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First U–Pb SHRIMP age for the Pilmatué Member (Agrio Formation) of the Neuquén Basin, Argentina: Implications for the Hauterivian lower boundary

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ABSTRACT

Ammonite-based biostratigraphic schemes for the Lower Cretaceous are fairly well refined across the world, from the standard zonation in the West Mediterranean province to the Boreal and Austral provinces in the northern and southern hemispheres, respectively. However, the lack of radioisotopic ages associated to the fossil-rich, Lower Cretaceous marine successions has hindered the accurate establishment of the numerical ages for the lower boundaries of its several stages (from Berriasian to Albian). Geochronological dating by U–Pb SHRIMP of a tuff layer that occurs within beds belonging to the *Holcoptychites neuquensis* Zone in the Pilmatué Member of the Agrio Formation in the Austral province (Neuquén Basin, Argentina) has resulted in an absolute age of 130.0 ± 0.6 Ma (2 sigma internal errors only) or 130.0 ± 0.8 Ma (including calibration and decay constant uncertainties). This age is interpreted to represent the time of eruption and thus the timing of the pyroclastic deposit. The H. *neuquensis* Zone is the equivalent of the A. *radiatus* Zone in the West Mediterranean province. Therefore, the obtained age is the first numerical data that could help constrain the Hauterivian lower boundary. Indeed, there is reasonable agreement with the latest proposed lower boundary of the Hauterivian at ~132.9 Ma. On the other hand, the duration recently established for this stage would be hard to reconcile with the stratigraphic record of the entire Hauterivian in the study region (northeastern Neuquén Basin). Therefore, the results of this contribution could also help to assess the extent of the Hauterivian and associated stages.

1. Introduction

Since the rapid development of geochronological methods and, particularly, since dating process allow obtaining highly precise absolute ages (e.g. < 1 my), one of the main application of these tools in stratigraphy is on the refinement of biostratigraphic charts, both regional and global ones, which have traditionally relied heavily on marine macro or micro invertebrates (ammonites, belemnites, foraminifers, radiolarians, etc.). This is particularly significant for the Lower Cretaceous, in which all the six comprising stages still await for final agreement on their boundary stratotypes and duration (Cohen, Finney, Gibbard, & Fan, 2013 (updated); Ogg & Hinnov, 2012). This is due to the fact that although the construction of biostratigraphic schemes for this stage has been a matter of intense research for a long time (see Reboulet et al., 2014 and references therein), the available radioisotopic dates tighten to biostratigraphic information have remained scarce worldwide, apart for a few exceptions (Aguirre-Urreta, Pazos, Lazo, Fanning, & Litvak, 2008, Aguirre-Urreta et al., 2015).

The Neuquén Basin, located in west-central Argentina, represents one of the main South American regions in terms of lateral and vertical continuity of Lower Cretaceous marine deposits (Howell, Schwarz, Spalletti, & Veiga, 2005). The Agrio Formation (De Ferrariis, 1968; Marchese, 1971; Weaver, 1931), deposited between the late Valanginian and early Barremian, covers vast areas of the basin with offshore, mostly fine-grained siliciclastic- and carbonate-rich facies, which hold a rich fossiliferous content of macro and micro invertebrates. The sedimentological, biostratigraphic and paleoecological significance of these fossils have been investigated for decades (see Aguirre-Urreta et al., 2011; Ballent et al., 2011; Spalletti, Veiga, & Schwarz, 2011; for synthesis). The

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research body based on the ammonite record of the Agrio Formation and bounding units allowed a detailed ammonite zonation (Aguirre-Urreta & Rawson, 1997; Aguirre-Urreta, Concheyro, Lorenzo, Ottone, & Rawson, 1999; Aguirre-Urreta, Rawson, Concheyro, Bown, & Ottone, 2005; Aguirre-Urreta, Mourgues, Rawson, Bulot, & Jaillard, 2007; Aguirre-Urreta, Pazos & et al., 2008; Aguirre-Urreta, Price, & et al., 2008), and the construction of a biostratigraphic chart that is undoubtedly the most consistent and complete of South America for that interval. However, radioisotopic ages for the same interval are almost absent, except for two dated tuffs within upper Hauterivian strata (Aguirre-Urreta, Pazos, & et al., 2008, 2015).

The aim of this contribution is to present the absolute age of a pyroclastic layer interbedded within lower Hauterivian mudstones of the Agrio Formation in central Neuquén Basin, which are well constrained within one ammonite zone (*Holcoptychites neuquensis* Zone). As this zone correlates with the Tethyan *Radiatus* Zone, which marks the entrance in the Hauterivian stage (Reboulet, 1996), the obtained numerical age allows for a discussion regarding the potential implications for this stage's lower boundary and the global time scale.

2. Geological setting

The Neuquén Basin is a giant sedimentary depression located on the eastern side of the Andes in west-central Argentina, between latitudes 32° and 40° South. It covers an area of over 200,000 km^2 (Fig. 1), and it is bounded by tectonically stable areas to the northwest (Sierra Pintada Block) and south and southeast (North Patagonian Massif). The sedimentary record of the Neuquén Basin includes continental and marine siliciclastics, carbonates, and evaporites, accumulated under a variety of basin styles between the Late Triassic to the early Cenozoic (Howell et al. 2005; Legarreta & Uliana, 1991).

From the Middle Jurassic to the Early Cretaceous, the Neuquén Basin evolved as a back-arc basin located inboard of the proto-Andean emergent magmatic arc, in the western margin of southern Gondwana (Fig. 1). Whereas a predominantly extensional stress regime associated with volcanism and deep-marine sedimentation was dominant in the westward intra-arc setting during that time, the back-arc Neuquén Basin developed under more regional thermal subsidence punctuated by several episodes of structural inversion (Howell et al., 2005; Vergani, Tankard, Belotti, & Welsink, 1995).

Between the Late Jurassic and Early Cretaceous (Berriasian-Hauterivian), the epeiric sea of the Neuquén Basin was characterized by a ramp-type profile in the eastern and southern margins (Legarreta & Gulisano, 1989; Legarreta & Uliana, 1991), but a steeper depositional profile toward the west (Spalletti, Veiga, Schwarz, & Franzese, 2008). Available paleogeographic reconstructions, based on paleomagnetic data, suggest a mid-latitude position for the basin during the Early Cretaceous (Somoza, 2011). During that interval, long-lived periods of highstand conditions were interrupted by significant events of relative sea-level fall, in turn followed by rapid transgression (Fig. 2). Relative sea-level drops triggered partial disconnection of the epeiric sea from the

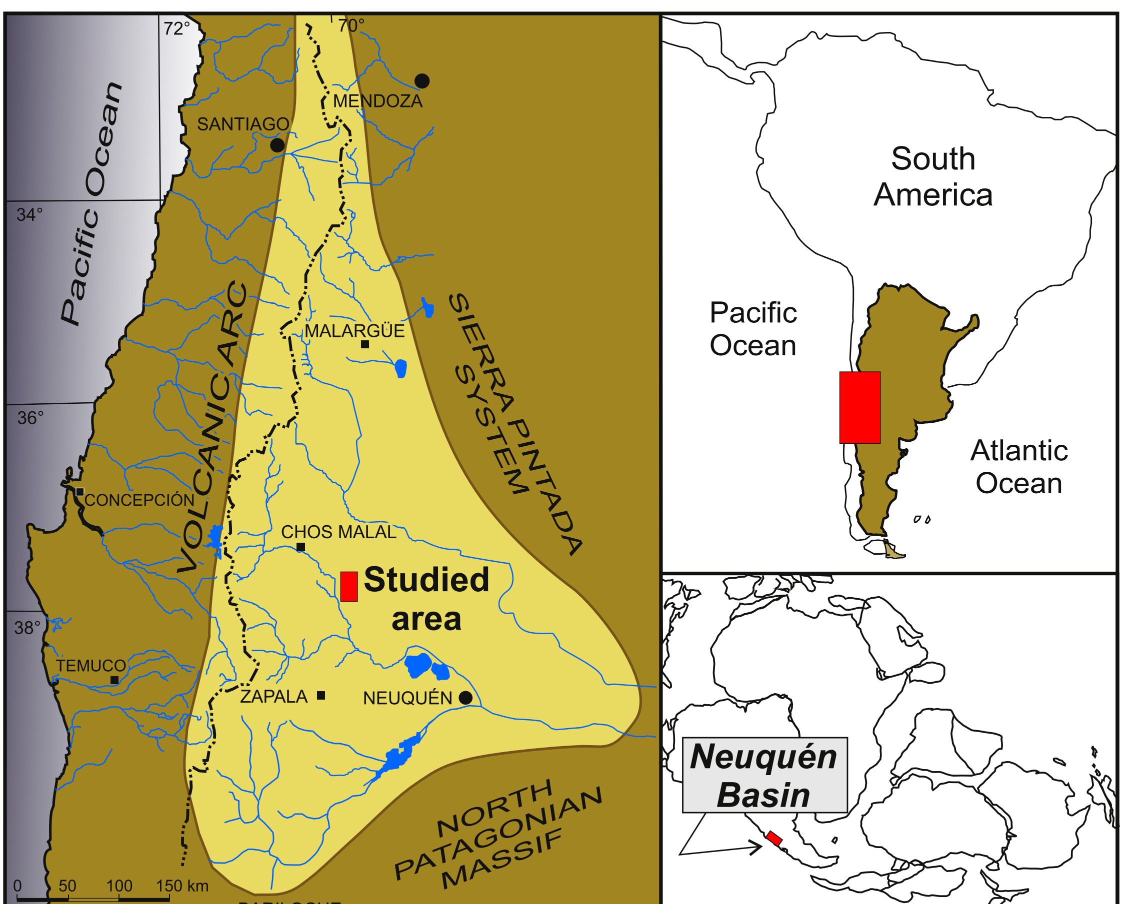

Fig. 1. Location map of the Neuquén Basin. Study area (shown in detail in Fig. 4) is boxed.

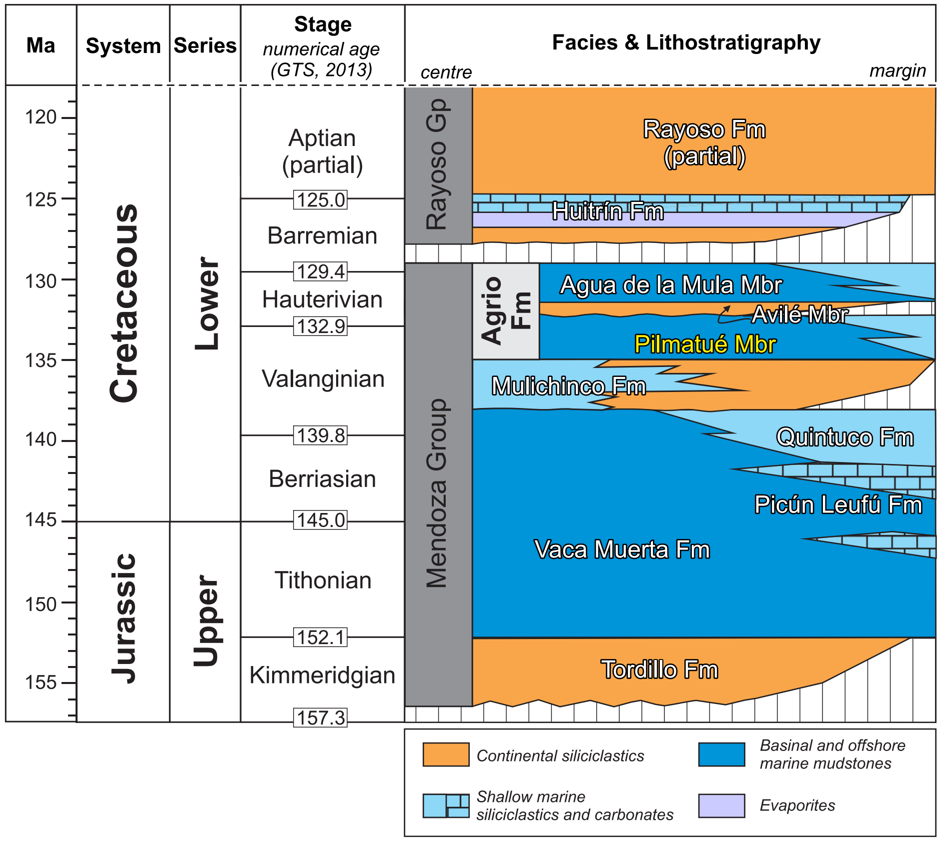

Fig. 2. Chronostratigraphy for the Kimmeridgian to Aptian of the Neuquén Basin in northern Neuquén Province (modified from Howell et al., 2005). The base of the Pilmatué Member of the Agrio Formation represents an abrupt transgression of the basin, following a relatively lowstand stage represented by the Mulichinco Formation (Schwarz et al., 2006). The age of the Huitrín Formation after Lazo and Damborenea (2011).

STAGE	ZONES	SUBZONES	UNITS
LOWER HAUTERIVIAN	*Weavericeras vacaensis*		Avilé Mbr
	Hoplitocrioceras gentilii	*H. gentilii*	Pilmatué Mbr
		H. giovinei	
	Holcoptychites neuquensis	*Olcostephanus (O.) laticosta*	
		H. agrioensis	★ Tuff layer
		H. neuquensis	
UPPER VALANGINIAN	*Pseudofavrella angulatiformis*	*Decliveites crassicostatus*	
		Chacantuceras ornatum	
		P. angulatiformis	
	Olcostephanus (O.) atherstoni	*Viluceras permolestus*	
		Karakaschiceras attenuatus	Mulichinco Fm
LOWER VAL.		*O. (O.) atherstoni*	

Fig. 3. Valanginian-early Hauterivian biostratigraphic scheme for the Pilmatué Member of the Agrio Formation (compiled from Aguirre-Urreta et al., 2005, 2011). Approximate location of the tuff layer is also shown.

Proto-Pacific, as well as the exposure and erosion of large areas of the basin (Howell et al., 2005). Three of these transgressive–regressive cycles, already recognized by pioneer geologists (e.g. Groeber, 1946; Weaver, 1931) are lithostratigraphically included in the Mendoza Group.

The Pilmatué Member is present all across the Neuquén Basin; it overlies the Mulichinco Formation in the southern and central sectors (Lazo, 2005; Schwarz & Howell, 2005; Spalletti et al., 2011), and time-equivalent carbonate deposits in the northernmost part of the basin (Sagasti, 2005). The basal boundary of the Pilmatué Member marks an abrupt deepening across the basin (Legarreta & Uliana, 1991; Schwarz, Spalletti, & Howell, 2006). South of the study area this unit overlies continental deposits of the Mulichinco Formation that grade into marine strata to the north (Fig. 2). In the study area the Pilmatué Member is abruptly truncated by continental (fluvial and eolian) deposits of the Avilé Member, which represents a second-order lowstand stage in the basin (Legarreta & Uliana, 1991; Veiga, Spalletti, & Flint, 2002).

In the southern and central sectors of the basin the Pilmatué Member mostly comprises marine deposits, ranging from offshore/basinal shales and marls to sandstones and pebbly sandstones representing shoreface deposits (Lazo, 2005; Schwarz, Veiga, & Spalletti, 2014; Spalletti et al., 2011). Although the unit is mostly composed of terrigenous sedimentary rocks, carbonate intrabasinal material is present throughout it, either forming carbonate-dominated packages or mixed with siliciclastic grains making hybrid deposits (Schwarz et al., 2014). Time-equivalent continental deposits (lower section of the Centenario Formation; Digregorio & Uliana, 1980), are present in the subsurface toward the eastern and southeastern margins of the basin. In the northern sector of the basin (Mendoza Province), the unit becomes highly enriched in carbonates and is composed entirely of basinal/offshore deposits (Sagasti, 2005).

A detailed ammonite biostratigraphic framework has been erected for the Pilmatué Member (Aguirre-Urreta et al., 2005, 2011), indicating that the unit would span from the upper Valanginian to the lower Hauterivian (Fig. 3). Where the unit overlies shallow-marine or continental deposits of the Mulichinco Formation, the basal grey to black shales typically hold an ammonite fauna which is indicative of the upper subzone of the *Olcostephanus atherstoni* Zone [i.e. O. (*Viluceras*) *permolestus*], or the younger *Pseudofavrella angulatiformis* Zone (Schwarz & Howell, 2005; Schwarz et al., 2011). However, in the westernmost sector of the basin, some authors would extend the base of the Pilmatué Member to green mudstones with ammonite horizons that belong the K. *attenuatus* Subzone of the O. *atherstoni* Zone (e.g. Aguirre-Urreta et al., 2005).

3. Stratigraphic context and description of the tuff layer

3.1. Stratigraphic context

Facies and stratigraphy of the entire Pilmatué Member in the central Neuquén Basin have been recently examined by Schwarz et al. (2014) in a 25 km-long sector, between 37°28′ and 37°42’ South Latitude. Complete stratigraphic sections of the unit were measured within that study at Mina San Eduardo, Río Neuquén and Loma Rayoso (Fig. 4). General trends from south to north suggest a fairly constant thickness (thinning northwardly from 700 m to 620 m) and a gradual reduction in the proportion of sandstones (Fig. 5).

Broadly speaking, the Pilmatué Member shows two distinct stratigraphic intervals in this region. The lower half is exclusively composed of fine-grained deposits, including black shales (mudstones with fissility), greenish terrigenous mudstones, grey calcareous mudstones (marls), and sandy mudstones (Fig. 5). In contrast, the upper half of the unit is characterized by fine-grained deposits interbedded with decameter-thick intervals comprising muddy sandstones, fine-grained sandstones, mixed sandstone-carbonate deposits and/or carbonates. The tuff layer reported in this contribution is found at 350 m from the base of the San Eduardo section, just above the first occurrence of the oldest shallow-marine deposits identified in the Loma Rayoso type section (Fig. 5).

The ammonite information for both sections collectively suggests that the base of the Pilmatué Member in this region corresponds to the P. *angulatiformis* Subzone of the P. *angulatiformis* Zone (Figs. 3 and 5). Additionally, it provides a constraint for the biostratigraphic span of the different stratigraphic intervals. The tuff layer is located about 125 m of the first occurrence of *Holcoptychites magdalenae*, which typically characterizes intermediate levels of the *H. neuquensis* Subzone (Aguirre-Urreta et al., 2005). It also occurs 105 m below the first occurrence of *Olcostephanus* (*O.*) *laticosta*, which characterizes the base of the highest

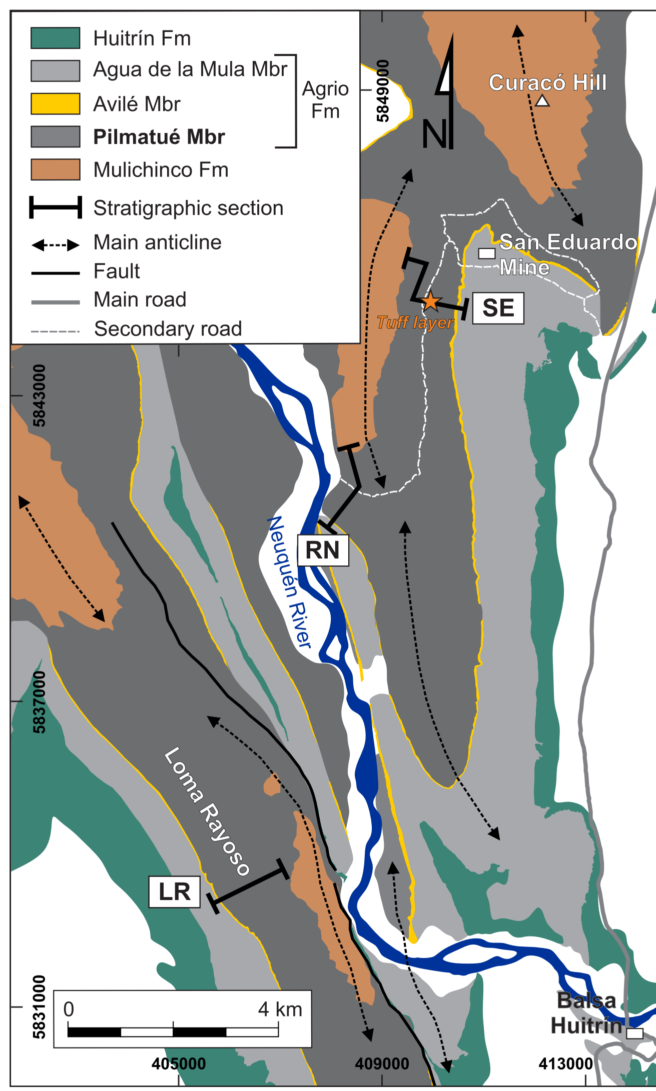

Fig. 4. Simplified geological map of the studied area, showing main stratigraphic sections of the Pilmatué Member analyzed by Schwarz et al. (2014). SE: San Eduardo section; RN: Río Neuquén section; LR: Loma Rayoso section. Location of the tuff layer is also shown in the San Eduardo section.

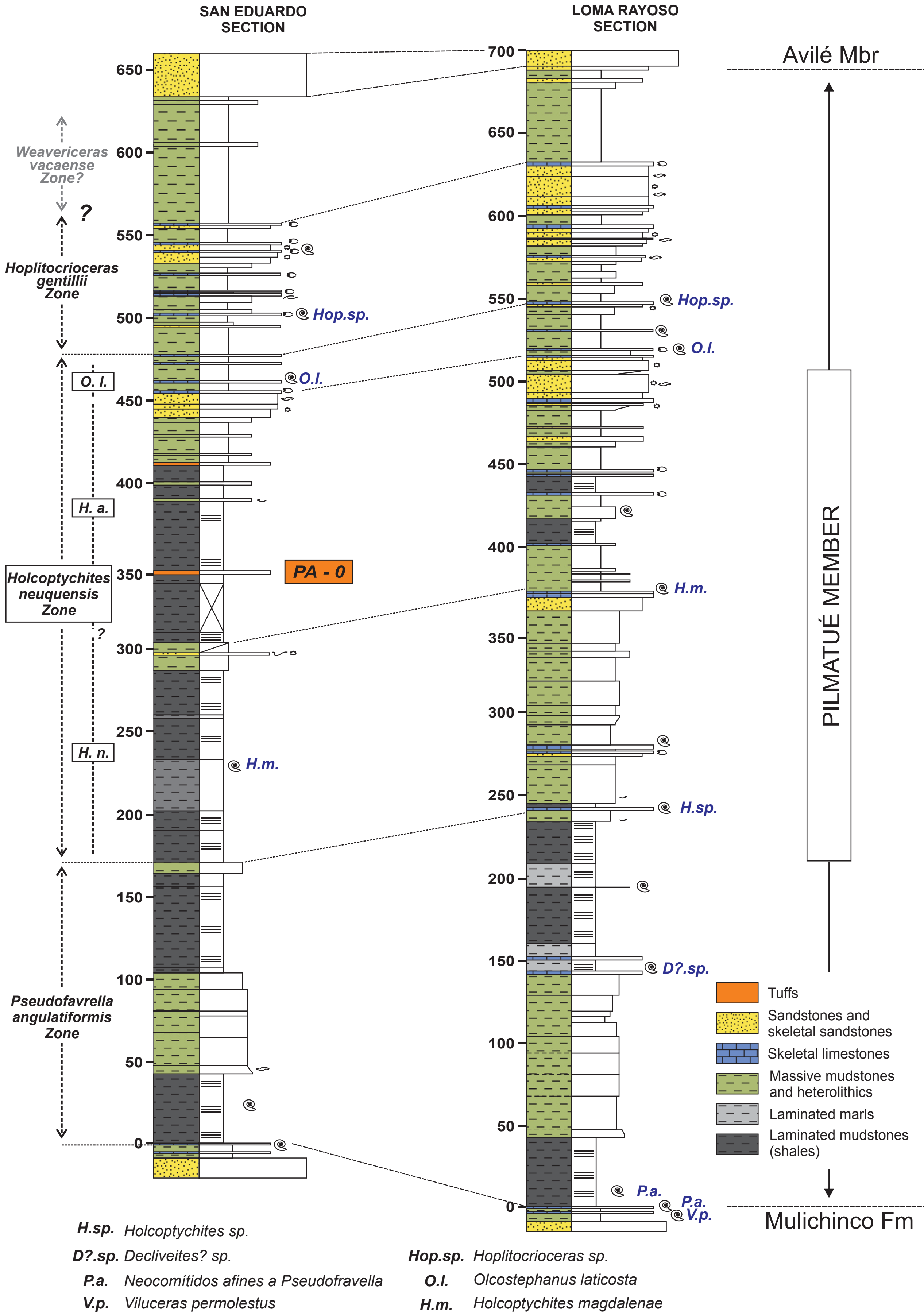

Fig. 5. Simplified sedimentological sections representing the stratigraphic record of the Pilmatué Member in the southernmost (Loma Rayoso) and northernmost (San Eduardo) regions of the studied area. The stratigraphic occurrence of key ammonite fauna and the resulting biozonation (see Fig. 3) is also shown. *H.n.*: *Holcoptychites neuquensis* Subzone; *H.a.*: *Holcoptychites agrioensis* Subzone; *O.l.*: Olcostephanus (O.) laticosta Subzone.

subzone of the *Holcoptychites neuquensis* Zone (Figs. 3 and 5). Therefore, according to the ammonite information, the tuff layer undoubtedly falls within the stratigraphic interval assigned to the *H. neuquensis Zone*, most likely within the H. *agrioensis* Subzone (Figs. 3 and 5).

3.2. Tuff layer description

The sampled tuff is 20 cm thick, continuous for more than 200 m, and interbedded with dark grey siliciclastic mudstones (Figs. 5 and 6A). This tuff/tuffaceous bed has a massive to laminated structure and a sandy texture (Fig. 6B), and is interpreted to have been deposited as a pyroclastic fall. Additional tuffaceous beds occur higher in the section, but their preservation was not as good as that of the studied sample.

Under the microscope the tuff is essentially composed of glass shards (>90%), with a preferential parallel disposition of the larger grains. According to mineral composition this rock can be classified as a rhyolitic, vitric tuff. The volcanic glass mostly comprises very angular shards (Fig. 6C), which are heavily altered to clay minerals and partially replaced by ferron oxides and fine-grained carbonates. The shards are relatively well sorted, with most grains in the fine sand fraction (~150 μm). Uncommonly, larger vitric grains (>350 μm) could be attributed to lithic fragments, or less likely, re-sedimented pumice material. Phenocrysts are rare, they range in grain size from fine to medium sand, and they correspond mostly to quartz, potassium feldspar (altered to sericite and kaolinite) and biotite. Significantly, rounded quartz grains are also present, suggesting a potential mixing of primary pyroclastic material with clasts taken by the wind from an external sedimentary source. Elongated, carbonate fragments with sparry calcite texture could represent the remains of marine invertebrates.

4. Analytical methods

For the geochronological study, the rock was crushed and milled by conventional methods. The grounded sample was passed through a 60 mesh nylon disposable sieve and washed. Heavy minerals were then separated using heavy liquids and magnetic methods. From this mineral concentrate, the zircon grains were handpicked, mounted in an epoxy disc, and ground and polished until nearly half of each grain was removed to expose a cross section. The mounts were photographed in transmitted and reflected light, and SEM imaged. Cathodoluminiscence images were used to target the magmatic rims of euhedral grains.

The sample was analyzed using the high resolution SHRIMP II ion microprobe at the Research School of Earth Sciences (Canberra, Australia), and analytical data were processed with the SQUID e Isoplot/Ex programs (Ludwig, 2001, 2003). Uncertainties for individual analyses (ratios and ages) are reported at the 1σ level, but errors in calculated weighted mean ages are 95% confidence limits. Thirty-one SHRIMP spots were analyzed in thirty zircon grains. The zircon population essentially consists of euhedral crystals with well-defined pyramidal terminations and their average length is

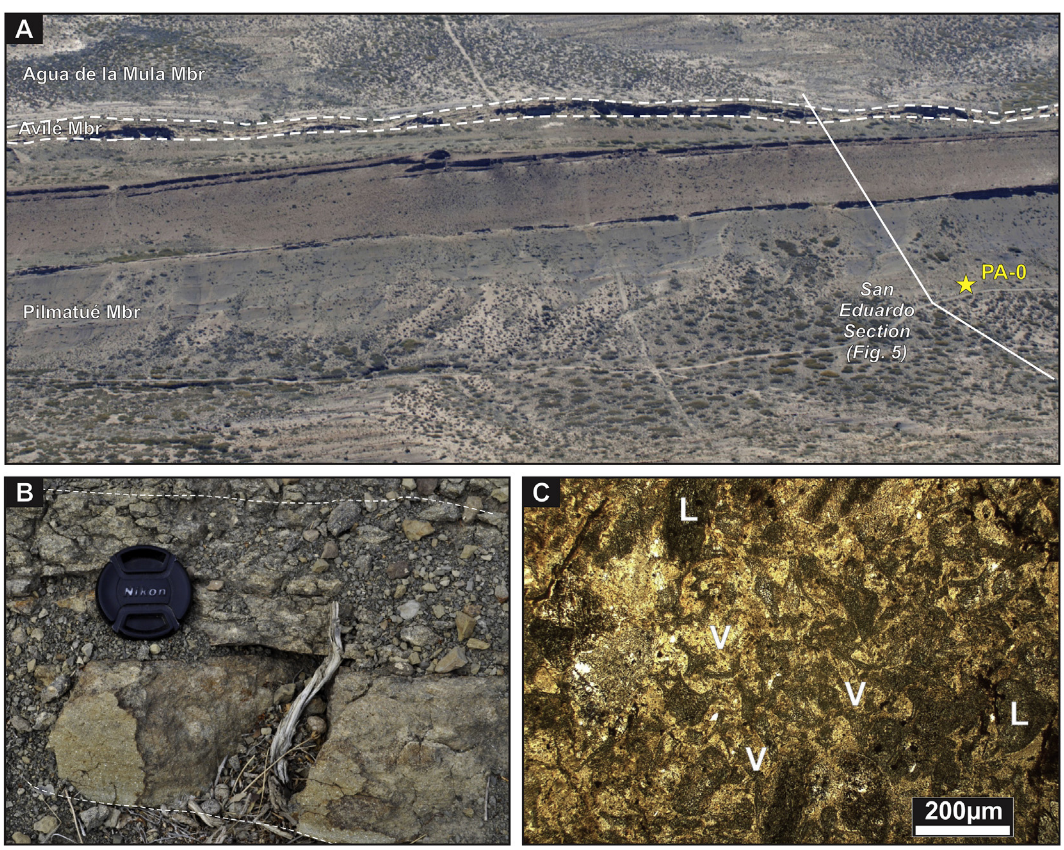

Fig. 6. A) General outcrop view of the upper interval of the Pilmatué Member in the San Eduardo Section, showing the location of the tuff layer (PA-0) and the sandstone-dominated units sticking out above it. The overlying Avilé Member and basal section of the Agua de la Mula Member are also indicated. B) Detailed outcrop view of the pyroclastic bed, showing a crudely laminated to massive structure and characteristic altered, whitish, pyroclastic/glass-dominated material. C) Microfotograph (crossed nicoles), showing that the analyzed bed is largely composed of glass hards (V), with minor contribution of quartz and uncommon larger grains, which could attributed to re-sedimented lithic fragments (L) in this case.

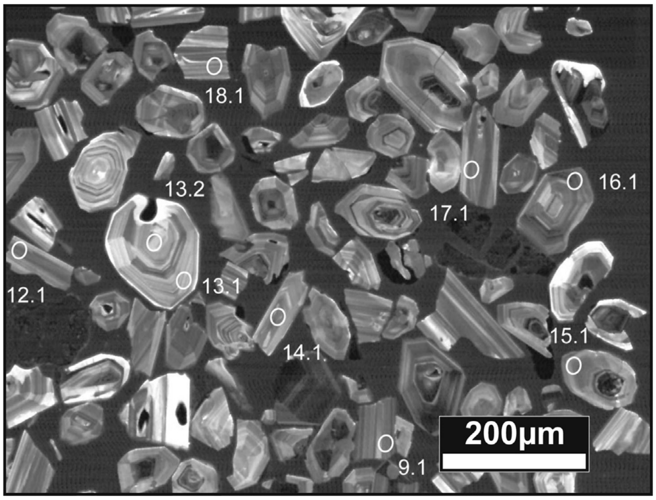

Fig. 7. CL image of mounted zircon grains from the PA-0 sample. Most of the zircon grains are not abraded and show well developed magmatic zoning.

about 85 μm (Fig. 7). Cathodoluminescence images show oscillatory zonation from center to border, which can be attributed to the crystallization process during a single igneous event (Fig. 7). Some grains have central cavities that suggest abrupt cooling in a subvolcanic or volcanic setting.

5. Geochronological results and implications

The geochronological results are shown in Table 1 and Fig. 8. The U–Pb isotopic data plotted in a concordia diagram showed highly consistent results with minor deviations. For further confidence one core-rim pair was analyzed, which shows that it is all part of the same magmatic crystallization. All the results represent a unique population in the Tera-Wasserburg diagram (Fig. 8A) and a simple, bell-shaped curve in the probability plot (Fig. 8B). The $^{206}Pb/^{238}U$ weighted arithmetic mean for all the analyzed zircon grains have a low deviation (MSWD = 1.4, probability = 0.083), with an average age of 130.0 ± 0.6 Ma (2 sigma internal errors only) or 130.0 ± 0.8 Ma (including calibration and decay constant uncertainties) (Table 1). This average age is interpreted to represent the time of eruption and therefore represents the age of the pyroclastic deposit.

On the basis of the refined biostratigraphic scheme for the Lower Cretaceous of the Neuquén Basin (Aguirre-Urreta & Rawson, 1997, 2001, 2010; Aguirre-Urreta et al., 1999, 2005, 2007), most of the Agrio Formation record spans from the upper Valanginian to the lower Barremian (Fig. 9). In this context, the grey to black shales of the base of the Pilmatué Member started its accumulation during the late Valanginian in the study area (*Pseudofavrella angulatiformis* Zone) and continued with marine sedimentation through the early Hauterivian (*Holcoptychites neuquensis*, *Hoplitocrioceras gentillii* and *Weavericeras vacaense* zones) (Fig. 9). The 130.0 ± 0.8 Ma age for the analyzed tuff represents the first absolute age for the Pilmatué Member of the Agrio Formation. Additionally, it also

Table 1
Summary of SHRIMP U–Pb results for zircon from sample PA-0.

Grain spot	U (ppm)	Th (ppm)	Th/U	^{206}Pb (ppm)	$^{204}Pb/^{206}Pb$	f_{206} %	Total				Radiogenic		Age (Ma)	
							$^{238}U/^{206}Pb$	±	$^{207}Pb/^{206}Pb$	±	$^{206}Pb/^{238}U$	±	$^{206}Pb/^{238}U$	±
1.1	860	588	0.68	15.5	0.000119	0.03	47.82	0.52	0.0489	0.0007	0.0209	0.0002	133.4	1.4
2.1	1040	767	0.74	18.3	0.000034	0.02	48.93	0.53	0.0488	0.0006	0.0204	0.0002	130.4	1.4
3.1	766	561	0.73	13.4	0.000045	0.12	49.11	0.54	0.0496	0.0007	0.0203	0.0002	129.8	1.4
4.1	428	258	0.60	7.6	0.000256	0.14	48.25	0.56	0.0498	0.0009	0.0207	0.0002	132.1	1.5
5.1	516	246	0.48	9.1	0.000155	<0.01	48.64	0.55	0.0483	0.0008	0.0206	0.0002	131.3	1.5
6.1	261	174	0.66	4.7	0.000584	0.40	48.21	0.60	0.0518	0.0011	0.0207	0.0003	131.8	1.6
7.1	543	354	0.65	9.3	–	0.05	50.05	0.74	0.0489	0.0008	0.0200	0.0003	127.5	1.9
8.1	763	404	0.53	13.5	–	0.00	48.54	0.54	0.0487	0.0008	0.0206	0.0002	131.5	1.5
9.1	677	483	0.71	11.9	0.000325	0.26	48.92	0.54	0.0507	0.0007	0.0204	0.0002	130.1	1.4
10.1	1103	878	0.80	19.4	0.000161	0.13	48.85	0.60	0.0497	0.0006	0.0204	0.0003	130.5	1.6
11.1	915	382	0.42	16.3	0.000109	0.10	48.37	0.59	0.0494	0.0006	0.0207	0.0003	131.8	1.6
12.1	814	516	0.63	14.6	0.000047	0.15	48.01	0.53	0.0499	0.0007	0.0208	0.0002	132.7	1.5
13.1	290	107	0.37	5.1	0.000558	0.11	49.22	0.59	0.0495	0.0011	0.0203	0.0002	129.5	1.6
13.2	228	113	0.49	3.9	0.000113	<0.01	50.45	0.65	0.0484	0.0013	0.0198	0.0003	126.6	1.6
14.1	585	435	0.74	10.2	–	0.24	49.39	0.64	0.0505	0.0008	0.0202	0.0003	128.9	1.7
15.1	701	474	0.68	12.5	–	0.05	48.30	0.53	0.0491	0.0007	0.0207	0.0002	132.0	1.4
16.1	1413	1267	0.90	24.3	–	<0.01	49.97	0.53	0.0482	0.0005	0.0200	0.0002	127.8	1.4
17.1	666	451	0.68	11.8	0.000189	<0.01	48.43	0.53	0.0485	0.0007	0.0207	0.0002	131.8	1.4
18.1	755	559	0.74	13.0	0.000091	0.17	50.04	0.55	0.0499	0.0007	0.0200	0.0002	127.3	1.4
19.1	435	346	0.80	7.7	0.000430	0.45	48.60	0.56	0.0522	0.0017	0.0205	0.0002	130.7	1.5
20.1	717	330	0.46	12.4	0.000155	0.09	49.62	0.55	0.0493	0.0009	0.0201	0.0002	128.5	1.4
21.1	624	378	0.61	11.0	0.000005	0.05	48.94	0.62	0.0490	0.0007	0.0204	0.0003	130.3	1.7
22.1	882	528	0.60	15.4	–	0.07	49.31	0.54	0.0492	0.0006	0.0203	0.0002	129.3	1.4
23.1	683	470	0.69	11.7	0.000270	0.04	49.97	0.55	0.0489	0.0007	0.0200	0.0002	127.7	1.4
24.1	1098	777	0.71	19.3	–	0.16	48.76	0.53	0.0499	0.0006	0.0205	0.0002	130.7	1.4
25.1	566	280	0.49	10.0	0.000151	0.18	48.61	0.55	0.0501	0.0008	0.0205	0.0002	131.0	1.5
26.1	1206	1033	0.86	20.9	0.000185	0.30	49.51	0.66	0.0510	0.0006	0.0201	0.0003	128.5	1.7
27.1	603	381	0.63	10.5	0.000196	<0.01	49.54	0.56	0.0481	0.0008	0.0202	0.0002	128.9	1.4
28.1	134	74	0.55	2.3	0.000374	0.14	50.23	0.71	0.0497	0.0016	0.0199	0.0003	126.9	1.8
29.1	950	560	0.59	16.7	0.000052	<0.01	48.89	0.53	0.0485	0.0006	0.0205	0.0002	130.5	1.4
30.1	89	34	0.38	1.6	–	0.58	48.90	0.77	0.0533	0.0034	0.0203	0.0003	129.7	2.1

[1] Uncertainties given at the one σ level.
[2] Error in Temora reference zircon calibration was 0.41% for the analytical session (not included in above errors but required when comparing data from different mounts).
[3] f_{206} % denotes the percentage of ^{206}Pb that is common Pb.
[4] Correction for common Pb for the U/Pb data has been made using the measured $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios following Tera and Wasserburg (1972) as outlined in Williams (1998).

determines a minimum age for the base of the *Holcoptychites neuquensis* Zone (Fig. 9), as the tuff layer is located immediately above ammonites assigned to intermediate levels of the *H. neuquensis* Subzone (Figs. 5 and 9).

The *H. neuquensis* Zone defined in the Neuquén Basin has been traditionally correlated with the *Acanthodiscus radiatus* Zone in the West Mediterranean Province (Aguirre-Urreta et al., 2005, 2007; Reboulet et al., 2014). Although this correlation remains provisional (Reboulet et al., 2014), this zone in the tethyan region marks the base of the Hauterivian (Fig. 9). Thus, it follows that the tuff layer reported and dated in this contribution would provide an estimated minimum age for the lower boundary of the Hauterivian, which remains to be dated, as several other Early Cretaceous stages, without well-established boundaries (Ogg & Hinnov, 2012). Considering that recent Global Time Scales have estimated an age model of 132.9 Ma (Cohen, Finney, Gibbard, & Fan 2013; 2013 updated, no error provided) for the Hauterivian lower boundary (Fig. 9), the absolute age obtained in this contribution is in a reasonable agreement with the proposed boundary.

The absolute age obtained in this contribution is also coherent with two tuff layers dated at the base and the top of the Agua de la Mula (upper) Member of the Agrio Formation (Fig. 9). The tuff horizon at the base was originally dated as 132.5 ± 1.3 Ma by SHRIMP (Aguirre-Urreta, Pazos, & et al., 2008), but more recently re-dated by higher-precision dating methods (ID-TIMS U–Pb geochronology), providing an age of 129.09 ± 0.4 (Aguirre-Urreta et al., 2015). In turn, the stratigraphically upper tuff provided a radioisotopic age of 127.42 ± 0.15 Ma (Aguirre-Urreta et al., 2015). These tuffs are also well constrained biostratigraphically by ammonites and can be correlated to the standard zonation of the West Mediterranean Province (Fig. 9). The lower horizon is close to the base of the upper Hauterivian, which in the Neuquén Basin is represented by the *Spitidiscus ricardii* (Fig. 9), partially equivalent to the *Subsaynella sayni* Zone in the Tethyan realm (Hoedemaeker et al., 2003; Reboulet et al. 2006). The upper tuff layer is close to Hauterivian-Barremian boundary (Aguirre-Urreta et al., 2015) (Fig. 9). Particularly important to this contribution, the age of 129.09 ± 0.4 for the base of the upper Hauterivian

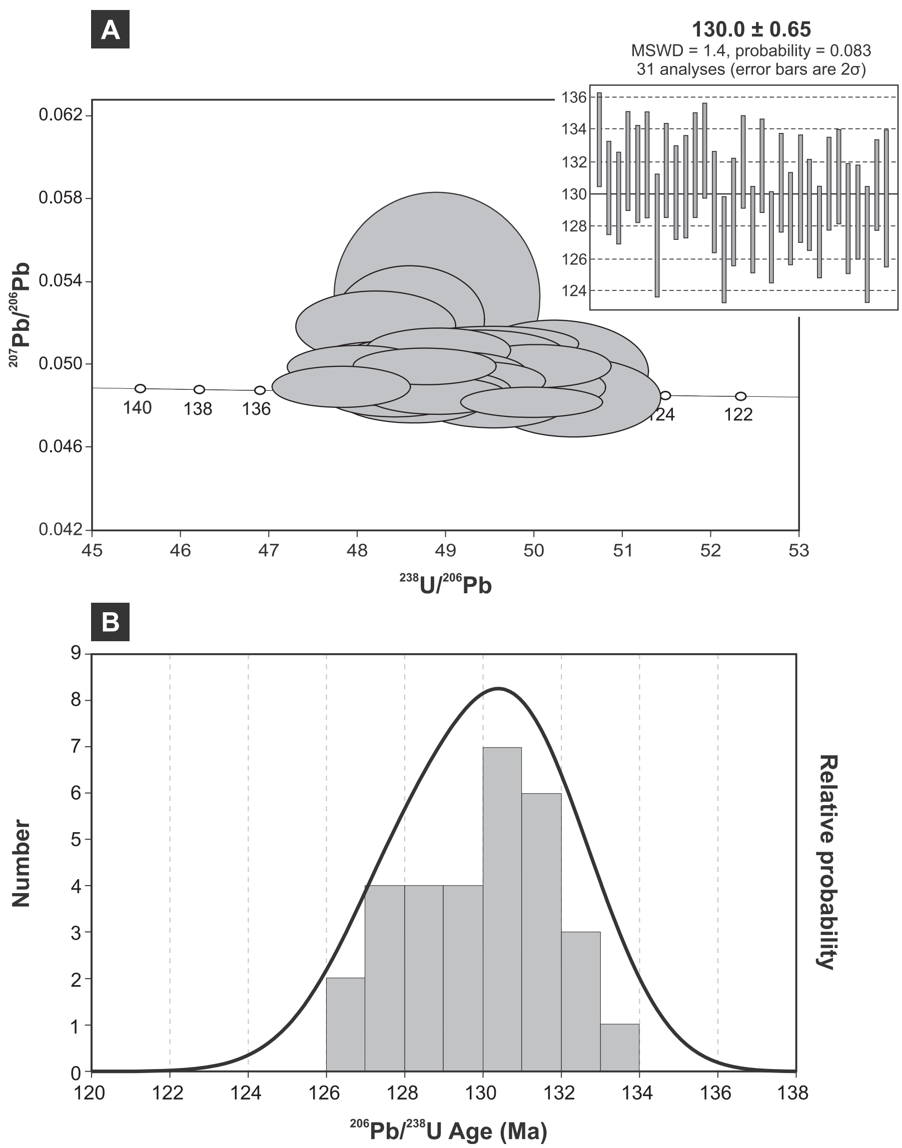

Fig. 8. Geochronological results for the analyzed tuff layer (PA-0). (A) Weighted mean age calculation (two sigma error) and Tera-Wasserburg concordia plot (one sigma error). The age uncertainty is given at 95% confidence limits and includes the uncertainty in the U/Pb ratio calibration of the reference zircon. (B) Probability versus age diagram.

would imply a *minimum* duration of 1 my for the lower Hauterivian.

Following the proposed correlation between the standard zonation of the West Mediterranean Province and the Neuquén Basin (Fig. 9), the absolute age of 130.0 ± 0.8 Ma for the pyroclastic deposit of the Pilmatué Member would be a time constraint for the numerical age of the Hauterivian lower boundary in the Neuquén Basin (for the origin of Cretaceous numerical ages see details in Ogg & Hinnov, 2012). This information can also be used to analyze the relationship between the estimated duration of a single stage and its stratigraphic record in a given basin. In the Neuquén Basin the Hauterivian is entirely represented by the Agrio Formation, which comprises the Pilmatué, Avilé and Agua de la Mula members (Figs. 2 and 9). Considering a duration of 3.5 my, as proposed in recent time scales (Cohen et al., 2013; 2013 updated), it follows that the stratigraphic interval from the first record of *Holcoptychites neuquensis* (i.e. base of the Hauterivian) to the tuff level of the Pilmatué Member would have demanded about 2.9 my (Fig. 9), whereas the rest of the Agrio Formation (upper part of the Pilmatué Member, plus the Avilé Member, plus the Agua de la Mula Member) would have deposited in only c. 0.6 my. Given the similar facies composition of the Pilmatué and the Agua de la Mula members in

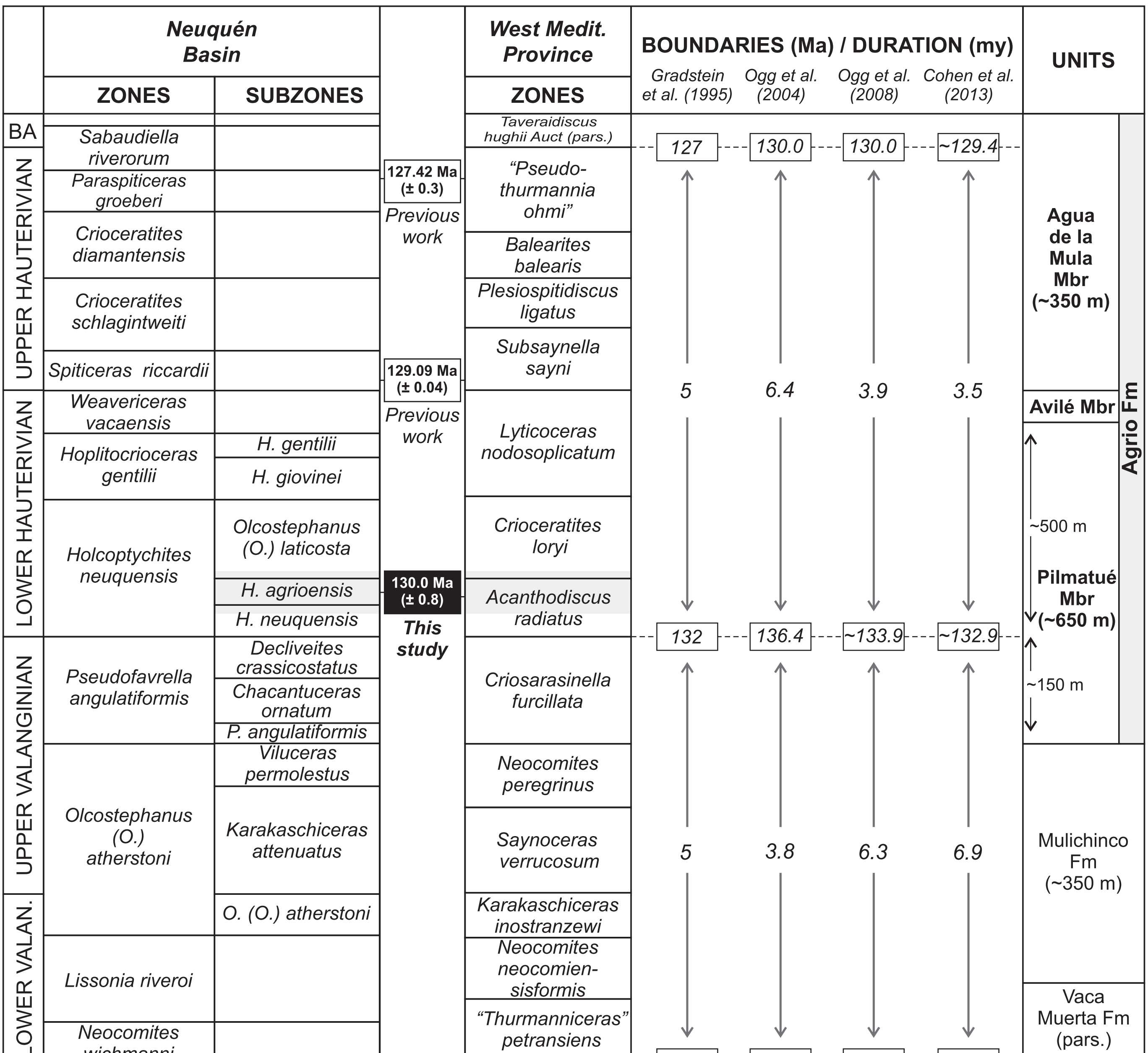

Fig. 9. Biostratigraphic scheme of the Valanginian and Hauterivian of the Neuquén Basin, proposed correlation with the West Mediterranean province (after Aguirre-Urreta et al., 2005; Reboulet et al., 2014), age models for different authors and lithostratigraphy for the northeastern region of the Neuquén Basin. The absolute ages for the Hauterivian of the Neuquén Basin are shown. The SHRIMP age reported here as well as the TIMS-derived age published by Aguirre-Urreta et al. (2015) are included. The reported age of this contribution would be in reasonable agreement with Gradstein et al. (1995) and Cohen et al. (2013) Hauterivian lower boundaries. On the other hand, assuming that basinal/offshore facies deposited under similar long-term accumulation rates similar, the relatively longer duration proposed in older global time scales (particularly by Gradstein et al., 1995) would fit better with the facies and stratigraphic thickness of the entire Agrio Formation in this region (Ogg, Agterberg, & Gradstein, 2004).

this central region of the basin (Spalletti et al., 2011), the resulting temporal intervals are inconsistent if we assume similar (low) long-term depositional rates, particularly for the basinal marine settings. However, including the recent results of Aguirre-Urreta et al. (2015), which suggest the Hauterivian/Barremian boundary should be placed c. 127 Ma, a longer duration of the Hauterivian, in the order of 5 my, could be considered. In this scenario, the lower Hauterivian stratigraphic record of the Pilmatué Member, about 500 m in thickness, could have been deposited in c. 2.5–3 my, whereas the upper Hauterivian record of the Agua de la Mula Member, about 350 m in thickness, would have taken c. 2–2.5 my (the thin continental deposits of the Avilé Member and its basal discontinuity are not considered for simplicity of comparison). This longer Hauterivian duration, which is similar to the one estimated in older time scales such as the one proposed by Gradstein et al. (1995) (Fig. 9) would fit better with the facies and the stratigraphic thickness of the Agrio Formation in the northeastern Neuquén Basin.

6. Final remarks

Geochronological dating by U–Pb SHRIMP of a tuff layer that occur within beds belonging to the H. *neuquensis* Zone in the Pilmatué Member of the Agrio Formation (earliest Hauterivian) has resulted in an absolute age of 130.0 ± 0.6 Ma (2 sigma internal errors only) or 130.0 ± 0.8 Ma (including calibration and decay constant uncertainties). This age is interpreted to represent the time of eruption and thus the timing of the pyroclastic deposit. As the H. *neuquensis* Zone is equivalent of the A. *radiatus* Zone in the Tethys realm, the obtained age is the first numerical data that could help constraining the Hauterivian lower boundary, and in fact, there is reasonable agreement with the latest proposed lower boundary at c. 132.9 Ma. On the other hand, the present proposed duration of the Hauterivian (relatively short) would be hard to reconcile with the stratigraphic record of the entire Hauterivian in the study region (northeastern Neuquén Basin).

The numerical age reported in this contribution from the Pilmatué Member, and likely forthcoming absolute ages from this and related units in the Neuquén Basin, are called to significantly help in defining the boundaries of several Lower Cretaceous stages, particularly the Valanginian, Hauterivian, and Barremian, which to date have heavily relied on correlation with sequences of magnetic anomalies, cyclostratigraphy and Sr isotope curves (McArthur et al., 2007). As more data are released and inconsistencies between estimated boundaries and the stratigraphic record are faced, it is likely that the limits and span of different stages such as the Hauterivian would have to be thoroughly reviewed.

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