

Palaeosalinity variations in the Early Cretaceous of the Neuquén Basin, Argentina: Evidence from oxygen isotopes and palaeoecological analysis

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Abstract

The Neuquén Basin is a stratigraphically- and economically-important Early Cretaceous depocentre located in west-central Argentina. The Early Valanginian to Early Barremian succession (upper Vaca Muerta, Mulichinco and Agrio Formations) contains a rich fossil record, with abundant bivalves and ammonoids. Palaeosalinities are determined systematically throughout the succession, based on an oxygen isotope analysis of unaltered oyster shells from two localities in Neuquén province. A total of 188 oyster samples from 52 stratigraphic levels were processed. A total of 52 mean values of $\delta^{18}\text{O}$ isotope are used to calculate palaeosalinities, assuming an estimated water temperature of 25 °C. The observed range of palaeosalinities, between the maximum and the minimum, is 19, which is in conflict with published accounts of this being a fully marine succession. The isotopic data are combined with independent faunal evidence to evaluate palaeosalinity variation both laterally and temporally. Significant fluctuations in water salinity are indicated, with a clear tendency to increase from brachyhaline to euhaline and near hyperhaline conditions through time. The fluctuations were probably due to dilution from normal marine water, caused primarily by variations in rainfall and continental runoff. In addition, the presence of a volcanic island arc along the western margin of the basin may have at least partially isolated the basin from the marine waters of the Pacific Ocean. Also, a gulf-shaped basin may have inhibited hydrodynamic exchange with the ocean while enhancing retention of continental waters.

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1. Introduction

The Neuquén Basin is a stratigraphically- and economically-very important Mesozoic to Late Tertiary depocentre located in

west-central Argentina (32°–40° S) primarily within Mendoza and Neuquén provinces (Fig. 1A). From Late Triassic to Late Tertiary times more than 7000 m of sedimentary, volcanoclastic and volcanic facies accumulated. During the Early Cretaceous the Neuquén Basin formed a large marine embayment connected to the Pacific Ocean, in which a variety of siliciclastic, carbonate and evaporitic facies accumulated. The embayment covered an area of over 120 000 km², had a triangular shape, its depositional surface was of low gradient and the depositional environment shallow (Howell et al., 2005). It had a magmatic arc along

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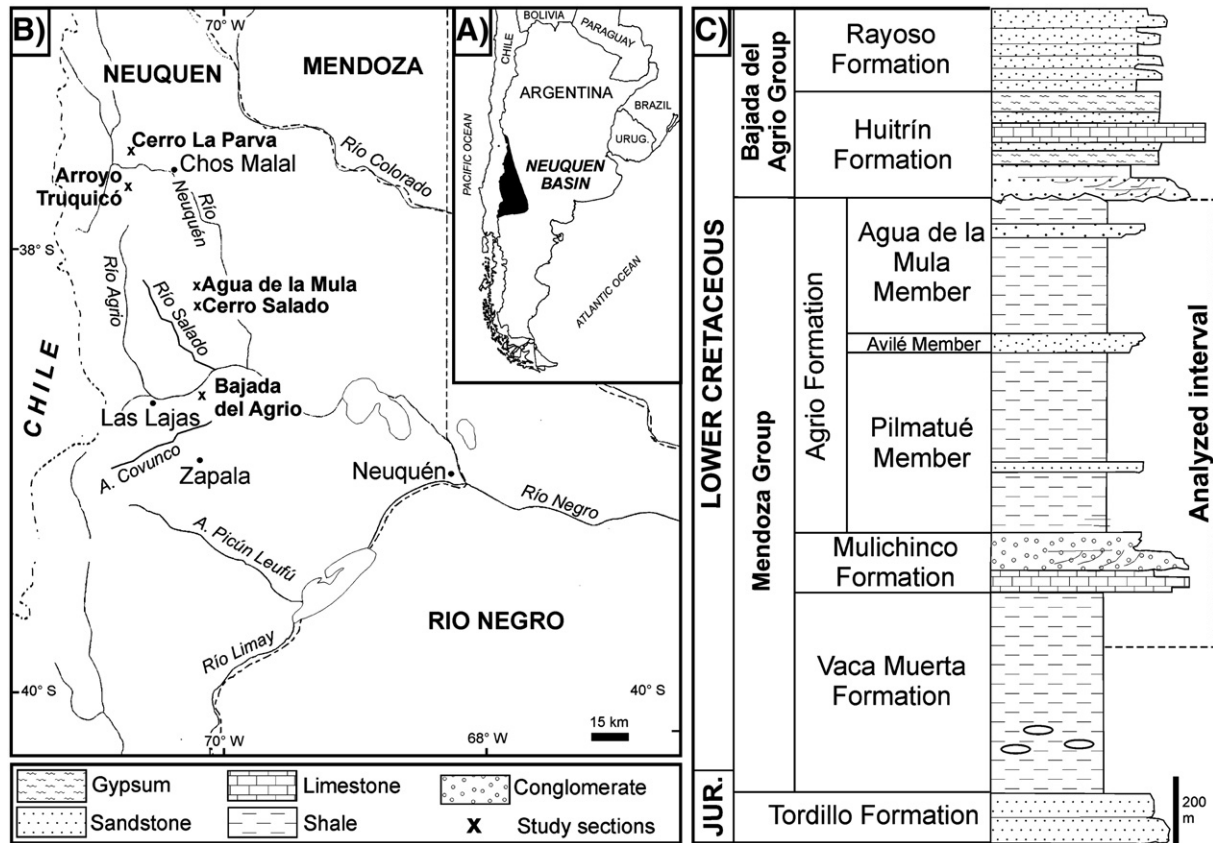


Fig. 1. Study area and units in Neuquén Province, Argentina. A, Location of the Neuquén Basin in west-central Argentina. B, Map of Neuquén showing the location of study localities. C, Subdivisions of the Mendoza Group with indication of the analyzed interval.

its western margin due to the onset of an active subduction zone since the Early Jurassic (Ramos, 1999). This arc probably restricted the entrance of oceanic waters from the west, especially during times of relative sea-level fall. Siliciclastic input was principally from the southeast and the waters deepened towards the north and west (Legarreta and Gulisano, 1989).

The Neuquén Basin contains one of the most remarkable fossil records of Early Cretaceous age in the world (Howell et al., 2005). Several detailed palaeontological works on the benthic faunas over the last six years have given new insights into the occurrence and composition of its benthic assemblages (see Lazo, 2004 and references therein). These assemblages are generally characterized by a highly diverse composition with up to 16 bivalve taxa combined with ammonoids, nautiloids, corals, and serpulids. In the past these assemblages were regarded as having lived in fully marine conditions, following the interpretation of the regional sedimentary facies (Weaver, 1931; Legarreta and Gulisano, 1989). However, the vertical and lateral variations of the assemblages have never been taken into account. Recent studies have suggested that these assemblages are highly variable in composition, taphonomy, and stratigraphy and it has been suggested that some of them may indicate deviations from normal marine salinity (Lazo, 2006, 2007). In particular the occurrence of monospecific mass aggrega-

tions of oysters and serpulids in the Mulichinco and Agrio Formations is very distinctive at outcrop: the first assemblages thought to reflect deviation from normal marine salinity (Lazo, 2004). However, this interpretation has never been tested properly by independent analysis (e.g. oxygen isotopes), the first results of which have just been obtained for the succession studied here (Aguirre-Urreta et al., in press). Other useful palaeoecological criteria to determine salinity, also considered here, have been reviewed by Fürsich (1994), but gregariousness in oysters and serpulids has not been fully exploited.

The aims of this work are: (1) to determine systematically palaeosalinities throughout a Lower Valanginian to Lower Barremian succession based on a detailed oxygen isotopic analysis of unaltered oyster shells from two localities in Neuquén province; (2) to compare the isotopic data with independent faunal evidence for palaeosalinity variation; and (3) to discuss possible causes and consequences of palaeosalinity variations in the basin.

It is important to note that fluctuations in salinity in the fossil record should be evaluated on both temporal and geographical scales because salinity may change periodically and also along a proximal–distal transect, as in recent bay or estuarine environments. Time-resolution of the macrobenthic assemblages studied here was estimated using the duration of an ammonoid zone (see below), while geographical changes

were evaluated only on the basis of distribution and thickness of the shell beds.

2. Stratigraphy

The succession studied embraces (from base to top) the highest Vaca Muerta, Mulichinco and Agrio Formations (Fig. 1C). These form part of the Mendoza Supersequence, which encompasses the Tithonian–Early Barremian interval (Legarreta and Gulisano, 1989). This supersequence was deposited during the last connection of the basin to the Pacific Ocean.

The area of study is located in central–north Neuquén. Data from different localities in this area have been gathered, from north to south, from Cerro La Parva, Arroyo Truquicó, Agua de la Mula, Cerro Salado and Bajada del Agrio (Fig. 1B). In Agua de la Mula, Salado Sur and Bajada del Agrio complete sections of the Agrio Formation crop out. In contrast, at Cerro La Parva and Arroyo Truquicó only the top of the Vaca Muerta Formation, the whole Mulichinco Formation and the lowest beds of the Agrio Formation are well exposed.

The Vaca Muerta Formation is a monotonous succession of finely stratified black and dark grey shales and lithographic lime-mudstones, 200–1700 m thick. It overlies the Tordillo Formation (Kimmeridgian) and is covered by the Quintuco or Mulichinco Formations. The Vaca Muerta Formation is interpreted as a restricted inner basin succession deposited under low benthic oxygen levels during the Tithonian–Early Valanginian (Legarreta and Gulisano, 1989). The Mulichinco Formation, deposited during the Valanginian, comprises a variety of environments ranging from gravel-rich fluvial braidplains to outer-shelf marine settings, reaching 400 m in maximum thickness (Schwarz and Howell, 2005). It is overlain by the Agrio Formation and the boundary is diachronous, becoming younger southward.

The Agrio Formation crops out extensively from Mendoza to Neuquén with important variations in thickness, lithology, and fossil content. Over much of the outcrop it can be divided into three members, reaching a combined thickness of up to 1600 m. The Pilmatué (lower) and Agua de la Mula (upper) members represent a mixed clastic-carbonate succession, comprising shales, sandstones, and limestones. They are interpreted as storm influenced shoreface to offshore deposits (Spalletti et al., 2001). The middle, or Avilé, Member is a continental unit of 180 m of maximum thickness, including fluvial, shallow lacustrine, playa-lake, and aeolian facies that accumulated discontinuously during a major regression in the mid Hauterivian (Rossi, 2001). The Agrio Formation is overlain by the Huitrín Formation. Except for the Avilé Member, the depositional environments are generally regarded as completely marine, based on the contained faunas.

Macrofossils in the upper (Valanginian) part of the Vaca Muerta and Mulichinco Formations are mainly ammonoids and bivalves, including oysters. The Agrio Formation has

an abundant and varied macrofauna, first described in detail by Weaver (1931). It is composed of bivalves, gastropods, nautiloids, ammonoids, corals, crustaceans, echinoderms, bryozoans, and serpulids, diverse trace fossils, and scarce vertebrate remains (ichthyosaurs, plesiosaurs and pycnodontid fishes).

In the study area the Early Valanginian to Early Barremian interval has been divided into 15 ammonoid zones/subzones by Aguirre-Urreta et al. (2005). This zonation can be followed from one locality to another and has allowed biostratigraphic dating of the oyster samples and macrobenthic assemblages. A composite section between Cerro La Parva and Agua de la Mula has been created in order to comprise the whole interval (Appendix A). The maximum and minimum values of palaeosalinity based on oxygen isotopes were calculated for each zone and subzone (see below). In each zone/subzone the main fossil assemblage is described and interpreted, and when possible an inference about palaeosalinity is made. The faunal approach is contrasted and complemented with the isotopic technique.

3. Materials and methods

3.1. Materials

The sampled oysters belong to the genera *Aetostreon* Bayle and *Amphidonte* (*Ceratostreon*) Bayle of the Family Gryphaeidae (see Malchus, 1990). *Aetostreon* forms a group of very inequivalved, very thick-shelled oysters whose adults were mainly soft bottom recliners that reached a large size (Rubilar and Lazo, 2003). Adult shells have a maximum height of 22 cm (Fig. 2, A–C). Specimens of *Aetostreon* occur sporadically through the succession. These oysters peak in abundance in the *Olcostephanus atherstoni* and *Neocomites* sp. Subzones and the *Crioceratites diamantensis* Zone. *Amphidonte* (*Ceratostreon*) includes a group of small oysters with inequivalved valves and chomata (Fig. 2D; Rubilar and Lazo, 2003). Adult shells reach a maximum height of 9 cm. These oysters are comma-shaped and have a large attachment area and conspicuous radial ribs. They usually encrust molluscs, corals, serpulids and carbonate concretions. They are recorded throughout the three studied units in all zones, being one of the most common bivalves in the succession. They formed occasional mass aggregations immersed in mud especially within the *Olcostephanus* (*O.*) *atherstoni* and *Olcostephanus* (*O.*) *laticosta* Subzones (see below).

Oyster samples were collected from 52 stratigraphic levels; 4 in the Vaca Muerta Formation, 2 in the Mulichinco Formation, and 46 in the Agrio Formation (sampled levels in Appendix A). Oysters, and thus samples, are unevenly distributed throughout the sequence, but were recovered from a variety of lithologies, most commonly from shell beds. Such beds range from loosely-packed pavements to shell-packed composite coquinas of tens of metres of maximum thickness. Most of the specimens were not in life position, especially the free-lying epifaunal *Aetostreon*.

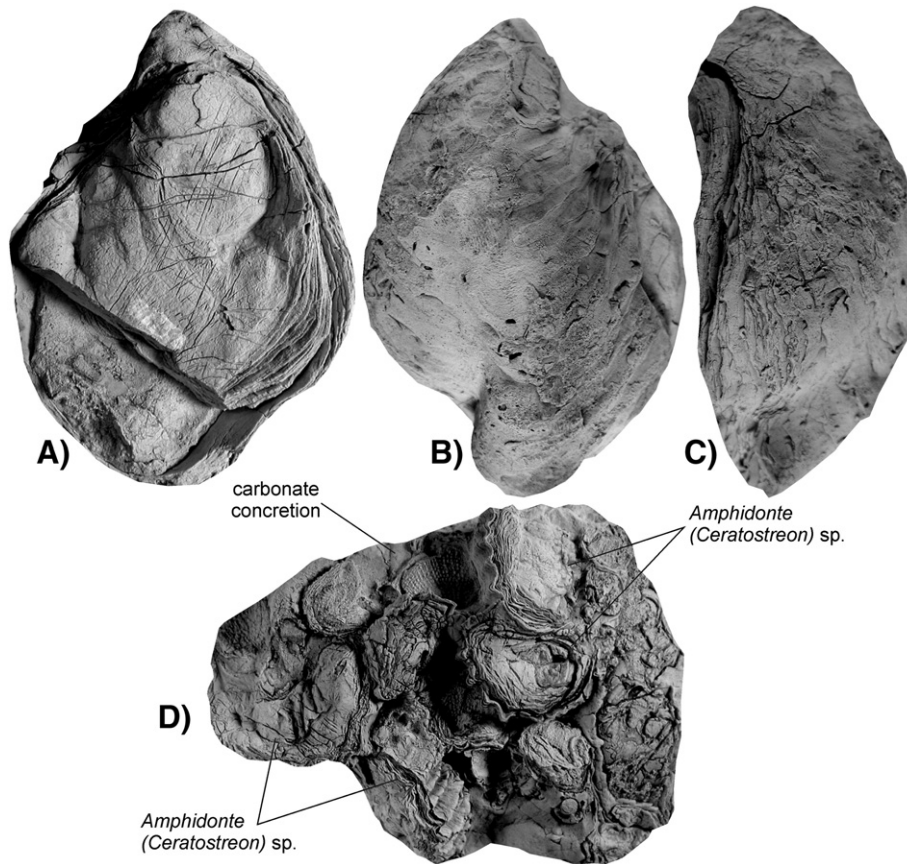


Fig. 2. Sampled oysters for the isotopic analysis. A–C, *Aetostreon* sp. CPBA 19769 in right lateral, left lateral, and anterior views; D, *Amphidonte* (*Cerastreon*) sp. CPBA 19968.1 various specimens in life position cemented to a carbonate concretion. All $\times 1$, from the Pilmatué Member of the Agrio Formation. Figures A–C from the *Neocomites* sp. Subzone, Late Valanginian, Cerro Salado; D from the *Hoplitocrioceras gentilii* Zone, Early Hauterivian, Agua de la Mula.

However, some *Amphidonte* (*C.*) were recorded in life position cemented to isolated hard substrates such as ammonoids and corals. Oysters showed minimal or minor external taphonomic alteration and thus suggest an autochthonous to slightly parautochthonous origin. Only adult left (i.e. thicker) valves were sampled, and one piece about 2 cm long was taken from each specimen. Sampling avoided obvious highly transported specimens or material from highly condensed shell beds. Thus each sampled oyster represents a low time-averaged association of much less than 0.5 My which is the estimated duration of an ammonoid zone/subzone in the studied succession. This magnitude of time-averaging is acceptable for the Mesozoic marine fossil record, corresponding to within-habitat time-averaged assemblages, and provides a good source for palaeoecological information (see Kidwell and Bosence, 1991).

Standard thin sections of sampled oysters were examined by petrographic methods and cathodoluminescence (CL). Luminescence signatures are caused by trace elements and provide clues to the diagenetic history of the carbonate under study. Chemically pure calcite normally shows blue CL, whilst Mn^{2+} is the primary activator and produces yellow-red emission. The presence of large amounts of Mn in carbonate

can be taken as an indicator of diagenetic alteration (e.g. Veizer, 1983; Marshall, 1992). The CL analysis described herein was performed using a Cambridge Image Technology cathodoluminescence CLMK4. Diagenetic alteration was not obvious by standard petrographic inspection. Under CL, most of the oysters were dully luminescent, whilst some growth bands adjacent to the shell margin, infilled microfractures, and the cement and material infilling borings were brightly luminescent (see Fig. 3 in Aguirre-Urreta et al., in press).

3.2. Microsampling and isotopic procedure

In order to obtain sufficient shell carbonate for isotopic analysis (in this case, 1 mg for each sample) without contamination from diagenetically-altered areas of the oyster, each sampled 2 cm-fragment of oyster shell was broken up with a vibrating microdrill. The external growth increments (shown by their chalky nature and by CL to be sometimes diagenetically-altered) of the shell margins were discarded. By drilling at the side of the broken shell, individual growth increments could be broken away and isolated. These growth increments were an average of 0.5 mm thick and up to 1 cm in diameter. Each growth

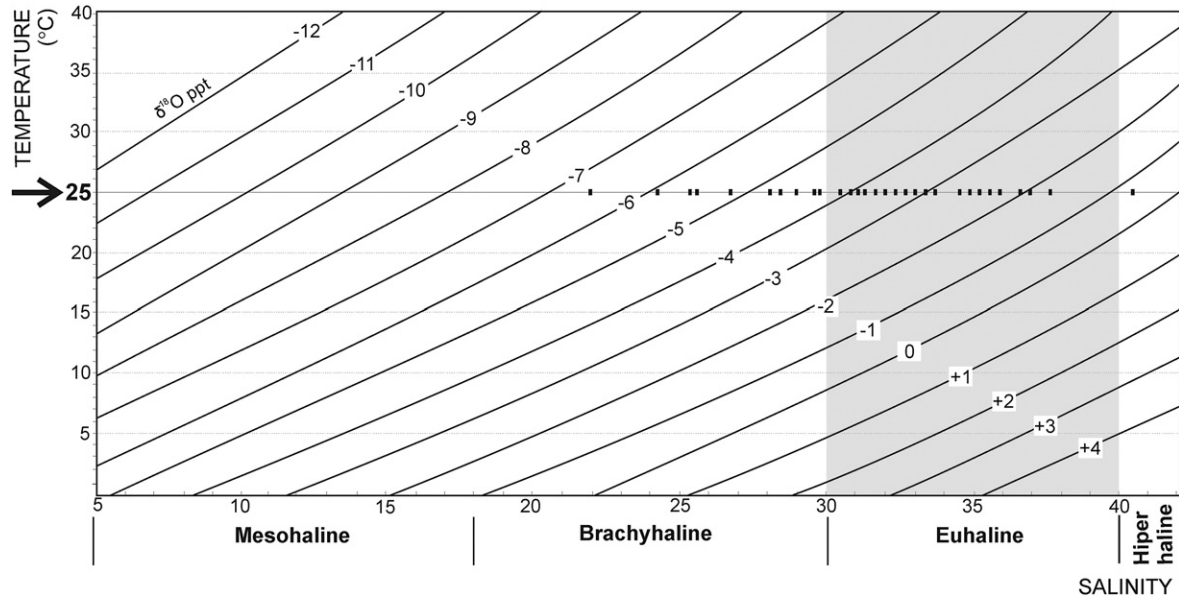


Fig. 3. Isopleths and plots of mean values of $\delta^{18}\text{O}$ at 25 °C to obtain 52 palaeosalinity ranges. Data from Appendix B.

increment was washed in de-ionised water in an ultrasonic bath for 5 min. The core of each growth increment was then drilled with a microdrill, avoiding fracture edges, hinge or growth tip areas. Each drilled powder was analysed separately, such that if some diagenetically-altered material dominated a sample, the aberrant result could be isolated. Each oyster had between 3 and 6 subsamples taken by this means, depending on the total shell thickness and number of growth increments. The 52 sampled 2 cm-fragments were thus subsampled providing a total of 188 oyster analyses. Thus, for many sampled levels there is more than one isotope measurement and mean and standard deviations were calculated for each one (see Appendix B). Standard deviations were generally low (mostly <1) and indicate that reproducibility of measurements are acceptable. ‘Vital effects’ (the secretion of carbonate by an organism not in isotopic equilibrium with the water within which it grew) and seasonal variations between growth increments, can also modify the $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ record. Importantly, the oxygen isotope composition of modern oyster shells is reported to be in close equilibrium with ambient water (e.g. Surge et al., 2001). As more than one, and often three or four growth increments were sampled for each oyster, we effectively time-averaged any seasonal record in the growth increments. A more detailed study of each growth increment could resolve the range of isotope values observed for each oyster into seasonal fluctuation: the range of results obtained from each layer sampled and from each oyster specimen suggests that such variations may be present, although the overall trend (see below) remains consistent. By analysing each layer of shell separately, we avoided mixing material from primary and secondary layers. The data are all plotted together on the isotope curve, and thus some of the spread in results may be due to both seasonal variation, and to different layers in the shell being analysed. The long-term trend is

however still consistent, showing that the range of these micro-variations is less than the long-term (geological) variation.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for oysters presented in this study were obtained using a GV Instruments Carbonate Acid Injector and GVI 2003 Mass Spectrometer, housed in the School of Planning, Architecture and Civil Engineering, Queen’s University, Belfast. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values obtained were calibrated against the internationally accepted International Atomic Energy Association carbonate standard NBS-19. Analytical reproducibility of the measurements is ± 0.2 per mil based upon replicate analyses. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data are reported in the conventional delta notation with respect to V-PDB.

3.3. Palaeosalinity determination by ammonoid zone/subzone

Calcite palaeotemperatures were calculated using the equation of Epstein et al. (1953) modified by Anderson and Arthur (1983) which was based primarily on molluscan data:

$$T(^{\circ}\text{C}) = 16.0 - 4.14(\delta c - \delta w) + 0.13(\delta c - \delta w)^2$$

where δc equals the oxygen isotopic composition of the calcite with respect to the V-PDB international standard and δw equates to the oxygen isotopic composition of the water from which the calcite was precipitated with respect to the SMOW standard. On inspection of the absolute oxygen isotope values derived from the oysters, it is apparent that temperature alone cannot account for the observed values. The oxygen isotope values are quite negative; the minimum mean value is -6.6‰ in level 11 in the *Lissonia riveroi* Zone of the Vaca Muerta Formation at Cerro La Parva (Appendix B).

Table 1
Synthesis of palaeosalinities derived from isotopic analysis and palaeoecological evidence from macrobenthic assemblages

	Ammonite zone/subzone	Age	Section	Unit	Type of water at 25 °C	Macrobenthic assemblages
15	<i>Paraspticerias groeberi</i>	Early Barremian		Agua de la Mula Mb, Agrio Fm	Euhaline to hyperhaline	Coral patch-reefs indicate salinities between 25‰ and 35‰
14	<i>Crioceratites diamantensis</i>	Late Hauterivian			Brachyhaline to euhaline	Macrobenthic elements point to euhaline waters
13	<i>Crioceratites schlagintweiti</i>				Euhaline	Macrobenthic elements point to euhaline waters
12	<i>Spitidiscus riccardii</i>	Early Hauterivian	Agua de la Mula	Pilmatué Mb, Agrio Fm	Euhaline	Small-sized benthic mollusk fauna associated with black shales would indicate poorly oxygenated seafloor rather than fluctuations in water salinity
11	<i>Weavericeras vacaensis</i>				Brachyhaline to euhaline	Macrobenthic elements point to euhaline waters
10	<i>Hoplitocrioceras gentilii</i>				Euhaline	Macrobenthic elements point to euhaline waters
9	<i>Olcostephanus (O.) laticosta</i>				Euhaline	Thick mass aggregations of small-sized oysters may indicate brackish waters
8	<i>Holcoptychites agrioensis</i>				Euhaline	Macrobenthic elements point to euhaline waters
7	<i>Holcoptychites neuquensis</i>				Brachyhaline to euhaline	Pavements dominated by small-sized <i>Modiolus</i> may indicate a deviation of normal marine salinity
6	<i>Neocomites sp.</i>				Late Valanginian	Euhaline
5	<i>Chacantuceras ornatum</i>	Early Valanginian	Cerro La Parva	Mulichinco Fm	Brachyhaline	Sparse benthic fauna with no indications of salinity
4	<i>Pseudofavrella angulatiformis</i>				Brachyhaline	Sparse benthic fauna with no indications of salinity
3	<i>Karakaschiceras attenuatus</i>				Brachyhaline	Lingulid brachiopods and gregarious oysters may indicate brackish waters
2	<i>Olcostephanus (O.) atherstoni</i>				Brachyhaline to euhaline	Thick mass aggregation of small-sized oysters may indicate brackish waters
1	<i>Lissonia riveroi</i>				Brachyhaline	Sparse benthic fauna with no indications of salinity, except thin shell bed with dispersed coral colonies of small size

Palaeosalinities from Appendix B; ammonoid zonation and ages from Aguirre-Urreta et al. (2005); classification of water follows Fürsich (1994).

Assuming an ice-free Ocean (i.e., a δ_{seawater} value of -1.0‰) and using the Anderson and Arthur (1983) equation, results in the most negative $\delta^{18}\text{O}$ values providing temperatures a little in excess of 45 °C , values clearly too high for the region, even during the Cretaceous greenhouse. Although small polar ice-sheets may have existed at times during the Cretaceous (Price, 1999) they were likely to have been of such a magnitude not to have imparted an imprint upon δ_{seawater} . Therefore if a reasonable temperature range is assumed then the isotopic composition of the waters from within which the organism grew can be estimated.

The temperature range of the Neuquén embayment may have been between about 15 °C and 25 °C , based upon independent General Circulation Modelling (e.g., Valdes

et al., 1996), but a temperature of 25 °C was selected to calculate palaeosalinities as it is best supported by records of coral assemblages, coral patch-reef facies, oolitic carbonates, and thick-shelled bivalves in the Agrio Formation (see Lazo et al., 2005). An estimated temperature was used instead of a temperature range to highlight palaeosalinity changes. Also records of evaporites, including halite, in the Avilé Member of the Agrio Formation suggest evaporation of water under an arid or semiarid warm climate during the deposition of at least part the Agrio Formation (see discussion).

Inferences regarding salinity can be derived using the salinity–temperature model of Railsback et al. (1989). The model assumes that the $\delta^{18}\text{O}$ of calcite precipitated in

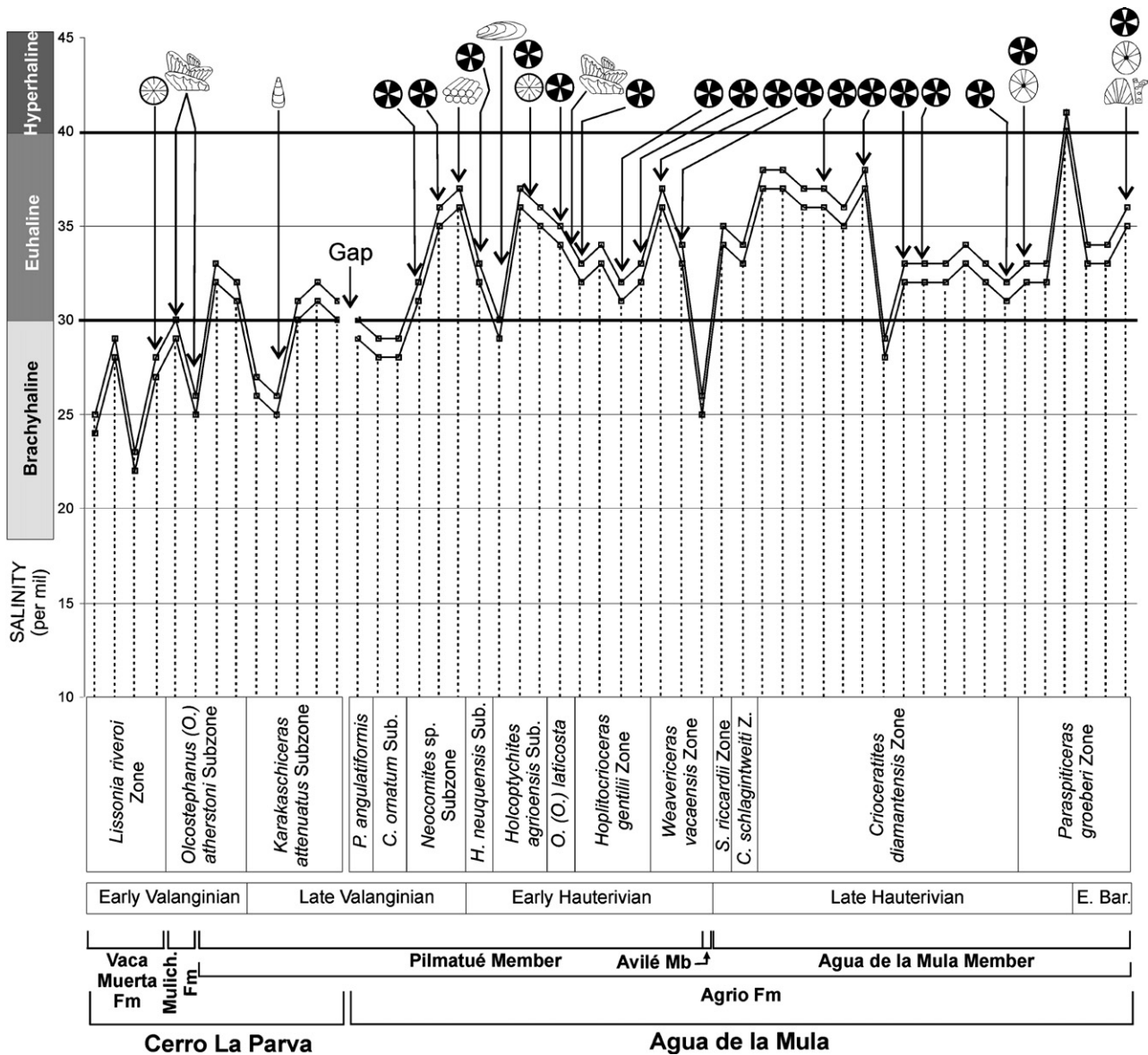


Fig. 4. Curve of palaeosalinity calculated from oxygen isotopes at 25 °C and distribution of macrobenthic assemblages. Key in Appendix A; data from Appendix B; ammonoid zonation and ages from Aguirre-Urreta et al. (2005).

equilibrium with seawater is determined by a combination of seawater temperature and $\delta^{18}\text{O}_{\text{seawater}}$, which can be related to salinity. It is also assumed that the Earth was ice-free with a $\delta^{18}\text{O}_{\text{seawater}}$ composition of -1‰ and mean salinity of mean seawater of 34. The values used for salinity and oxygen isotopic composition are those calculated by Shackleton and Kennett (1975). Each isopleth indicates the possible combination of temperature, calculated using the equation of Anderson and Arthur (1983), and salinity that correspond between calcite of a given isotopic composition and seawater (Fig. 3). Palaeosalinities were calculated by plotting the mean $\delta^{18}\text{O}$ values ($n=52$) on Fig. 3 using an estimated temperature of 25°C (see Appendix B). Then fifteen salinity ranges were obtained using maximum and minimum palaeosalinities of each of 15 ammonoid zone/subzones (Appendix B, Table 1). A

similar approach has also been used by Fassell and Bralower (1999) and Price and Mutterlose (2004).

4. Interpretation of the palaeosalinity curve

The observed range of palaeosalinities, between the maximum and the minimum, is 19, which is very surprising for a supposed fully marine sequence (Fig. 4). It is important to note that despite the absolute values of palaeosalinity, which are dependent on the estimated temperature discussed before, the observed range of 19 is significant enough to strongly suggest that deviations from normal marine salinity occurred throughout the studied Early Cretaceous sequence.

It is apparent from Fig. 4 that from Early Valanginian to Early Barremian times there were significant fluctuations in

water salinity in the Neuquén Basin with a clear tendency to increase from brachyhaline to euhaline and roughly hyperhaline conditions through time. During most of the Valanginian, from the *Lissonia riveroi* Zone to the middle of the *Neocomites* sp. Subzone, brachyhaline waters probably prevailed, although we have a sample gap corresponding to the *Olcostephanus (Viluceras) permolestus* Subzone. The minimum palaeosalinity record occurs near the top of the Vaca Muerta Formation. The likely predominance of brachyhaline waters during the deposition of the top beds of the Vaca Muerta Formation, the Mulichinco Formation and lowest beds of the Agrio Formation is related to a relative sea-level fall in the Early Valanginian *L. riveroi* Zone proposed by Gulisano et al. (1984). This drop in sea-level of more than 100 m was induced partially by tectonic inversion within the basin (Vergani et al., 1995). During the fall the coastline shifted about 100 km towards the north. In many localities basinal black shales (top of Vaca Muerta Fm) were replaced by a number of continental, marginal marine and shallow marine environments deposited over a second-order sequence boundary corresponding to the Mulichinco lowstand wedge or sequence set defined in Schwarz and Howell (2005).

In particular at Cerro La Parva black shales were replaced by storm- and wave-dominated marine deposits interpreted as a lowstand systems tract (LST) in the uppermost *L. riveroi* Zone to the middle part of the *Olcostephanus (O.) atherstoni* Subzone (Schwarz and Howell, 2005). This significant relative fall is coincident with a decrease in palaeosalinity of 5 reaching the lowest value of the study samples in level 11 in the Vaca Muerta Formation. The succeeding transgressive systems tract (TST) is composed of carbonate cycles, including large mass aggregation of oysters, interpreted as a low-energy ramp setting subjected to very low clastic input. The TST corresponds to the upper *O. (O.) atherstoni* Subzone and lower *Karakaschicerias attenuatus* Subzone. Here the rate of relative sea-level rise increased rapidly and steadily, but palaeosalinity changed more slowly. It shows a general increasing tendency, but with two minima in levels 31 and 38 in the Mulichinco Formation within the *O. (O.) atherstoni* Subzone. The highstand systems tract has the same facies as the TST, but with an aggradational and progradational stacking pattern and a limited sediment supply (Schwarz and Howell, 2005). The HST spans from the *K. attenuatus* Subzone to the lowest *O. (V.) permolestus* Subzone. Palaeosalinity above level 38 tend to increase, but again there are fluctuations and not a steady increment.

From the *Chacantuceras ornatum* Subzone onwards palaeosalinity increases and stays generally below 30, in a quasi permanent euhaline condition, but reaching a maximum in a roughly hyperhaline environment in the Late Hauterivian–Early Barremian *Paraspiticeras groeberi* Zone. During most of the deposition of the Agrio Formation the palaeosalinity fluctuated within the euhaline zone with significant minimums at the base of the *Holcoptychites agrioensis* Subzone, towards the top of the *Weavericeras vacaensis* Zone and in the middle of the *Crioceratites*

diamantensis Zone. The minimum in palaeosalinity near the top of the *W. vacaensis* Zone could be related to the succeeding deposition of the Avilé Member which has been interpreted as a lowstand systems tract deposit. A decrease in palaeosalinity of 8 is recorded just before the strong erosion promoted by the sea-level fall and consequent exposure of the Agrio shelf. The rest of the fluctuations are probably related to minor changes in the relative sea-level during periods of highstand base-level.

5. Description and palaeoecological interpretation of macrobenthic assemblages

In this palaeoecological analysis three sections have been measured: Agua de la Mula, Cerro Salado and Bajada del Agrio. Previous detailed stratigraphic and taphonomic studies at these localities indicate that the macrobenthic assemblages are autochthonous or slightly parautochthonous with no evidence of significant lateral transport, and have a maximum degree of time-averaging of approximately 0.5 My (Lazo, 2006). Thus short-term (<0.5 My) fluctuations are not considered here as they are time-averaged to some extent. The degree of time-averaging was estimated by the maximum duration of an ammonoid zone/subzone for the Early Cretaceous. Condensation of individual ammonoid zones has not been recorded in the study localities.

A number of macrobenthic assemblages, which are described below, have been identified in the field. Some of them are proposed as palaeosalinity indicators and are compared to palaeosalinity values derived from the isotopic data.

5.1. Mass aggregations of oysters

Oysters and serpulids may switch from a solitary mode of life to a gregarious habit under the influence of fluctuations in water chemistry, even though successful establishment and development of an oyster or serpulid reef depends on a combination of geological, physical, chemical, and biological factors (see Ten Hove and van den Hurk, 1993; Livingston et al., 2000).

The lowermost beds of the Pilmatué Member of the Agrio formation are represented by the *Olcostephanus (O.) atherstoni* Subzone (2 in Table 1) in Cerro La Parva. In this subzone there is a mass aggregation of oysters of approximately 13 m of maximum thickness and more than 100 m of lateral extension embedded in shales (levels 30–31 in Appendix A). It comprises oysters of the subgenus *Amphidonte (Ceratostrongylus)*. These oysters are small-sized and they occur cemented to each other forming monospecific masses that are very similar to Recent oyster reefs. Schwarz and Howell (2005) have also recorded these mass aggregations in the same locality. They pointed out that they were built on a low-energy ramp system subjected to sediment starvation and stressed marine conditions during a transgressive systems tract.

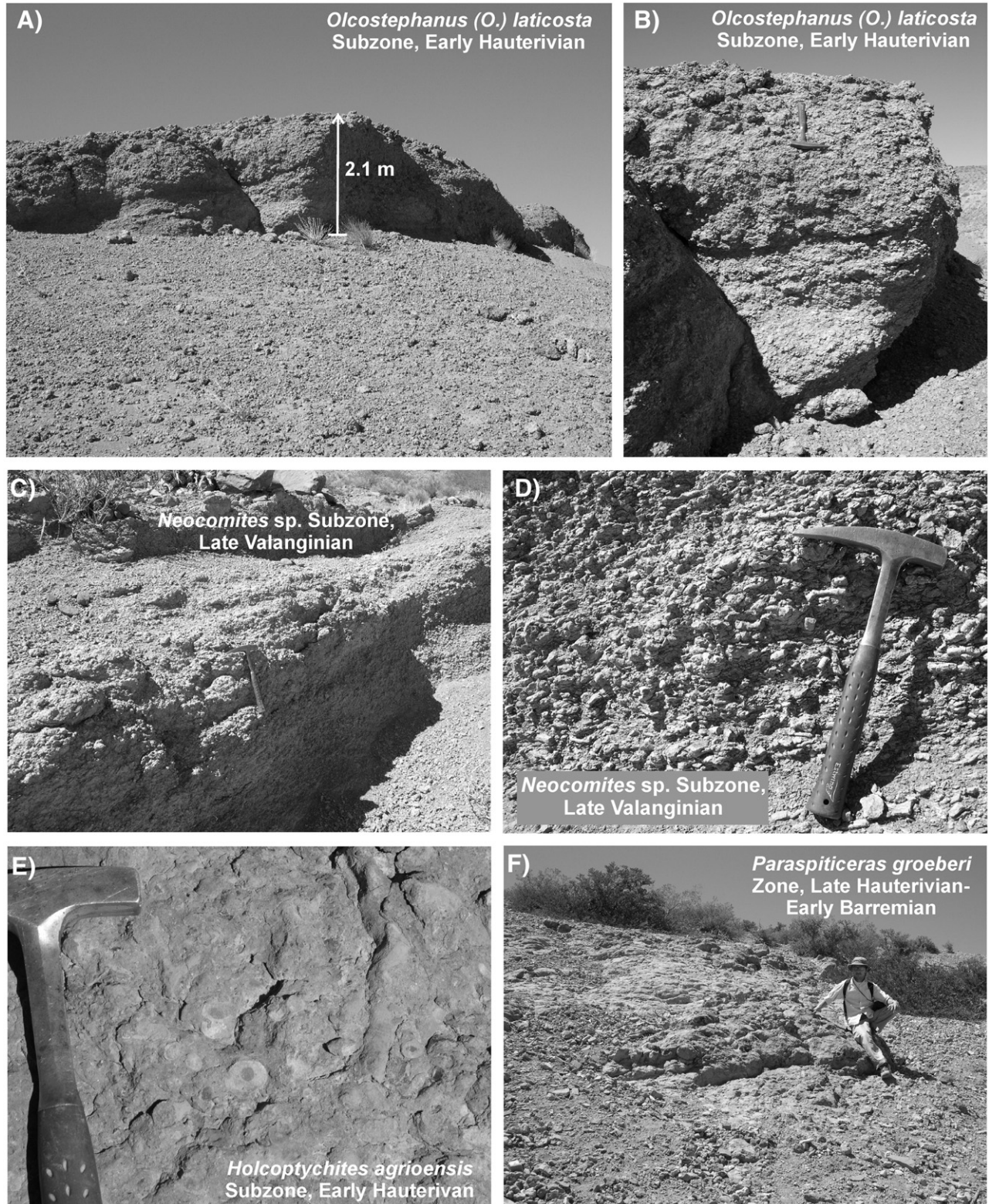


Fig. 5. Field pictures of studied macrobenthic assemblages. A, B, Mass aggregation of the oyster *Amphidonte* (*Ceratostreon*) sp. immersed in shales; 2.1 m thick and approximately 30 m of lateral extension; *Olcostephanus* (*O.*) *laticosta* Subzone, Early Hauterivian, Bajada del Agrio; note the composite nature of the mass aggregation. C, D, Mass aggregation of the serpulid *Parsimonia antiquata* (Sowerby); around 2 m in thickness, *Neocomites* sp. Subzone, Late Valanginian, Bajada del Agrio. E, Coral assemblage composed of ramose and global colonies belonging to *Columastrea antiqua* (Gerth) and *Placocoenia neuquensis* Gerth; colonies may reach 20 cm in height; *Holcoptychites agrioensis* Subzone, Early Hauterivian, Bajada del Agrio. F, Coral patch-reef facies recorded near the top of the Agua de la Mula Member of the Agrio Formation; bioherms may reach 1 m in height; *Paraspiticerus groeberi* Zone, Late Hauterivian–Early Barremian, Agua de la Mula. Hammer is approximately 30 cm long.

Recent examples of mass aggregations of oysters occur in muddy bottoms in bays of lower salinities in the Gulf of Mexico, and in the North Sea in places where salinities stay below 34 because of the slightly brackish Western European coastal current (Hedgpeth, 1954; Stenzel, 1971). The range of salinity calculated for levels 30–31 is brachyhaline, which is highly concordant with ranges of salinities of existing bays in the Gulf of Mexico (Texas and Florida) where oyster reefs currently develop (Table 1; Ladd et al., 1957; Livingston et al., 2000; Surge et al., 2001).

In the *Olcostephanus (O.) laticosta* Subzone (9 in Table 1) in Agua de la Mula there is also a record of mass aggregation of the same oysters, although in this locality they are poorly expressed as the masses are only about 5 cm thick (above level 63 in Appendix A). The thickest aggregations of oysters in this subzone occur in Cerro Salado and Bajada del Agrio, where they may reach 2.1 m in maximum thickness and approximately 30 m in lateral extension (Fig. 5, A–B). Only one oyster sample was analyzed in this subzone and the result suggests euhaline conditions. Although this sample does not reach the values of the *O. atherstoni* Subzone, this salinity may have been enough to enhance small patches of aggregated oysters. There was probably a salinity gradient between Agua de la Mula and Bajada del Agrio, because in the latter the mass aggregations reached a maximum expression in thickness and lateral extension. Cerro Salado and Bajada del Agrio are located nearer to the continental runoff area that is located towards the southeast of Neuquén. This position within the basin may have enhanced also wider ranges of salinity than in Agua de la Mula.

5.2. *Lingulid brachiopods*

The *Karakaschiceras attenuatus* Subzone (3 in Table 1) is characterized by an alternation of shell beds and shale levels (see Appendix A). The composition of shell beds may be variable, although bivalves and macrurous decapods are dominant. Most notable is a shell bed dominated by a small lingulid brachiopod that may indicate a non-marine salinity at Arroyo Truquicó. Brachiopods are extremely rare in the Agrio Formation, especially in Neuquén. Recent lingulid brachiopods live in brackish to intertidal environments suggesting a notable tolerance of changes in salinity. The lingulids recorded in the *K. attenuatus* Subzone have not been studied properly yet, so their systematic and palaeoecological affinities are still unknown. However, it is likely that they tolerated comparable changes in salinity to their modern counterparts. In addition, small-sized oysters presumably in a gregarious habit are also recorded, forming shell beds of approximately 1.5 m thickness. These gregarious oysters may also indicate brackish waters. The range of salinity calculated from $\delta^{18}\text{O}$ data is brachyhaline to euhaline, which is compatible with the range of salinities of Recent oyster reefs.

5.3. *Mass aggregations of serpulids*

In the *Neocomites* sp. Subzone (6 in Table 1) mono-specific mass aggregations of serpulids occur in shales (level 30 in Appendix A; Fig. 5, C–D). The serpulids belong to *Parsimonia antiquata* (Sowerby), a well-known species recorded in the Early Cretaceous of Europe. These aggregations are lenses that reach 2 m of maximum thickness near Bajada del Agrio. They present a dense shell-packing of cementing serpulids in a fine-grained matrix. Serpulid tubes are encrusted by small-sized oysters. Recent mass aggregations of serpulids occur in stressed aquatic settings as for example lagoons, bays, and fiords. They can acquire a gregarious life habit under a range of salinities, from brachyhaline to hyperhaline waters (Ten Hove and van den Hurk, 1993). The range of salinity calculated in level 30 is euhaline (Table 1). This range overlaps partially with the range of salinities of recent mass aggregations of *Serpula vermicularis* Linnaeus located in Ardbear Lough (Ireland) where they live in salinities of 25–34 (Bosence, 1979).

5.4. *Monospecific pavements of Modiolus*

In the *Holcoptychites neuquensis* Subzone (7 in Table 1) there are a number of monospecific pavements of the bivalve *Modiolus* Lamarck that are immersed in shales (above level 33 in Appendix A). Their shells are very thin and small. They occur articulated and with low degrees of encrustation by small oysters. Recent *Modiolus* has an endobysate life habit in intertidal to subtidal environments in brachyhaline to euhaline waters (Stickney and Stringer, 1957; Stanley, 1970). The predominance of a small-sized benthic bivalve with thin shell may suggest a deviation from normal marine salinity, but a lowered oxygen level or a combination of both factors cannot be discarded (see Lazo, 2004). The range of salinity calculated in this subzone is euhaline which is concordant with the inferences made from Recent *Modiolus*.

5.5. *Coral assemblages and coral patch-reef facies*

Towards the top of the *Lissonia riveroi* Zone there is a thin shell bed dominated by bivalves, but also with dispersed coral colonies (level 28 in Appendix A). These colonies are ramose and small-sized (<2 cm in diameter). Both the small size and low abundance point to a very unfavourable environment for corals. A lowered salinity could have been one of the factors controlling the development of colonies, as it falls in the brachyhaline zone in this level.

In the *Holcoptychites agrioensis* Subzone (8 in Table 1) there is a benthic assemblage dominated by small ramose and globose coral colonies (between levels 44 and 45 in Appendix A). They are recorded in a composite coquina composed of amalgamated individual coquinas with dense shell-packing containing a high diversity assemblage of

bivalves. The occurrence of corals reaches a maximum towards Bajada del Agrio (Fig. 5E). The absence of overgrowth between colonies and their small size suggest that these colonies had a restricted growth because of unfavourable conditions, and they managed to form a low meadow on a sandy and partially bioclastic substrate (see Lazo, 2004). The unusual presence of abundant corals, even though not reef builders, indicates that salinity may have been euhaline. The range of salinity calculated for these levels is brachyhaline to euhaline which is highly concordant with inference made from corals.

Near the top of the *Paraspiticeras groeberi* Zone (15 in Table 1) there are coral patch-reef facies at a number of levels (level 40 Appendix A; see Lazo, 2005; Lazo et al., 2005). These facies contain a combination of flat, globose, conical, and ramose colonies that may reach approximately 1 m in maximum height (Fig. 5F). Scleractinian corals are the main component, even though sponges, bryozoans, regular echinoids, bivalves, and gastropods are also recorded (Lazo et al., 2005). The absence of coalescent corals and the limited lateral extension of these facies, which is restricted mainly to Agua de la Mula and Bajada del Agrio, suggests that corals constituted a patch-reef. The range of salinity calculated in this level is euhaline which is roughly concordant with the modern growth window of hermatypic corals, which grow best in waters between 25 and 35 (James and Bourque, 1992).

5.6. Echinoid assemblages

In the *Paraspiticeras groeberi* Zone there are two levels yielding regular and irregular echinoids (levels 33 and 40 in Appendix A). The first record includes reworked *Pygorynchus* sp. and *Coenholectypus* sp. in oolitic facies, while the second includes the regular *Leptosalenia* sp. in coral patch-reef facies (see Lazo et al., 2005). Echinoids have been always viewed as stenohaline organisms. The calculated salinities in levels 33 and 40 are euhaline which is concordant with the inferences made from Recent echinoids.

5.7. Highly diverse macrobenthic assemblages

These assemblages are composed of at least seven macrobenthic taxa including bivalves, gastropods, and serpulids. They are recorded throughout the Pilmetué Member of the Agrio Formation from the *Neocomites* sp. Subzone to the base of the *Weavericeras vacaensis* Zone. Typically these assemblages are dominated in abundance by bivalves and include many taxa that are traditionally accepted as stenohaline, for example Astartidae, Bakeveliidae, Pectinidae, Pholadomyidae, and Trigonioidea. They are recorded in shoreface to offshore facies characterized by a well-oxygenated soft and patchy bioclastic substrate and temperate to warm water temperature (see Lazo, 2004). Water salinity of these zones stays mainly in the euhaline

zone which is concordant with records of highly diverse benthic fauna.

5.8. Other macrobenthic assemblages

Macrobenthic elements in the *Spitidiscus riccardii* Zone (12 in Table 1) are characterised by their small size (less than 2 cm) and moderate richness. They are concentrated into pavements of disperse to loose shell-packing, intercalated with black shales. Signs of encrustation and bioerosion are absent. The dark colour indicates high organic content that in turn is typical of dysoxic or anoxic seafloors (Tyson et al., 2005). The presence of an association of small-sized shells and absence of encrusters also indicates an oxygen-controlled substrate (see Wignall, 1993). The benthic elements do not indicate a deviation from normal marine waters. The development of dysoxia can be linked to deeper stratified water mass (see Lazo et al., 2005). In this zone only one oyster sample was analyzed. It was taken near the base of this zone, about 60 cm above the top of the Avilé Member. The result is a euhaline salinity concordant with the recorded benthic assemblage.

Most of the *Lissonia riveroi* Zone and the *Pseudofavrella angulatififormis* and *Chacantuceras ornatum* Subzones are characterized by a rather sparse benthic fauna at least in the study localities (1, 4, 5 in Table 1). At present, there is no significant information regarding salinity from benthic elements in these zones, but it is most likely brachyhaline. Perhaps the low abundance of benthic element was due to a lowered salinity, but other factors, for instance oxygen levels and type of substrate, cannot be yet discarded.

6. Causes and consequences of palaeosalinity variations in the basin

The observed fluctuations in palaeosalinity were likely due to dilution from normal marine water, caused primarily by variations in rainfall and continental runoff. The Neuquén Basin was probably subjected to climate change as it was located at the boundary of two climatic regions, arid to the north and warm temperate with seasonal rainfall to the south (see Sagasti, 2005). It is also important to note that the presence of a volcanic island arc along the western margin of the basin may have at least partially isolated the basin from the marine waters of the Pacific Ocean. The shape of the basin is also important, because a gulf-shaped basin may have inhibited the hydrodynamic exchange with the ocean while enhancing retention of continental waters. There is no evidence to support the presence of a lagoon-barrier system within the Neuquén Basin, although large mass aggregations of oysters may have isolated part of the embayment at times.

The Pilmatué and Agua de la Mula Members of the Agrio Formation have long been considered as deposited under fully marine conditions as ammonoids are recorded

throughout the sections. However, ammonoids are not recorded in every bed and they were presumably swimmers that at times may have immigrated temporarily into waters slightly diluted from normal marine conditions. Moreover, fluctuations in salinity may have been the cause of death of many truly marine organisms, for instance ammonoids and inoceramids.

There is a good correlation between inferred palaeosalinity values and the distribution of some macrobenthic assemblages, especially the mass aggregations of oysters and serpulids. It appears that oysters and serpulids switched from a solitary to a gregarious life habit within a salinity range of 21–33, showing that lowered salinity is one of the factors controlling the development of such aggregates. However, as in modern settings, other factors such as substrate consistency, temperature, sedimentation rate, disease and availability of food particles may have played a role. In fact, records of oyster and serpulid aggregates are scattered irregularly through the succession, indicating that factors other than palaeosalinity were also important in their formation. Other faunal evidence regarding changes in palaeosalinity in the studied units is scarce. Simeoni (1988) analyzed the Foraminiferida recorded in the Agrio Formation near Bajada del Agrio. She found an association of *Conorboides* sp. and *Epistomina* cf. *E. ornata* Roemer in a 60 m thick interval recorded towards the top of the Agua de la Mula Member, probably within the *Crioceratites diamantensis* Zone. This association was proposed as an indication of reduced palaeosalinity, and concurs with our data.

The distribution of the faunal assemblages indicates that not only did palaeosalinities fluctuate through time but also there was probably a north–south orientated palaeosalinity gradient. Aggregations of oysters and serpulids in the Pilmatué Member are significantly larger towards the south indicating that dilution from marine waters was more pronounced or prolonged over time in the southern region of the basin. Interestingly there is sedimentary evidence that freshwater input and clastic influx during highstands was from the south which supports this interpretation (see Eppinger and Rosenfeld, 1996). The sedimentological evidence suggests periodic freshwater influxes as well as longer-term palaeosalinity changes. Our isotopic analysis of the oyster shells accounts only for the longer-term trends, when inter-annual variations in rainfall could have briefly and significantly altered salinities. This may well explain the spread of oxygen isotope values we record for each horizon/specimen, even though the overall trend is still visible that conforms to our facies analysis.

It should also be noted that records of evaporites, including halite, in the Avilé Member indicate a brief interval of enhanced salinity, with evaporation of water under an arid or semiarid warm climate occurring during the deposition of at least part of the Agrio Formation (Rossi, 2001; Legarreta, 2002; Veiga et al., 2005). Similar evaporites occur in the Chorreado and Troncoso Members of the

overlying, predominantly non-marine Huitrín Formation. However, although temperature changes may influence the $\delta^{18}\text{O}$ isotope values and thus give a spurious palaeosalinity, temperature cannot account for an increase in 19 of palaeosalinity. An approximate temperature rise in 19 °C would have been necessary between the Valanginian and Barremian to attain such an increase. There is no evidence supporting such an increase in temperature during the Early Cretaceous.

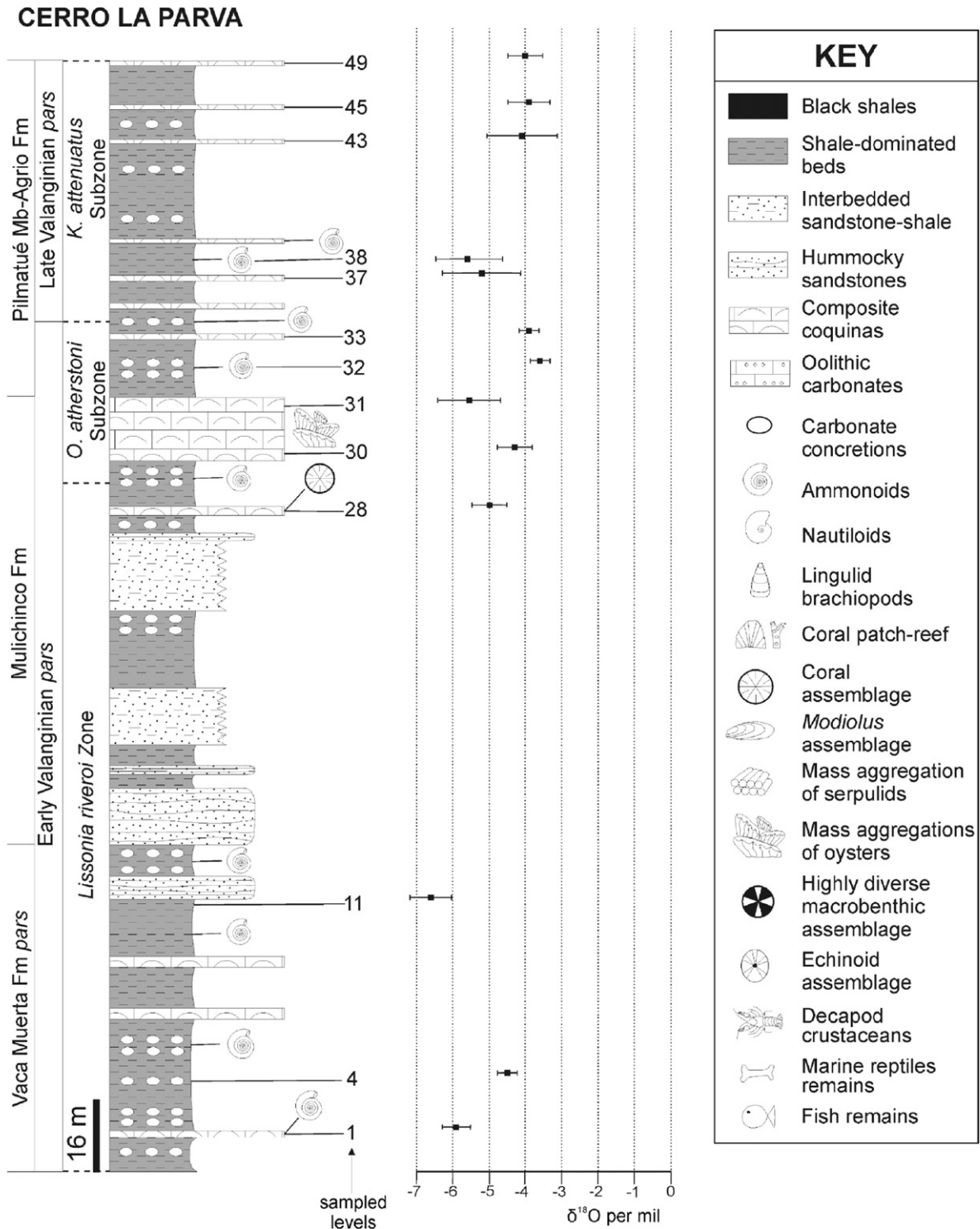
7. Conclusions

- This case study shows that the Neuquén Basin experienced significant changes in water salinity in the order of 19 during the Early Cretaceous. These changes are indicated by both isotopic and faunal studies. They were caused primarily by variations in continental runoff and seasonal rainfall in a semi-enclosed basin.
- Periodic dilution from normal marine salinity occurred especially during the Valanginian (from the top of the Vaca Muerta Formation to the middle of the Pilmatué Member of the Agrio Formation) when brachyhaline waters prevailed. However, euhaline waters predominated during the deposition of the Hauterivian to Early Barremian Agua de la Mula Member of the Agrio Formation.
- Lateral changes in faunal assemblages indicate that salinity changed in a north–south trend, being lower towards the south in Bajada del Agrio.
- Although the occurrence of ‘marine’ fossils and typical ‘marine’ sedimentary facies provide a generalized indication of the depositional environment, taken alone they may not be sufficient to provide an accurate picture. A combination of strategies may be more useful to understand complex settings such as the Neuquén Basin. Sometimes the so-called ‘marine’ invertebrates may indicate salinities different from normal marine.
- Gregarious oysters and serpulids and monospecific assemblages of small-sized *Modiolus* or lingulids have proved very useful for indicating deviations from normal marine salinity, while coral colonies and high diversity benthic assemblages are, as expected, indicative of marine waters.

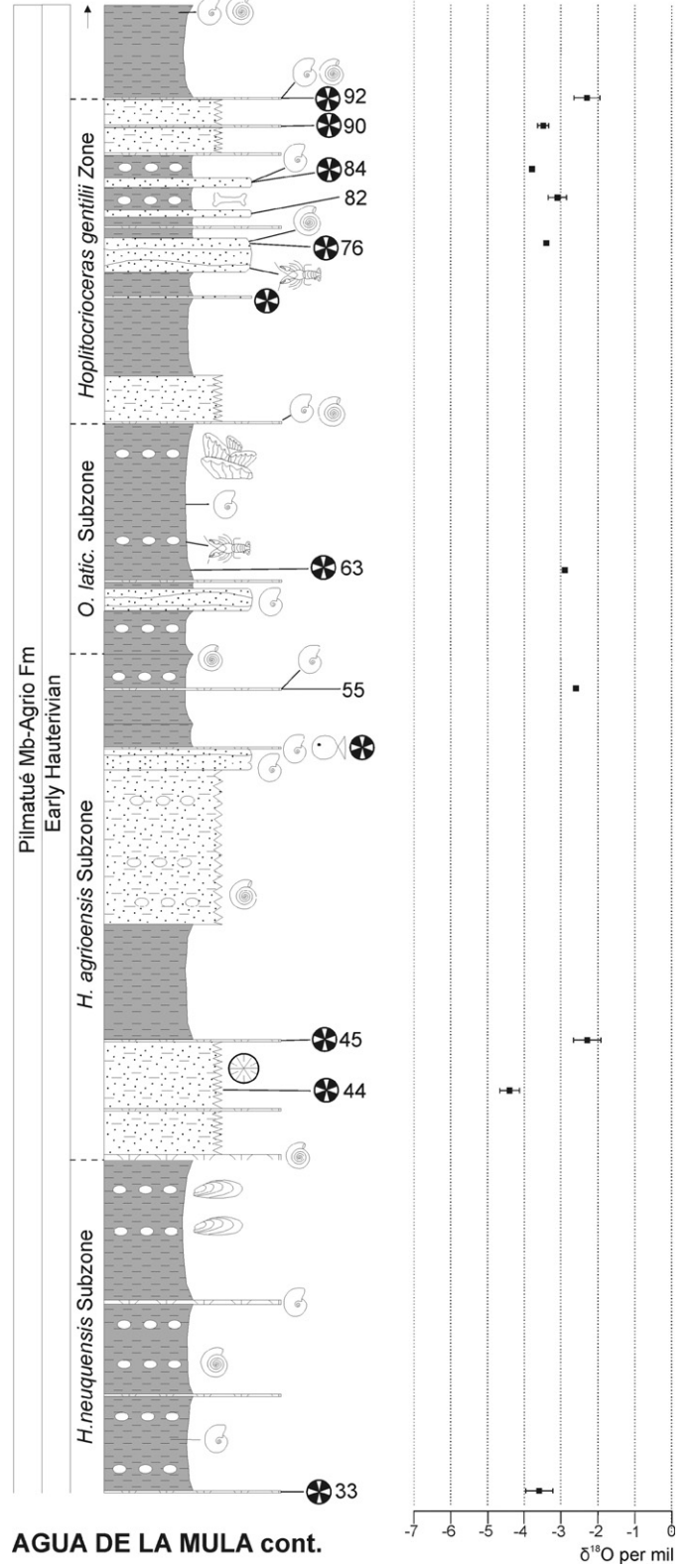
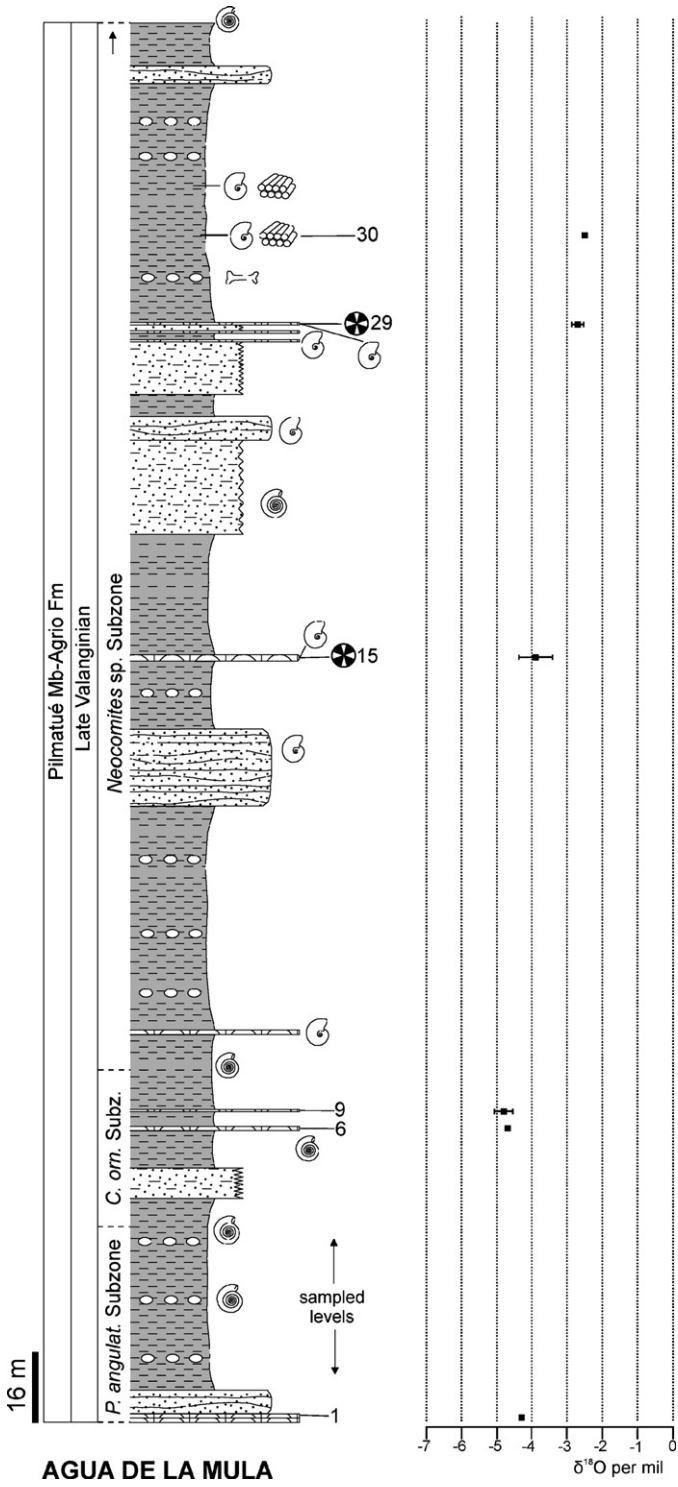
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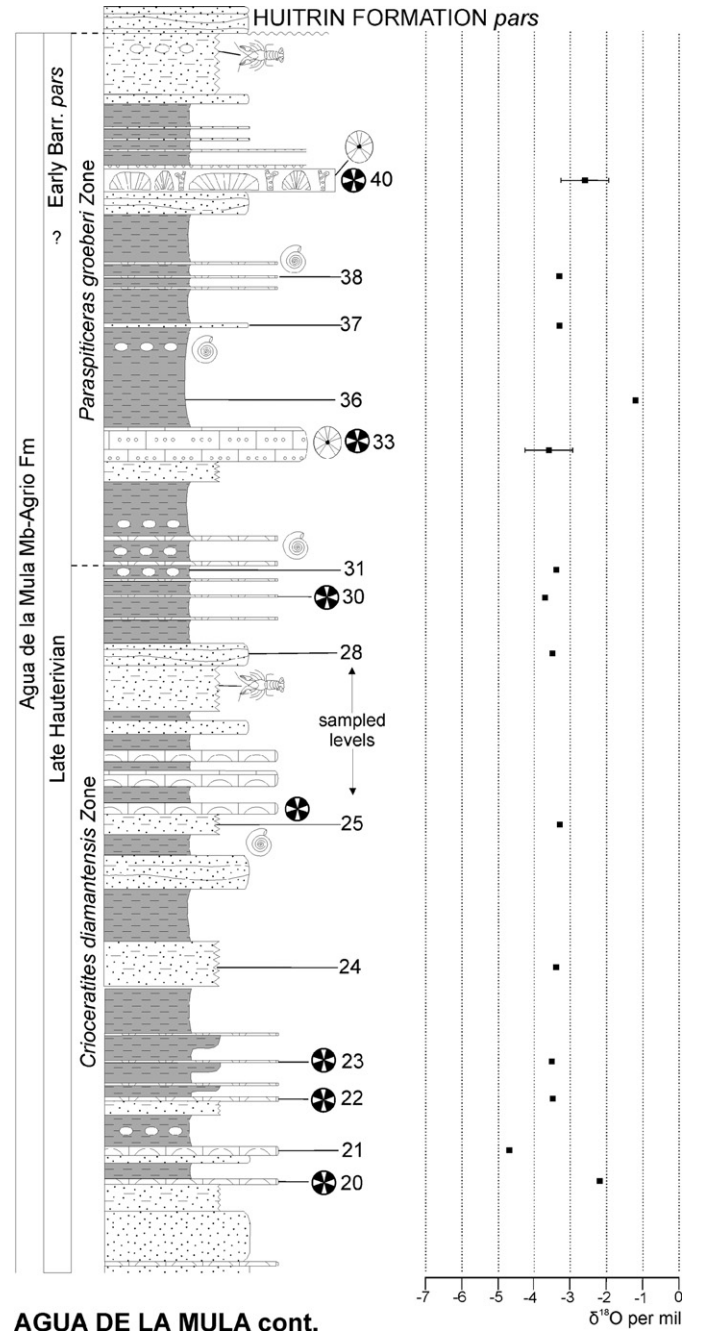
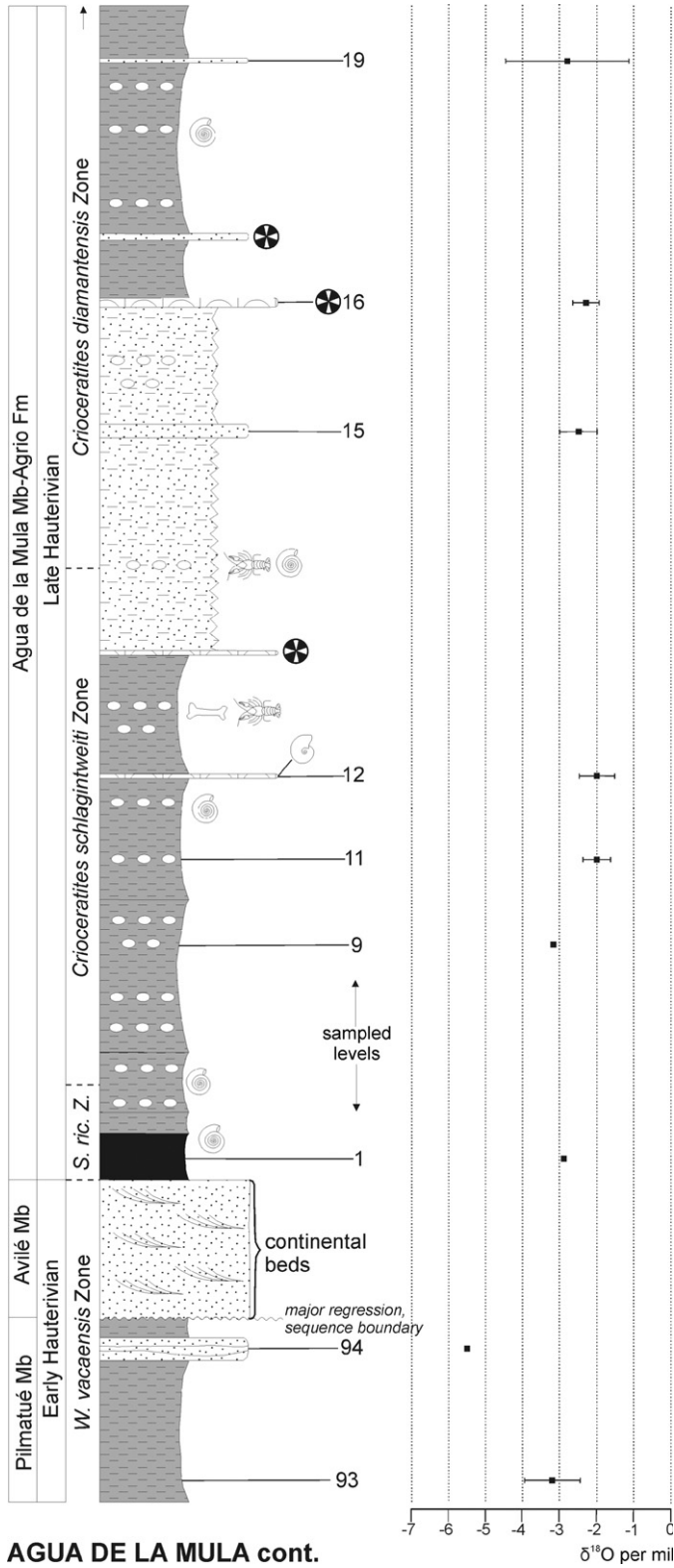
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Appendix A



Appendix A. Detailed stratigraphic sections at Cerro La Parva and Agua de la Mula localities comprising the top of Vaca Muerta Formation and the Pilmatué and Agua de la Mula Members of the Agrio Formation. Mean and standard deviation of $\delta^{18}\text{O}$ values by sample (stratigraphic level) and position of the studied macrobenthic assemblages are shown (see Appendix A for details). Ammonoid zonation and ages from Aguirre-Urreta et al. (2005) and lithofacies from Lazo et al. (2005).





Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.palaeo.2007.12.008.

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