore or inner ramp marine environments where the accumulation of the “Quintuco facies” took place (Figs. 7 and 8). However, the wind-induced geostrophic currents can show important deflections due to the Coriolis Effect (Ekman component), generating an important cross-shelf oriented displacement from shallow to deep areas (Figs. 7 and 8). It is clear then that the Ekman component must be considered as an effective mechanism for offshore-directed transport of the preferentially resuspended carbonate particles from the inner ramp regions to the foreset areas of the intraplatform clinoforms.

On the other hand, it is highly probable that under storm conditions, characterised by intense wind activity, the erosion processes of the “Quintuco facies” were accentuated in the inner ramp due to the increase in wave height accompanied by the circulation of residual tidal currents (Figs. 7 and 8). These storms are also very effective transport/accumulation agents, as their action leads to an intensification of sediment resuspension and dispersal mechanisms, with the expansion and cross-shelf exchange of the plume of suspended particles and the consequent increase of their inputs in the direction of offshore environments (cf. Traykovski *et al.*, 2000; Lentz and Fewings, 2012; Ralston *et al.*, 2013; Wang *et al.*, 2014; Schieber, 2016; Pang *et al.*, 2020).

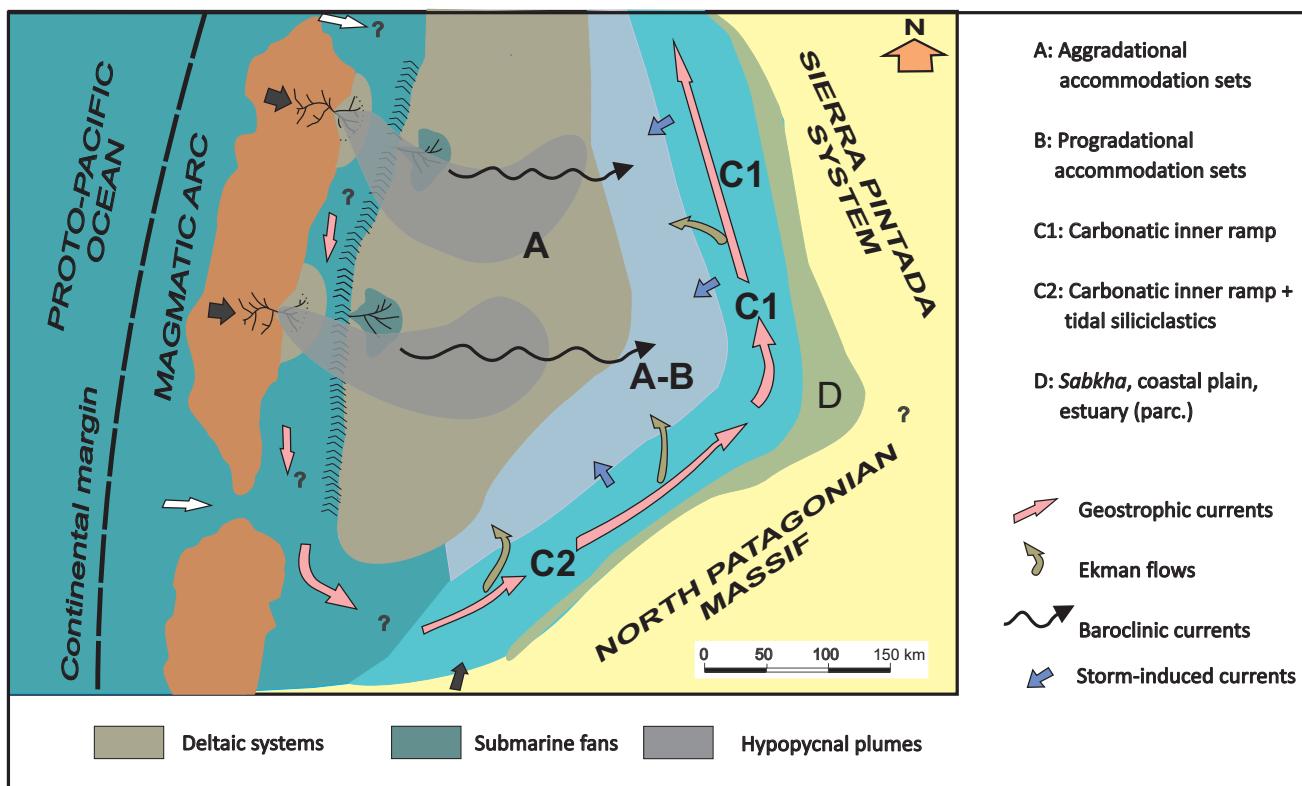


Figure 8. Conceptual model of the main marine current systems responsible for the redistribution and sedimentation of particles towards the outer ramp and basinal sectors of the Neuquén Sea during the Tithonian–Berriasián interval.

The fine-grained siliciclastic components

In the hybrid successions of the “Vaca Muerta facies”, the contribution of siliciclastic particles has been voluminous and persistent, especially in the hundreds of meters thick aggradational accommodation sets (Fig. 4B). Two main questions arise in relation to the origin of the siliciclastic particles; one refers to the source areas and the other to the mechanisms that produced their continuous arrival at the seafloor over ca. 7 my.

Regarding the provenance of siliciclastics, it is important to note that during the Tithonian–early Berriasián along almost the entire eastern and southern margins of the Neuquén Embayment, no sedimentary systems efficient enough to provide considerable volumes of terrigenous components to the marine basin have been identified (Íñigo *et al.*, 2018). Neither extensive and integrated fluvial drainage networks nor well-developed deltaic systems are defined in these coastal regions (Fig. 8). The deficit in the contribution of extrabasinal materials can be explained by the existence of continental areas with low relief and predominantly

dry climatic conditions. Under these circumstances, it could be assumed that terrigenous siliciclastic components could have been contributed by aeolian dust storms such as in present offshore Mauritania (Michel *et al.*, 2011; Klicpera *et al.*, 2015); however, the virtual absence of dune deposits in the marginal areas and the scarce participation of sands along the eastern marine margin of the Neuquén Embayment do not support this alternative.

Towards the southwestern margin of the basin, in the inner ramp facies, shallow marine carbonate deposits and siliciclastic sands/muds accumulated especially by tidal action (Spalletti *et al.*, 2000; Zeller *et al.*, 2015b). These sediments are associated with fluvial, deltaic and estuarine systems at different evolutionary stages of the sedimentary record (Leanza, 1993; Moyano Bohórquez, 2004; Paz *et al.*, 2019). The marginal or transitional record of this system is composed of thin and fine-grained interdistributary bay facies, mouth bars dominated by heterolithic deposits and poorly developed channels suggesting both low efficiency and tidal dominance. Although these systems may have provided a small part of the siliciclastic fine-

grained components that contributed to the offshore/basinal deposits, they cannot be invoked to explain the enormous volume of siliciclastic particles that characterise the Tithonian-Berriasián record of the “Vaca Muerta facies” in the basinal distal most settings of the Neuquén Sea.

At the same time, along the western flank of the basin, a magmatic arc developed in a continuous meridian direction (Fig. 8), roughly parallel to the active continental margin of western Gondwana

(Legarreta and Uliana, 1991; Howell *et al.*, 2005; Spalletti, 2013). This topographic barrier was probably dissected by relatively narrow corridors that connected the Neuquén Sea with the proto-Pacific Ocean (Spalletti *et al.*, 2000; Macdonald *et al.*, 2003; Spalletti, 2013) and contributed to the restricted connection of the Neuquén Basin with the consequent development of oxygen-deficient conditions in the deeper marine waters.

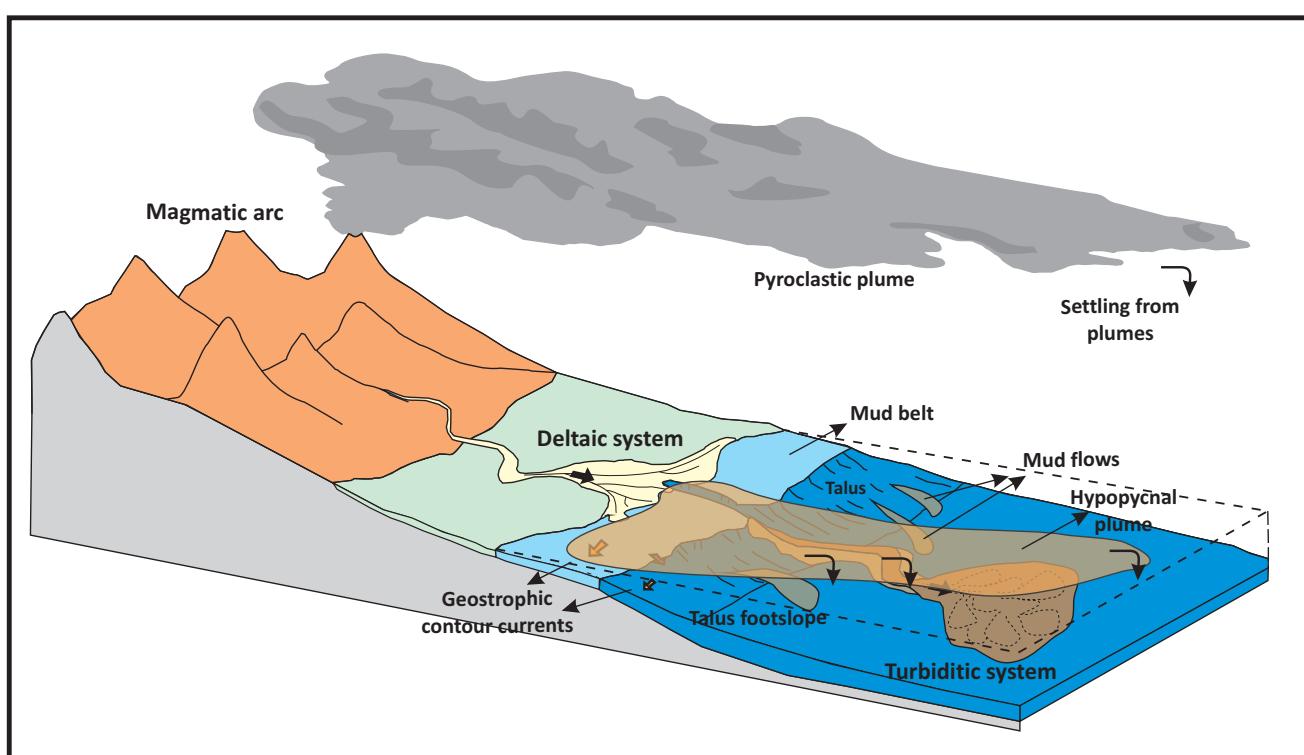


Figure 9. Schematic depositional model for the western (magmatic arc) margin of the Neuquén Sea during the Tithonian–Berriasián interval.

Marine deposits generated by gravitational sediment flows (high- and low-density turbidity currents, large-scale landslides) were identified in the western and deepest sector of the basin (Leanza *et al.*, 2003; Spalletti *et al.*, 2008; Spalletti, 2013). These features suggest the existence of a high-gradient zone on the active western flank of the basin and a seafloor profile with slope break and slope development, as well as the existence of efficient drainage networks in the magmatic arc region (Fig. 9). It is clear then that during the Tithonian–Berriasián there was a very high effectiveness of terrigenous contributions from the west (Fig. 9) where, in addition to the relief associated with the development of the magmatic

arc, there were much wetter climatic conditions compared to the rest of the marginal areas of the Neuquén Basin.

However, the limited basinward extension of the gravity flow deposits suggests that the resulting hyperpycnal flows were not efficient enough to produce the wide distribution of fine-grained sediments throughout the basin interior. This was most likely related to the marked stagnation and density stratification of the Neuquén Sea waters and thus to the development of a persistent pycnocline. The activity of geostrophic bottom currents in subpycnocline waters, suggested by Paz *et al.* (2022a), could not have been effective as it would

have produced a strong alteration of the system erasing the pycnocline and oxygenating the bottom waters. Therefore, it is inferred that much of the fine-grained particles were supplied to the marine basin by hypopycnal suspension plumes (Fig. 9) sourced either from one or multiple river mouths (cf. Vic *et al.*, 2014; Wu *et al.*, 2014; Luo *et al.*, 2017). This siliciclastic supply was probably combined with intermittent pyroclastic plumes and ash falls produced by active volcanism located along the Andean magmatic arc (Fig. 9). Worth to mention, marine hypopycnal plumes have been tracked in the marine environment at distances of hundreds of kilometres from the river mouth (Hopkins *et al.*, 2013; Shanmugam, 2019). Because of their low density they run at shallower depths and/or along the thermo-halocline without affecting the dominant physicochemical conditions in the substrate (Fig. 10). Under these circumstances, we suggest that the dispersal of the fine suspended particles of the plumes may have been driven by baroclinic currents controlled by vertical variations in seawater density, which are usually associated with internal tidal waves propagating along the boundary between waters of different density (the pycnocline, Fig. 10) (cf. Shanmugam, 2013; Wright, 2014). It is worth noting that mudflow deposits located preferentially on the foresets of the Vaca Muerta clinoforms (Fig. 7) would be the result of the baroclinic currents

turnover around the contact between the marine ramp substrate and the pycnocline.

In conclusion, while thermohaline geostrophic currents and/or wind-induced marine currents redistributed the terrigenous fine-grained material in the inner ramp sectors of the basin, in the basinal and offshore settings of the Neuquén Sea, the dispersal of fine suspended sediments could have been produced from suspension plumes mobilised by marine currents that travelled for long distances above the pycnocline (Figs. 8 and 10).

DISCUSSION ON THE DEPOSITIONAL MODEL FOR THE “VACA MUERTA FACIES” IN THE NEUQUÉN SEA

The geographical, tectonic and climatic conditions under which sedimentation of black shales occurred in the Neuquén Basin during the Tithonian–Berriasián were extremely peculiar. The generation of these deposits is ultimately the result of a complex interaction of factors controlled by climate, oceanography, tectonic setting, and basin evolution, among which the circulation and oxygenation levels of marine waters, the existence of warm waters, the organic productivity (nutrient input), the accommodation (input/subsidence ratio), and the superimposition of short-term climatically induced variations on sea-level change stand out.

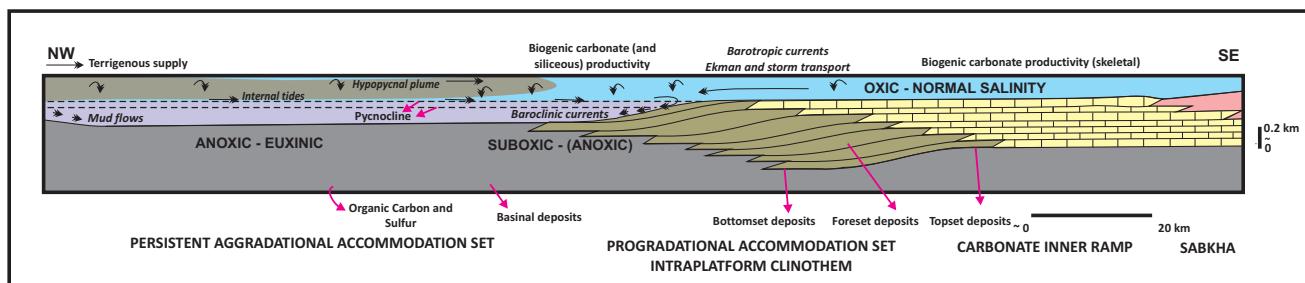


Figure 10. Inner ramp-basinal depositional model reconstructed for the Tithonian–Berriasián interval on the Vaca Muerta–Quintuco System.

The main attributes of the basin during the Tithonian–Berriasián are (1) its generation in an epicontinental sea surrounded to the east and southeast by cratonic areas and to the west by a magmatic arc generated by subduction of the proto-Pacific plate beneath the continental crust of western Gondwana; (2) the persistence of marked

hypoxic conditions over very extensive basinal regions determined by a strong regional, persistent and stable pycnocline reducing vertical mixing of the water column; (3) comparatively shallow depth (100–400 m (Mitchum and Uliana, 1985; Rodríguez Blanco *et al.*, 2022) of the Neuquén Sea, which resulted in a limited volume of the sub-pycnocline

water mass and facilitated benthic oxygen depletion; (4) connection of the Neuquén Sea with the eastern proto-Pacific Ocean, characterised by extreme shallowing of the oxygen-minimum zone, through shallow marine corridors that crossed the region of the active magmatic arc; (5) a long period of high glacio-eustatic highstand; (6) warm, arid to semi-arid climate along the eastern flanks of the basin and somewhat wetter towards the western basin margin represented by the orographic system of the magmatic arc. Although these six attributes were key elements in shaping the overall stratigraphic sequence, the cyclical vertical stacking of the Vaca Muerta fine-grained deposits also suggests productivity variations due to climatic oscillations of different periodicity (Kietzmann *et al.*, 2015), caused by orbital changes that affected the level of solar radiation over the Earth's surface.

The depositional features and the circumstances under which the accumulation of the Tithonian–Berriasián deposits in the Neuquén Basin occurred can only be partially compared to those of modern marine environments exhibiting widespread seafloor anoxia. The epicontinental character of the basin bears some similarities with the Hudson Bay, the Gulf of Carpentaria, the Baltic Sea, and the Black Sea. As in the Neuquén Basin during the Tithonian–Berriasián, the seawater depth in the first three examples is shallow (40 to 120 m; Algeo *et al.*, 2008); however, they differ in that they are located in humid regions and therefore receive important volumes of fluvial waters. On the other hand, the Black Sea shows similar environmental conditions to the Neuquén Basin, since it is located in a steppe continental region (average annual rainfall of 346 mm). However, the depth of the Black Sea is much greater and widespread, as it reaches more than 2,200 m in the central and deepest sector of the basin (cf. Poulos, 2023), while in the Tithonian–Berriasián Neuquén Sea the slopes were steeper only along the western flank of the basin and spent over short distances from uplands (arc) to the axis of the depocenter (Spalletti, 2013).

The sedimentary cycles comprising the “Vaca Muerta facies” in the aggradational sequence sets, essentially composed of fine-grained rocks rich in organic matter but with variable proportions of carbonates and siliciclastic particles, have a great lateral continuity that can be followed for hundreds of kilometres. The regional persistence of these

deposits implies the uniformity of environmental conditions and the synchronism of changes in the properties of the water mass over large distances. These features can only develop under a stable and persistent pycnocline. Vertical mixing must have been significantly reduced and the pycnocline must have been relatively strong to maintain oxygen-deficient conditions in subpycnocline waters over wide areas for long intervals.

While anoxic conditions persisted permanently in the aggradational sequence sets, oxygenation levels varied from anoxic to suboxic in the marine substrate of the progradational sequence sets, precisely because the pycnocline was located at depths where the clinoforms accumulated (Fig. 10). Due to the large regional extent of the clinoforms and their very low gradient, a small variation in the position of the pycnocline led to relatively large changes in oxygenation on the seafloor. If it is assumed that the location of the pycnocline varied according to global climatic changes, it must be concluded that in periods with lower relative insolation (comparatively colder) physicochemical conditions at the sedimentary interface in the topsets and in the shallower part of the foresets changed from anoxic to suboxic, whereas in climatic periods with higher insolation (warmer) the tendency was towards a generalization of anoxia in wide areas of the deepest Neuquén Sea.

CONCLUSIONS

During the Tithonian–Berriasián a thick and widespread succession of organic-rich sediments (“Vaca Muerta facies”) accumulated in the basinal and outer ramp setting of the back-arc Neuquén Basin, which was connected to the proto-Pacific Ocean through gaps in the magmatic arc. The sedimentary record is essentially composed of mixed or hybrid (siliciclastic-carbonate) fine-grained deposits accumulated under anoxic to suboxic conditions as a result of widespread and persistent starved conditions in the basinal areas of the Neuquén Sea. Aggradational and progradational accommodation sets are recognized in the “Vaca Muerta facies”. The aggradational set accumulated in the more distal (basinal) areas of the marine setting and is composed of a thick and widely distributed succession of organic-rich silty and clayey mudstones with varying proportions of

hemipelagic (siliciclastic) and pelagic (essentially carbonates) components. The progradational sets, characterised by clinoform geometries with topset, foreset and bottomset configurations, extend hundreds of kilometres both along and across the depositional dip, and are located between the inner ramp and the deeper sectors of the basin. Carbonate contents increase as one moves from the more distal deposits of the aggradational accommodation sets to the shallower deposits of the progradational accommodation sets. The increase in the proportion of these components in the clinoform deposits is attributed to resuspension and dispersal of particles and grains from the carbonate-rich inner ramp deposits ("Quintuco facies") by currents oriented cross-shelf, and related either to storms and/or to deflection by the Coriolis Effect (Ekman component) of highly efficient geostrophic contour currents flowing at depths above the pycnocline. In the "Vaca Muerta facies" the supply of terrigenous siliciclastic particles has been voluminous and persistent over 7 my, and the main source for these components was most likely the magmatic arc located to the western flank of the Neuquén Basin. Due to the marked stagnation and density stratification of the Neuquén Sea waters, much of the terrigenous fine-grained particles were probably dispersed in the basinal and offshore settings of the basin by suspension plumes mobilised by baroclinic currents that travelled for long distances above the pycnocline.

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