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First U–Pb SHRIMP age of the Hauterivian stage, Neuquén Basin, Argentina

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Abstract

A high-resolution ion-microprobe (SHRIMP) U–Pb zircon age from a tuff layer intercalated in the ammonoid bearing sedimentary succession of the Neuquén Basin in Argentina provides a robust geochronologic date to add to the absolute ages and to improve the relative chronology of the Early Cretaceous Hauterivian stage. The tuff layer appears interbedded between shales of the upper member (Agua de la Mula) of the Agrio Formation within the *Spitidiscus riccardii* ammonoid zone (base of the Late Hauterivian) yielding a date of 132.5 ± 1.3 Ma. This date confirms and supports an accurate correlation between the ammonoid biostratigraphy of the Neuquén Basin with the Western Mediterranean Province of the Tethys during the Early Cretaceous and matches with the most recently published time scale. It also casts doubts on the validity of K–Ar ages on glauconite-grains recently reported from the Lower Cretaceous of the Vocontian Basin of France.

Keywords: U–Pb SHRIMP geochronology; Biostratigraphy; Lower Cretaceous; Hauterivian; Neuquén Basin; Tethys

Resumen

Una edad U–Pb en circón realizada mediante una microsonda iónica de alta resolución (SHRIMP) de un nivel de toba intercalado en una sección sedimentaria de la cuenca Neuquina portadora de amonites provee un dato geocronológico robusto para incrementar las edades absolutas y mejorar la cronología relativa del piso Hauteriviano del Cretácico temprano. El nivel de toba aparece intercalado entre lutitas del miembro superior (Agua de la Mula) de la Formación Agrio dentro de la zona de amonites de *Spitidiscus riccardii* (base del Hauteriviano tardío) y arrojó una edad de 132,5 ± 1,3 Ma. Este dato confirma y sostiene una correlación precisa entre la bioestratigrafía de amonoideos de la cuenca Neuquina y la Provincia Mediterránea Occidental del Tethys durante el Cretácico temprano y coincide con la más reciente escala de tiempo publicada. También pone en duda la validez de edades K–Ar en granos de glauconita recientemente informadas para el Cretácico Inferior de la cuenca Vocontiana de Francia.

Palabras clave: Geocronología U–Pb SHRIMP; Bioestratigrafía; Cretácico inferior; Hauteriviano; Cuenca Neuquina; Tethys

1. Introduction

Biostratigraphic zonations for the Early Cretaceous in southern South America have been up today based on direct correlations with the Tethyan standard ammonoid zones (e.g. Aguirre-Urreta et al., 2005) but constraints of

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this inter hemispheric correlations from precise geochronological methods in South America were not previously reported.

The Neuquén Basin located in North Patagonia is famous for a well exposed sedimentary record, rich fossil content, and very productive oil and gas reservoirs in subsurface. Our studies were focused in the Lower Cretaceous marine succession spanning the Berriasian to the Lower Barremian based on a detailed ammonoid biostratigraphy achieved by Aguirre-Urreta and Rawson (1997). Further work on ammonoids combined with nannoplankton and palynology has not only improved the biostratigraphic understanding of the Lower Cretaceous of the basin but also provided a very good correlation scheme with the Tethyan standard zonation (Aguirre-Urreta et al., 1999, 2005; Bown and Concheyro, 2004).

The time scale for the Berriasian to Barremian stages of the Cretaceous was mainly determined by Tethyan ammonoid zones that have been calibrated with the M-sequence of magnetic polarity chrons. Not reliable radiometric ages permitted precise stratigraphic controls for that time-interval. In consequence, the major biostratigraphic events were calibrated to the magnetic polarity time scale for estimation of possible absolute ages (Ogg et al., 2004).

Recently, Fiet et al. (2006) proposed an alternative calibration of the Lower Cretaceous stage durations. It was based on absolute radiochronologycal dating on condensed horizons that provided an absolute time frame combined with orbital chronology applying cyclostratigraphy. Their cyclostratigraphy was supported by ammonite biostratigraphy. Ten horizons, spanning the Lower Hauterivian–Upper Albian were dated by K–Ar ages on glauconite grains yielding ages from 123.3 ± 1.7 to 96.9 ± 1.4 Ma.

The present study is underpinned by the fact that most of the Andean basins were closely associated with active magmatic arcs, and so possibilities of finding tuffaceous layers interbedded with the marine beds bearing ammonites were highly expectable. The appearance of such tuffs layers is crucial to U–Pb dating because the results would give robust absolute dates of the Early Cretaceous. However, tuffs prove to be very rare and a single one tuff layer was found interbedded with black shales of the *Spitidiscus riccardii* ammonoid zone in Agua de la Mula Member of the Agrio Formation. This zone is one of the most extended zones in the Neuquén Basin, and it is very well correlated with the lower *Subsaynella sayni* zone of the Tethys, marking the base of the Late Hauterivian. The obtained date of 132.5 ± 1.3 Ma (SHRIMP U–Pb zircons) is the first precise absolute age that validates the ammonoid biostratigraphy and reinforces the robust correlation between the Neuquén Basin and the Tethys. More important globally, it also provides a close match with the recently published time scale for the Lower Cretaceous by Ogg et al. (2004).

2. Geological background

The Neuquén Basin is located at the foothills of the Andes (32°–40°SL) (Fig. 1a) in a normal subduction segment (Jordan et al., 1983). In the north, it forms a narrow belt along the Andes, including part of the Chilean and Argentine Principal Cordillera, while south of 36°SL, the basin expands towards the eastern foreland forming a large embayment.

The first geological studies were carried out towards the end of the 19th century. More recently, a selection of significant ensuing studies, prompted by the important hydrocarbons reservoirs found in the basin, are by Gulisano et al. (1984), Legarreta and Uliana (1991, 1999), and Veiga et al. (2005), among many others.

The Neuquén Basin is a retro-arc basin with a complex history mainly controlled by the changing tectonic setting of the western margin of Gondwana (Ramos and Folguera, 2005). It encompasses a Late Triassic-Early Cenozoic succession of several thousand meters of thickness of sedimentary rocks that reflects many intervals of sedimentation during calm (black shales) and more variable paleoenvironmental conditions. It is bounded to the NE by the Sierra Pintada Massif and to the SE by the North Patagonian Massif, while its western margin was a volcanic arc (Fig. 1a). This volcanic arc had an extraordinary development from Early Jurassic to Albian times where widespread volcanic and pyroclastic rocks covered most of the axial part of the Principal Cordillera. The volcanic front at those times showed a quasi-static position. However, at the latitude of the Neuquén Basin, only small patched expositions of Early Cretaceous volcanic rocks are preserved because most of them are under a thick cover of Cenozoic volcanic successions (Ramos, 1999).

The infill of the Neuquén Basin during the Early Cretaceous is represented by the Andean cycle of Groeber (1953). This cycle comprises both marine and continental deposits that are assembled in the Mendoza Group. The marine Tithonian-Early Valanginian record is represented by organic dark shales with calcareous nodules (Vaca Muerta Formation, Tithonian-Berriasian), and thinly laminated limestones (Quintuco Formation, Berriasian-Valanginian). The paleogeography was complex during the Early Valanginian, when a regression took place, and there was a coexistence of continental and volcaniclastic deposits, marine shales and thick carbonate deposits of the Mulichinco and Chachao Formations. A widespread transgressive phase started in the late Early Valanginian with the deposition of the shales, sandstones and limestones of the Agrio Formation (late Early Valanginian–Early Barremian). This is the upper unit of the Mendoza Group and is covered unconformably by the fluvial, aeolian sandstones, evaporites and limestones of the Huitrín Formation which marks a regression and the disconnection of the Neuquén Basin with the Pacific Ocean during Barremian times.

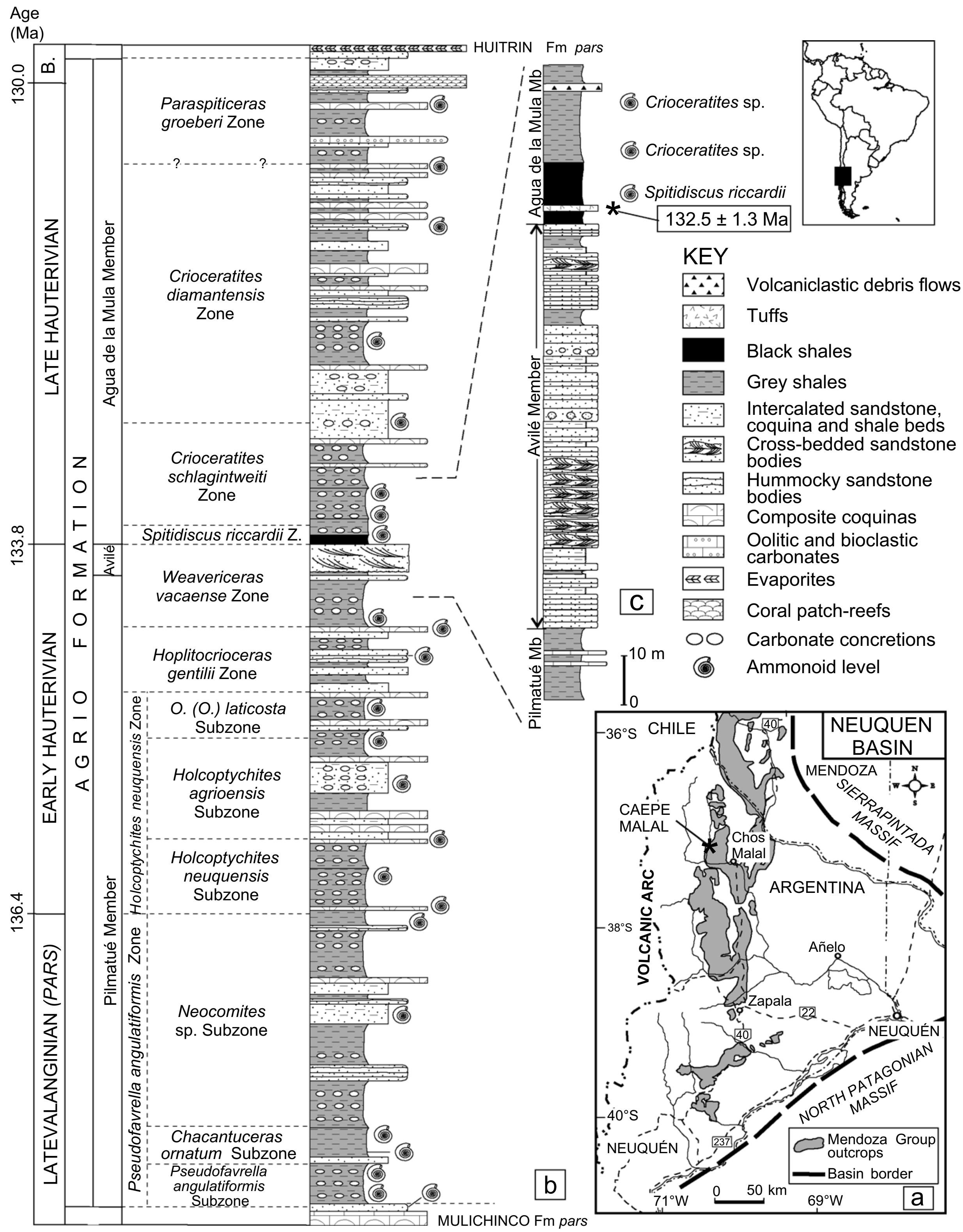

Fig. 1. (a) The Neuquén Basin in west-central Argentina showing outcrops of the Mendoza Group, basin borders and location of studied locality. (b) Lithic log of the Agrio Formation in Agua de La Mula section with ammonoid zonation. (c) Detailed log of part of the Agrio Formation in Caepe Malal section with location of the tuff layer. Numerical timescale after Ogg et al. (2004). B, Barremian.

3. The Agrio Formation

The Agrio Formation was defined by Weaver (1931) near Bajada del Agrio in Neuquén. In this section the unit reaches nearly 1200 m and is divided in three members: Pilmatué, Avilé and Agua de la Mula (Leanza and Hugo, 2001). The Pilmatué Member is mainly composed of massive claystones and shales interbedded with thin layers of packstones and wackestones containing abundant marine mollusks (Fig. 1b). Towards the top of the lower member the fine grained deposits became dominant. The middle member or Avilé Sandstone, 30–40 m thick in most areas, is represented by yellowish coarse sandstones, often with crossbedding of fluvial and aeolian origin (Gulisano and Gutiérrez Pleimling, 1988). It provides an excellent marker horizon in the basin. It contains no marine fossils and has been interpreted as a lowstand wedge produced by a rapid relative sea-level drop during mid Hauterivian times (Legarreta and Gulisano, 1989). The Agua de la Mula Member is composed largely of massive dark shales in the lower part and grey calcareous shales interbedded with sandy limestones and sandstones in the upper part again containing abundant mollusks and other fossil invertebrates (Fig. 1b).

The Agrio Formation has been interpreted as a storm-dominated shallow marine environment, with mixed siliciclastic and carbonate sedimentation (Brinkmann, 1994; Spalletti et al., 2001). The abundance of ammonoids has permitted to accurately date the Agrio Formation by the zonation proposed by Aguirre-Urreta and Rawson (1997) and more recently, by Aguirre-Urreta et al. (2005), combining ammonoids, calcareous nannoplankton and palynomorphs.

As recently stated by Howell et al. (2005) the knowledge of the basin is mainly based on the study of outcrops of the NE and SE passive margins of the basin. As a result of that, the sedimentary sections of the Agrio Formation lacked any evidence of the coetaneous activity of the western volcanic arc. Our search in the westernmost outcrops (Fig. 1a) of this unit permitted to identify a single tuff layer in the locality Caepe Malal (37°11′S, 70°23′W).

The succession in that locality includes the 15 topmost meters of the Pilmatué Member, 83 m of the Avilé Member, 480 m of the Agua de la Mula Member of the Agrio Formation and stratigraphically upward the Huitrín Formation (Figs. 1 and 2). The tuff is 1.2 m thick and is located 7 m above the top of the Avilé Member, within the calcareous black shales yielding *Spitidiscus riccardii* that conform the base of the Agua de la Mula Member. The sampled tuff layer can be followed for more than 8 km of outcrop along strike. It is a vitric tuff-type formed almost exclusively by unwelded volcanic shards and exhibit low content of quartz and plagioclase crystaloclasts; open spaces are filled by secondary carbonates. For this reason, major elements analysis has an anomalous high LOI (Lost of Ignition) value (10.22%); in consequence, SiO_2 content (67.26%), and other major elements as well, are less than expected. The rock corresponds to the rhyodacite/dacite field according to Nb/Y vs. Zr/TiO_2 trace elements classification diagram (Winchester and Floyd, 1977). Tectonic discrimination plots for trace elements, such as Th–Hf–Ta of Wood (1980), evidence an arc affinity for the analyzed sample. Moreover, trace element patterns show typical arc-type signature on mantle and MORB normalized spider diagrams; they show an enrichment of Large Ion Lithophile Elements (LILE) relative to High Filed Strength Elements (HFSE) which reflect subducted-derived magmas sources (Hildreth and Moorbath, 1988; Pearce, 1983).

Besides the tuff layer, higher up in the succession in Caepe Malal, several subaqueous volcaniclastic debris flows have been recognized. They are composed mainly of abundant feldspar, micas, volcanic rock fragments and volcanic quartz immersed in a matrix with glass in devitrification process to chert and clays. In outcrops these levels sometimes are amalgamated (1.2 m thick) and exhibit inverse grading and lenticular geometry. Stratigraphically upward they became rare and in thin section grains are profusely replaced by calcite. These volcaniclastic debris flows and the tuff layer are crucial evidence for active volcanism related to the arc located not far away to the west. Both the tuff layer and the first of these volcaniclastic subaqueous debris flows are shown in Fig. 2.

4. U–Pb SHRIMP geochronology

The zircons from the tuff sample are in general elongate grains, mostly euhedral with pyramidal terminations, or

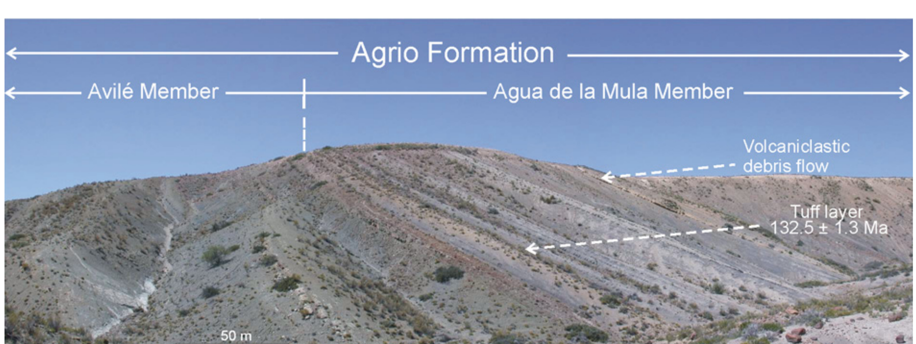

Fig. 2. Panoramic view of the Agrio Formation in Caepe Malal with location of the tuff layer and the first subaqueos volcaniclastic debris flow.

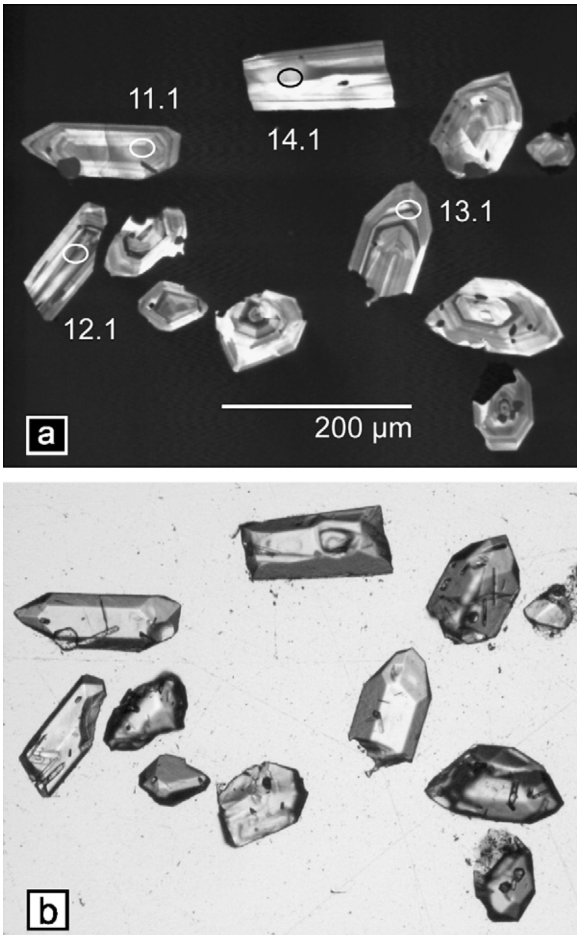

Fig. 3. Representative cathodoluminescence image (a) and transmitted light photo (b) of zircons.

are fragments of such grains (Fig. 3). There are more equant grains present, also euhedral. Zircon grains were separated from total rock samples using standard crushing, washing, heavy liquid (Sp. Gr. 2.96 and 3.3), and paramagnetic procedures. Hand selected zircon grains were placed onto double-sided tape, mounted in epoxy together with chips of the reference zircons (Temora, and SL13), sectioned approximately in half, and polished. Reflected and transmitted light photomicrographs were prepared for all zircons, as were cathodoluminescence (CL) Scanning Electron Microscope (SEM) images. These CL images were used to decipher the internal structures of the sectioned grains and to ensure that the ~20 μm SHRIMP spot was wholly within a single age component within the sectioned grains. These images reveal a dominantly simple oscillatory zoned internal structure to the sectioned zircon grains.

The U–Th–Pb analyses were made using SHRIMP II at the Research School of Earth Sciences, The Australian National University, Canberra, Australia, following procedures given in Williams (1998), and references therein. Each analysis consisted of 6 scans through the mass range, with the Temora reference zircon grains analyzed for every three unknown analyses. The data have been reduced using the SQUID Excel Macro of Ludwig (2001). The Pb/U ratios have been normalized relative to a value of 0.0668 for the Temora reference zircon, equivalent to an age of 417 Ma (see Black et al., 2003). Uncertainty in the U–Pb calibration was 0.72% for the SHRIMP II session. The U and Th concentrations are relative to the SL13 zircon which has 238 ppm U. Twenty grains have been analyzed (Table 1). The analysis of grain 19 is significantly younger with a $^{206}Pb/^{238}U$ age of ~123 Ma (Fig. 4). The area analyzed is near the broken tip of a relatively large elongate grain and although there is no clear evidence for disturbance/alteration from the CL image or transmitted light photomicrograph the area is interpreted to have lost radiogenic Pb. The other 19 analyses form a coherent single group on the Tera-Wasserburg plot. However, on the relative probability plot, with stacked histogram the data do not form a simple bell-shaped curve. Rather the distribution is skewed towards the younger side, with a dominant peak at about 133 Ma. A weighted mean of the $^{206}Pb/^{238}U$ ages for all 19 analyses has little scatter in excess of that attributable to experimental error (MSWD = 1.3) giving a mean age of 131.6 ± 1.3 Ma. However, as some of the zircons have been affected by post igneous crystallization effects, as is apparent in grain 19, then we interpret that small but significant amounts of radiogenic Pb loss has occurred giving rise to the skewed relative probability distribution. If the 4 analyses that yield $^{206}Pb/^{238}U$ ages less than 130 Ma are excluded (i.e. those giving rise to the skewed distribution) then the weighted mean is 132.5 ± 1.3 Ma (MSWD = 0.56, uncertainty at 95% confidence limits) (Fig. 4). This is interpreted to provide the best estimate for the crystallization age of the igneous zircon from this tuffaceous rock.

5. Implications for the chronology of the Hauterivian Stage

The Hauterivian Stage was originally defined in Neuchâtel, Switzerland (Renevier, 1874) and the ammonoid-rich sections in southeastern France are the present day reference for this stage. Its base is recognized in the Tethys by the first appearance of the ammonite *Acanthodiscus radiatus* (Bruguière) while the base of the succeeding Barremian stage is marked by the lowest occurrence of the ammonite *Taveraidiscus hugii* (Ooster) (Hoedemaeker et al., 2003; Reboulet et al., 2006).

The base of the Upper Hauterivian in the Tethys was traditionally marked by the appearance of the ammonite *Subsaynella sayni* (Paquier) but more recently the last occurrence (LO) of the nannofossil *Cruciellipsis cuvillieri* (Manivit) has been recommended as a worldwide marker for the base of the Upper Hauterivian by Mutterlose et al. (1996). Although this proposal has several advantages due to the easy recognition and lack of taxonomic problems with *C. cuvillieri* and its global distribution (Mutterlose et al., 1996), there are some disadvantages regarding its LO in the Mediterranean Province of the Tethys. The LO of *C. cuvillieri* in France is in the upper part the

Table 1
SHRIMP U–Pb Zircon data for tuff layer at Caepe Malal, Neuquén Basin

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	297	127	0.43	5.1	0.000176	0.19	49.616	0.626	0.0501	0.0012	0.0201	0.0003	128.4	1.6
2.1	165	102	0.62	3.0	0.000177	0.34	47.797	0.682	0.0514	0.0016	0.0209	0.0003	133.0	1.9
3.1	262	150	0.57	4.8	–	0.40	47.450	0.635	0.0519	0.0013	0.0210	0.0003	133.9	1.8
4.1	360	215	0.60	6.4	0.000270	0.30	48.000	0.587	0.0511	0.0011	0.0208	0.0003	132.5	1.6
5.1	319	163	0.51	5.7	0.000437	0.24	48.019	0.599	0.0506	0.0015	0.0208	0.0003	132.6	1.7
6.1	680	517	0.76	12.3	0.000239	0.22	47.520	0.534	0.0504	0.0008	0.0210	0.0002	134.0	1.5
7.1	350	156	0.45	6.3	0.000216	0.15	47.999	0.590	0.0498	0.0011	0.0208	0.0003	132.7	1.6
8.1	323	184	0.57	5.8	0.000328	0.17	47.450	0.592	0.0500	0.0012	0.0210	0.0003	134.2	1.7
9.1	188	114	0.61	3.3	0.001686	0.47	49.487	0.700	0.0523	0.0016	0.0201	0.0003	128.4	1.8
10.1	259	135	0.52	4.7	0.000240	0.14	47.634	0.756	0.0498	0.0013	0.0210	0.0003	133.8	2.1
11.1	222	119	0.53	3.9	0.000682	0.42	48.467	0.651	0.0520	0.0015	0.0205	0.0003	131.1	1.8
12.1	441	290	0.66	7.9	0.000106	0.00	47.987	0.735	0.0487	0.0010	0.0208	0.0003	133.0	2.0
13.1	463	293	0.63	8.3	0.000417	0.28	48.038	0.566	0.0509	0.0010	0.0208	0.0002	132.4	1.6
14.1	148	78	0.52	2.6	–	0.71	48.373	0.720	0.0543	0.0018	0.0205	0.0003	131.0	2.0
15.1	300	181	0.60	5.2	0.000555	0.19	49.331	0.625	0.0501	0.0012	0.0202	0.0003	129.1	1.6
16.1	114	37	0.33	2.0	0.001132	0.65	48.020	0.774	0.0539	0.0021	0.0207	0.0003	132.0	2.1
17.1	262	200	0.76	4.6	0.000325	0.26	48.601	0.639	0.0507	0.0019	0.0205	0.0003	131.0	1.7
18.1	247	129	0.52	4.3	0.000495	0.04	49.517	0.654	0.0489	0.0014	0.0202	0.0003	128.8	1.7
19.1	277	182	0.66	4.6	0.000333	0.12	51.902	0.825	0.0494	0.0013	0.0192	0.0003	122.9	2.0
20.1	539	521	0.97	9.5	0.000170	0.11	49.017	0.572	0.0495	0.0009	0.0204	0.0002	130.0	1.5

Notes:

1. Uncertainties given at the one σ level.
2. Error in Temora reference zircon calibration was 0.72% for the analytical session. (not included in above errors but required when comparing data from different mounts).
3. –denotes that no ^{204}Pb was detected.
4. f_{206}% denotes the percentage of ^{206}Pb that is common Pb.
5. Correction for common Pb made using the measured $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios following Tera and Wasserburg (1972), as outlined in Williams (1998); the so called ^{207}Pb correction method).

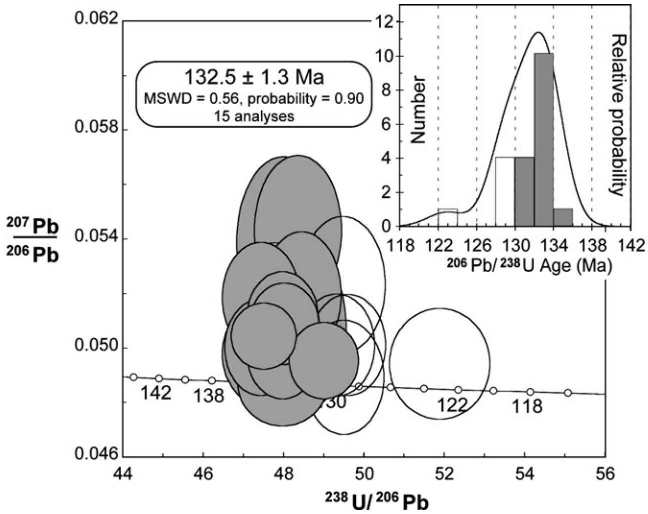

Fig. 4. Tera-Wasserburg concordia plot of the calibrated total $^{238}U/^{206}Pb$ ratios versus the total $^{207}Pb/^{206}Pb$ ratio. Analyses plotted as one sigma error ellipses. Inset is a probability density plot with stacked histogram; analyses used for the weighted mean $^{206}Pb/^{238}U$ age calculation are shaded, those unshaded are interpreted to have lost radiogenic Pb. The age uncertainty is given at 95% confidence limits and includes the uncertainty in the U/Pb ratio calibration of the reference zircon. Plots and calculations based on ISOPLOT of Ludwig (2003).

ammonite zone of *S. sayni* (Bergen, 1994); in Italy Channell et al. (1995) placed it at the base of the magnetic chron M8 (lower part of the *S. sayni* zone) while Ogg et al. (2004) located it within the M8, in the middle part of the *Plesiospitidiscus ligatus* ammonite zone in the Upper Hauterivian. More recently, McArthur et al. (2007) placed the LO of *C. cuvillieri* at the base of M8, but correlated it with the base of *L. nodosoplicatum* ammonite zone in the Lower Hauterivian. Ogg et al. (2004, Fig. 19.1), Hoedemaeker et al. (2003, Fig. 1) and Reboulet et al. (2006, Table 1) maintained that the traditional base for the Upper Hauterivian is the lowest occurrence of the ammonite *Subsaynella sayni*, a criterion that is followed here.

In the Neuquén Basin, the *Spitidiscus riccardii* zone was proposed for shales with *Spitidiscus* at the base of the Agua de la Mula Member, immediately overlying the Avilé Member and was originally correlated with the *Lyticoceras nodosoplicatum* ammonite zone (Aguirre-Urreta and Rawson, 1997). Further research in the ammonite faunas of the Neuquén Basin modified this correlation. First, the occurrence of *Olcostephanus (Jeannoticeras) agrioensis* Aguirre-Urreta and Rawson in the *Olcostephanus (O.) laticosta* subzone (*Holcoptychites neuquensis* zone) indicates a correlation with the *Olcostephanus (Jeannoticeras) jeannoti* subzone of France (upper part of the *Crioceratites loryi* Zone) (Aguirre-Urreta and Rawson, 2001). Second, the occurrence of *Olcostephanus (Olcostephanus) variegatus* (Paquier) in the upper part of the *Hoplitocrioceras giovinei* subzone (*Hoplitocrioceras gentilii* zone) suggests a correlation of the *H. giovinei* subzone with the *O.(O.) variegatus* biohorizon in the base of the *Lyticoceras nodosoplicatum* zone (Aguirre-Urreta and Rawson, 2001). Thus, the *Spitidiscus riccardii* zone of the Neuquén Basin is presently correlated with most of the *Subsaynella sayni* ammonite zone of the Mediterranean Province (Aguirre-Urreta et al., 2005, 2007; Rawson, 2007). There are two species, *S. riccardii* Leanza and Wiedmann and *Spitidiscus* sp. nov. (Aguirre-Urreta and Rawson, 1997, Fig. 7f and g). The last one is almost identical to species from the *Subsaynella sayni* zone in France, while *Crioceratites apricus* (Giovine) from the overlying *Crioceratites schlagintweiti* zone in the Neuquén Basin is virtually indistinguishable from forms belonging to the *Subsaynella sayni* to *Plesiospitidiscus ligatus* zones of the Tethys (Fig. 5). Besides the ammonites, there is also good agreement with the nannoplankton biostratigraphy. In the Neuquén Basin, the LO of *Cruciellipsis cuvillieri* is recorded within the *S. riccardii* zone in the locality Pampa Tril (Bown and Concheyro, 2004) while in other localities (Agua de la Mula and Mina San Eduardo) the LO coincides with the base of the *C. schlagintweiti* zone, and appears to be consistent with its global extinction level, corroborating the ammonite correlation with the *S. sayni* zone of the standard Mediterranean sequences of the Tethys proposed by Aguirre-Urreta et al. (2005, 2007).

Therefore, the new U–Pb SHRIMP date provides a close age constraint for the base of the Late Hauterivian not only for the southern Hemisphere, but also based on the robust biostratigraphic correlations, it is an important direct support for the age of the Early-Late Hauterivian boundary in the Tethyan region. Although the age obtained of 132.5 ± 1.3 Ma, has a relatively small error, the time interval bracketed by these values poses the base

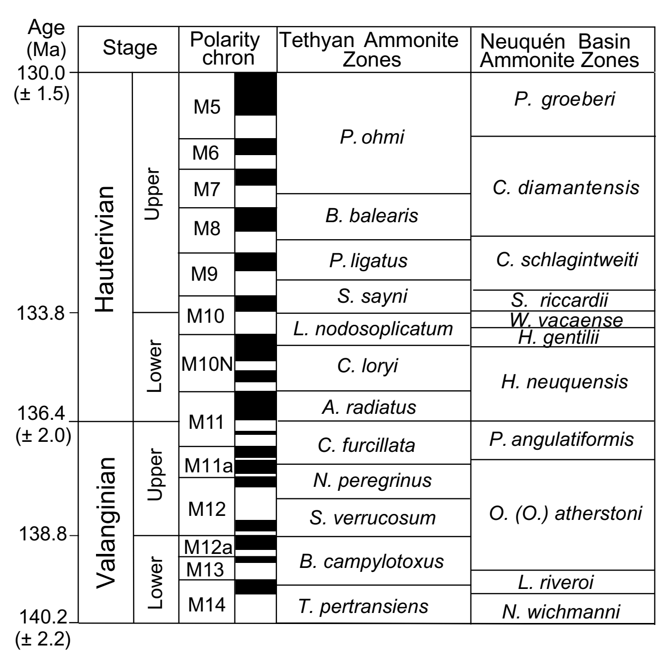

Fig. 5. Correlation chart of the Valanginian–Hauterivian Tethyan and Neuquén Basin ammonoid zones and polarity chrons. Timescale in Ma from Ogg et al. (2004), magnetostratigraphy from Channell and Erba (1992), Tethyan ammonoid zonation from Hoedemaeker et al. (2003), and Neuquén Basin ammonoid zonation from Aguirre-Urreta et al. (2005).

of the Late Hauterivian within the errors of the proposed values based on magnetostratigraphic and biostratigraphic chronology (Ogg et al., 2004).

When comparisons are done between the glauconitic ages offered by Fiet et al. (2006) and their extrapolated cyclostratigraphy ages with those proposed by Ogg et al. (2004) differences as great as 12 Ma stand for the lower and upper boundaries of the Hauterivian Stage. A glauconitic horizon within the *Acanthodiscus radiatus* zone of the Lower Hauterivian gave a K–Ar age of 123.6 ± 1.7 while another glauconitic level within the *Taveraidiscus hugii* zone in the base of the Barremian yielded a K–Ar age of 118.3 ± 1.7 (Fiet et al., 2006). Thus, these authors bracketed the Hauterivian between 124.1 ± 0.4 and 118.8 ± 0.4 Ma. It is considerable younger than the 136.4 ± 2.0 and 130.0 ± 1.5 Ma ages previously proposed by Ogg et al. (2004). The large differences may be due to the methodology applied by Fiet et al. (2006). Glauconites were considered ideal minerals for isotopic dating of sedimentation time due to their genetic and mineralogical characteristics, but according to Smith et al. (1998) and more recently to Sandler and Harlavan (2006) glauconites should not be used for dating purposes as they frequently record ages which are too young, apparently because of weak argon retention. Clauer et al. (2005) in their case study of Eocene sections argued that relatively young glauconite ages do reflect the time of formation but this time is long and depends on later interactions with circulating fluids.

Our high-resolution ion-microprobe (SHRIMP) U–Pb zircon age of 132.5 ± 1.3 Ma constitutes a reliable tie point for the base of the Upper Hauterivian and supports the proposal of Ogg et al. (2004) for the Hauterivian stage boundaries.

6. Conclusions

As pointed out by Ogg et al. (2004) when the Late Jurassic and Early Cretaceous are compared with the high precision of Late Cretaceous time scale, this interval is nearly devoid of precise ages and was mainly calibrated based on biostratigraphy or magnetic polarity chrons. Therefore, our high-resolution ion-microprobe (SHRIMP) U–Pb zircon age constitutes the first reliable tie point for the base of the Upper Hauterivian and supports the presently accepted Hauterivian stage boundaries.

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